

# **JAC: Jena Atomic Calculator**

## **— User Guide, Compendium & Theoretical Background —**

<https://github.com/OpenJAC/JAC.jl>

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### Atomic representations

- Configuration-based expansions
- Restricted active spaces (layer-by-layer)
- CI+perturbation theory; Gamov states
- Approximate Green functions, ...

### Processes & properties

- Transition probabilities
- Excitation, ionization & recombination
- Auger, DR, Rayleigh-Compton, multi- $\gamma$
- Hyperfine & Zeeman splitting; plasma
- Isotope shifts, Lande & form factors

### Atomic cascades

- Average single-configuration approach
- Multiple-configuration approach
- Incorporation of shake-up & shake-off
- Ion & electron distributions, ...

### Symbolic Racah algebra

- Wigner symbols, special values
- Symmetries & recursions
- Symbolic sum rule evaluation
- Spherical harmonics & tensors

Interactive High-Level Language

# JAC

## Jena Atomic Calculator

A Julia implementation for  
atomic computations.

Open-source applications  
in physics, science and  
technology.

### Atomic responses

- Field-induced processes & ionization
- High-harmonic generation
- Particle-impact processes
- Charge exchange

### Time evolution

- Liouville equation for statistical tensors  
& atomic density matrices
- Atoms in intense light pulses
- Angle & polarization-dep. observables

### Atomic descriptors

- Feature transform. & machine learning
- Bi-spectra of electronic densities
- Subshell & coupling descriptors
- Atomic fragments & effective charges

### Semi-empirical estimates

- Weak-field ionization rates
- Asymptotic behaviour & formulas
- Stopping powers
- Plasma Stark broadening, ...

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## A few remarks about this User Guide & Compendium ahead:

- **Goals of this User Guide & Compendium:** While a large (huge) number of publications have contributed to the progress in atomic physics and theory over the years, they have lead also to different research fields as well as rather diverse designations and notations, with many of them hard to resolve in detail. — With this Compendium, we aim to **establish a common language in which the results are easier communicated and (hopefully) applied by others researchers**. Indeed, such a common language must aim to comprise (1) precise and analogue designations for (the same or) analogue physical quantities; (2) the same or obviously modified mathematical syntax in formulas for the same physics; and (3) quite similar but still distinguishable (mathematical) symbols for similar but distinguishable quantities.

While this goal is rather ambitious and hard to achieved in practice, I shall explain below some of the concepts and difficulties below, which I tried to (partly) overcome in this Compendium on computational atomic physics.

- **Goals of this User Guide & Compendium:** First, this Compendium **contains all expressions and formulas that are implemented in JAC** as well as many more. Such a compilation will make it explicit which which of the *physics* is (partly) implemented already within the toolbox, and which other topics are close to an implementation. Apart from those topics *not yet considered in JAC*, most chapters of this Compendium therefore contain basic information also from other research fields that might benefit from this toolbox. Overall, however, no attempt is made (and I wouldn't feel able) to provide further details about these fields; nonetheless, we hope to capture curiosity and, perhaps, find new supporters of JAC by this way.
- **Symbols and formulas:** A good deal of (modern) research paper are quite difficult to follow because quantities are either not explained at all or because little care is taken about (additional) assumptions, their dependencies or simply because of an overload of notations. Moreover, the (parametric) dependencies of physical quantities are often not shown, or authors are not even aware about them. Here, **we aim to (partly) overcome these missing dependencies and the the overloading of designated or alias name and symbols**. In a good number of research paper, indeed, the same symbols have different (and by far no obvious) meaning, or different symbols are used for the same quantity, either within the same or from one to the next publication by the same authors.
- **Symbols and formulas:** In physics, there is a wide believe that symbols can be used quite freely, as long as they are properly explained. While this is *formally* true from a technical viewpoint, such a carelessness can indeed hamper considerably the work of other people, and will make certain case studies unfeasible. Of course, we can write Newton's famous law for a 1-dimensional motion either:  $m \ddot{x} = F$  or  $x \ddot{F} = m$ , if all the symbols are carefully introduced. However, such a freedom is of little help since a careful introduction of all entities becomes elaborate with increasing complexity, and one might even not be fully aware of the precise definition of all quantities at most of the times. From a physical viewpoint, strictly speaking, a re-definition of symbols requires knowledge about *all* assumptions that were made prior to

their first use. I guess, hardly anyone will spontaneously be able to recall most or, at least, most of these assumptions about the quantities as they appear in some derivation or discussion. — **This Compendium therefore aims to make assumptions about as well as the notations and dependencies of various entities in atomic physics (much) more explicit**, than what is typically found in most research papers. No claim is made that this is always done in a *wise* and final manner.

- **Expressions and formulas:** This Compendium provides first of all a compilation of expressions and formulae, with less focus on their detailed derivation. In fact, many of the underlying derivations are lengthy enough, so that they are not or only rarely repeated by other researchers in the field. Of course, this Compilation should not discourage young people to re-think and re-do certain derivations in good detail, and sometimes with their very own success to find *new* insights into physics. Nonetheless, such derivations will be made less often as the size and complexity of (intermediate) expressions increase. Many of the formulas below are (simply) taken from the literature, adapted in their notations and/or checked for their consistent use in the literature. (In some other cases, I was earlier involved myself in the derivations.) No claim is made that all these formulas are correct or correctly ‘translated’ into the chosen notation. Both, misprints and misunderstandings are readily possible; **despite of all these difficulties, the search for common and appropriate notations for all physical quantities has taken enormous effort but is considered as ‘main prize’ of this Compendium.**
- **Parametric dependence of amplitudes and derived quantities:** From the viewpoint of elementary mathematics, we easily accept expressions such as

$$f(x, y; a) = \int_b^\infty dz g(x, y; a) h(y, z; b) \quad \text{for } b > 0,$$

as long as we know which values the explicit variables  $x, y, z$  and the parameters  $a, b$  may take. We even accept such expressions if the detailed derivation of this formula is not known at a given time. Nonetheless, the physical interpretation of such formulas is quite easy as long as the *dependencies* are clear. In physics, in contrast, we all-too-often find formulas, in which the dependencies cannot be resolved by the reader, and sometimes also by the authors themselves. An *educational guess* is then needed to resolve the expression. For example, the radiative recombination (RR) plasma rate coefficient describes the rate of an ion to recombine by (direct) photoemission for one particle per *unit* volume. For a plasma with electron temperature  $T_e$ , this rate coefficient is often written as

$$\alpha^{(\text{RR})} = \int_0^\infty dE E \sigma^{(\text{RR})} \exp\left(-\frac{E}{T_e}\right)$$

without telling much about the cross section  $\sigma^{(\text{RR})}$ , nor its dependencies or about the energy  $E$  that appear here in this expression. Moreover, in which ‘units’ should all these entities be utilized? — A more detailed analysis of the radiative recombination process will reveal that the RR plasma rate coefficient depend parametrically on the temperature of the plasma  $T_e$  and the initial (ground) level  $(\alpha_i \mathbb{J}_i)$  of the ion,

while the (set of) final states of the recombined ion determine the approximation that is used in a particular computation. Moreover, the structure of the radiation field (multipole fields) need to be specified but are typically restricted to the electric-dipole component. A more explicit notation with all entities in atomic units [!] then reads as

$$\Downarrow$$

$$\alpha^{(\text{RR})}(T_e; \alpha_i \mathbb{J}_i) = \frac{4}{\sqrt{2\pi} m T_e^{3/2}} \int_0^\infty dE E \left[ \sum_{\alpha_f \mathbb{J}_f, \mathbb{M}} \sigma^{(\text{RR})}(E; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; \mathbb{M}) \right] \exp\left(-\frac{E}{T_e}\right) [\text{a}_0^3 \text{s}^{-1}],$$

and where the major complexity now arise from determining the relevant final levels  $(\alpha_f J_f)$  and all the associated cross sections. Here,  $(\alpha_i \mathbb{J}_i)$  refers to the initial  $N$  electron bound level of the ions that recombines into any bound  $N + 1$  electron level. While it is sometimes still mentioned the ions are initially taken in their ground level, I haven't seen serious discussions how the summation over the  $N + 1$  electron *resonances*  $(\alpha_f \mathbb{J}_f)$  should be made in practice. Although, no doubts, several codes perform reasonable approximations to this (multiple-infinite) summation over all final states, the overall structure of these rate coefficient and, in particular, the truncation of the final states will usually remain intransparent. **Such a simple example shows that better insight into the physics is often already obtained if the dependencies are made explicit.**

- **Hierarchy of approximations and prior assumptions:** Many (frequently) applied expressions in atomic physics are obtained, once a series of different assumptions and approximation were made before. While such an hierarchy of approximation is crucial for a successful description of physics, not all approximations are necessarily consistent with each others and, hence, may weaken some derivation significantly. By showing the assumptions made for an expression, the risk of computational pitfalls will be reduced.
- **Same designation, different physics:** There is little misunderstanding of scientific terms (and notation) possible if the subjects, where these terms are used, are sufficiently separate from each other. The use of scientific terms becomes however more problematic if there exist both, overlap and differences in their meaning and detailed designation. The use of (common) short designations and symbols then cause quickly confusion. This confusion can be (partly) overcome if the notations is made more explicit, and as done extensively in this Compendium. The opposite, different designations but the same physics, is easier to resolve but still requires extra effort. **Likely, some readers may feel the partly redundant notations in this Compendium a little point for their own work but may still benefit, if they need to understand and apply expressions from neighbored fields.**



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## 1.1. Computational atomic physics: Challenges & difficulties

### Contemporary challenges of computational atomic physics:

- (i) Developement of (practical) **many-body techniques** which account for all relevant electron-electron correlation contributions, and **which can be improved systematically**. These many-body techniques can be based on both, extended quantum electro-dynamical (QED) but also much simpler approximations, whenever *ab-initio* computations become unfeasible. Since the fine-structure constant and, hence (almost) all inner-atomic interactions, is known with very high accuracy, emphasis should be placed first of all on a detailed and much better understanding of many-electron effects in the behaviour and response of atoms and ions.
- (ii) Support of atomic spectroscopy to make **time-consuming experiments necessary just as benchmarks of atomic theory** but no longer in order to *collect* data for other research areas. This support requires the treatment of a (very) large number of atomic properties, processes and responses, and just as the JAC toolbox is aiming for, cf. section 1.2. It also requests for a critical evaluation of computational methods as well as a careful estimate of theoretical uncertainties in atomic computations.
- (iii) Highly-accurate predictions for various **fundamental physics studies (and experiments) in exploring “new physics”**. When compared to high-energy physics, such atomic experiments are performed at rather low costs, although they may still provide hints towards new concepts and interactions in physics owing to their (extremely) high accuracy. By using systematically-enlarged representations of atomic states, small remaining deviations between theory and experiment may indicate fundamental processes that are still omitted from theory. This approach has been utilized, for instance, in studying parity-nonconserving interactions, for atomic clocks as well as in the search of variations of the fine-structure constant.
- (iv) **Electron dynamics in intense and spatially-structured light fields**. While a first generation of these studies have often been successfully performed *without* considering much of the electronic structure of the target atoms, forthcoming experiments will reveal further details about the strong-field interaction, only if the time-dependent wave functions of the atoms and ions are taken into account. Such studies of atoms in in intense fields make it also necessary to deal with time-dependent atomic density matrices at different level of sophistication.

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- (v) Diagnostics in astro (and plasma) physics in order to support large space missions and to improve our understanding of the Universe; in fact, more than 99 % of all visible matter in the Universe is expected in a plasma states and subject to conditions that can hardly be re-produced in the laboratory.
- (vi) Use of **machine-learning techniques** to quickly generate large data sets for astrophysical observations and for the dynamical evolution of complex atomic (and molecular) systems.

### Difficulties for the implementation and use of atomic theory:

- I have been involved in the computation of atomic properties and processes for more than two decades. During this time, I had to follow through various theoretical (and experimental) studies, from research papers to *ad-hoc* compilations of formulas to conference contributions. Frankly speaking, I found myself struggling on certain details again and again. Often, there has been taken little care by the authors about notations and the dependence of physical in the formulas, or more generall about the reader. In practice, a few lines in such texts can literally turn into several pages of precise mathematics (notations).
- **Difficulties for applying atomic theory:** From the recent study of  $\gtrsim 250$  papers, that have been screened or analyzed for the implementation of JAC, the following observations were made:
  - (1) Although the *physics* is reasonably clear in a large fraction of papers, the notations (and formulas) can often not be resolved in good detail;
  - (2) Use of *ad-hoc* notations (and names) that do *not* properly support a consistent 'physics picture';
  - (3) Missing bindings of arguments and indices in formulas, for instance:
    - + Polarizability:
    - + Opacities:
  - (4) Assumptions and limitations (of given expressions) are often not mentioned or are incomplete, i.e. these expressions are valid only for special cases that are not transparent for the reader;
  - (5) Hierarchy of approximations is often not explained (and sometimes not even justified) from the viewpoint of physics;
  - (6) Reasoning in the derivation of formulas is not made explicit (enough) with regard to the underlying assumptions.

## 1.2. Goals of the JAC toolbox

### Goals, purpose and use of JAC:

- The **Jena Atomic Calculator (JAC)** provides tools for performing atomic (structure) calculations at various degrees of complexity and sophistication. This toolbox has been designed to calculate not only **atomic level structures and properties** [g-factors, hyperfine and isotope-shift parameters, etc.] or **transition amplitudes between bound-state levels** [dipole operator, parity non-conservation, etc.] but also a large number of atomic processes including (atomic) transition probabilities, Auger rates, photoionization cross sections, radiative and dielectronic recombination rates as well as cross sections and parameters for many other (elementary) processes.
- Apart from **interactive (atomic) computations**, JAC also facilitates the simulation of **atomic cascades, atomic responses, the time-evolution of statistical tensors, the symbolic simplification of expressions from Racah's algebra** as well as various **semi-empirical estimates** of atomic properties. Indeed, JAC provides a diverse and wide-ranging, yet consistent set of methods which can be applied in different fields of atomic physics and elsewhere. In addition, the JAC module has been designed to readily support the display of level energies, electron and photon spectra, radial orbitals and several others entities.
- **Goals of JAC:** For many (modern) application of atomic structure theory, it is crucial indeed to integrate different atomic processes within a single computational toolbox in order to ensure good self-consistency of all generated data. JAC here aims to provide a very flexible user interface for different computational tasks, including a simple communication between the different parts of the program. In the past, sophisticated user interfaces often hampered the application of codes for people other than the authors (and sometimes even for them). **JAC aims to combines the strengths of previous atomic (structure) codes and to clearly enlarge the range of applications.**
- **Goals of JAC:** Since many methods for dealing computationally with quantum many-particle physics have first been applied to atoms and ions, JAC aims to retain and to advance this knowledge, and to make it usable by future AMO scientists. In JAC, the treatment of the electron continuum follows those of the FAC code but also goes well beyond it.
- In order to support these goals, several **types of computation** are distinguished within the JAC toolbox, and which are summarized below.
- **To find (the details about) individual features of the JAC program, see the index or search for keywords/phrases in this User Guide.**
- **Design of JAC:** The design of these tools has been based on an analysis of typical user requirements and a hierarchical structure of the code.
- With the design and development of JAC, we also aim to identify (emerging) problems from AMO science and to support rapid scientific progress for the AMO community.

## 1. Overview about JAC. Structure of this User Guide

- **Theoretical background of JAC:** Since the theoretical background and data, implemented in JAC, have been extracted from quite many sources, we also hope to develop JAC as a **repository of previous experience with electronic structure calculations of atoms in different environments**, and that is to be further refined, expanded and developed here.
- **Use of JAC:** Applications of the JAC toolbox range from simple estimates for various atomic properties and processes upto full-scale atomic simulations. Since performance is crucial for many applications, the goal is to demonstrate performance comparable FAC, GRASP, RATIP and other atomic structure codes.
- **Use of JAC:** The source code, an extensive documentation as well as a number of tutorials and examples are available from our Web site <https://www.github.com/sfritzsche/JAC.jl>.
- **Comparison with other computational communities:** When compared to astro and particle physics, and even if compared to quantum chemistry, the AMO community has placed less emphasis over the last decades in developing and maintaining robust and user-friendly software tools for its own applications and for those in related fields.
- **Estimates of theoretical uncertainties:** Although the uncertainty quantification of computationally-generated data is still a great challenge for theoretical (many-particle) physics, uncertainty estimates are crucial for assessing the quality of predictions and for discriminating different models. An evaluation of the uncertainties is therefore an important part of atomic computations.
- **Estimates of theoretical uncertainties:** There are two major strategies in order to estimate the uncertainty of theoretical (computed) atomic data: (1) By enlarging and monitoring the size of state vector representations or (2) by deriving upper uncertainty limits for the computed results. Until the present, however, the second approach has been found less useful in practice, mainly because of the large (or often even huge) uncertainty bounds that are obtained eventually.

## Types of computations:

- In the JAC toolbox, different types of computations are distinguished and can be easily controlled by the user without much prior knowledge about the code. Here, these different types of computations are briefly summarized, while all further details are given below in this User Guide.
- **Atomic computations, based on a set of explicitly specified electron configurations:** A typical computation, that is based on explicitly specified electron configurations, refers to level energies, atomic states or to either **one (or several) atomic properties** (for selected or all levels from a given multiplet). In addition, these atomic computations can provide also the rates and cross sections of just **one selected atomic process**. For all further details about the call and control of these computations, see the supported amplitudes, properties and processes in Sections 6–8 below.



- **Computation of atomic representations:** JAC supports the automatic generation of various atomic representations, such as an atomic *mean-field*, configuration-interaction as well as restricted active-space (RAS) expansions. In particular, the RAS computations refer to the automatic and stepwise representation of atomic state functions and level energies due to a user-specified (and, hence, restricted) active space of orbitals as well as due to a given number and/or kind of virtual excitations to be included. Such **RAS computations are internally always performed stepwise** in JAC by utilizing the self-consistent field (orbitals) from some prior step. See Section 4 for all further details about atomic representations.
- **Interactive computations:** In an interactive computation, the **functions/methods of the JAC program are applied interactively, either directly within the REPL or by just writing a short JULIA script**, in order to compute energies, expansion coefficients, transition matrices, rates, cross sections, etc. An interactive computation typically first prepares and generates (instances of) different data structures of JAC, such as orbitals, (configuration-state) bases, multiplets, and later applies these computed data in subsequent steps in order to obtain the desired information. Of course, **all methods from JAC and its submodules can be utilized also interactively**, although some specialized methods are typically available and help facilitate the computations. Like most other JULIA functions, the functions and methods from the JAC toolbox can be seen as (high-level) language elements in order to perform atomic computations at various degrees of sophistication.
- **Atomic cascade computations and simulations:** A cascade computation typically refers to **three or more charge states of an atom that are connected to each other by different atomic processes**, such as photoionization, Auger emission, radiative transitions, etc. Different (cascade) *schemes* and *approaches* have been predefined in JAC in order to deal with atomic cascades. The user has to specify the particular atomic processes that are taken into account for the individual steps of the cascade. Apart from cascade computations, (cascade) simulations make then use of a pre-calculated list of (many-electron) amplitudes, rates and/or cross sections in order to derive different ion, photon and/or electron distributions and spectra. **In Jac, cascade computations and cascade simulations are always handled independently.** See section ?? for further details about these cascade computations and simulations.
- **Atomic responses:** Atomic response computations (will) provide access to various **responses of atoms and ions to some incident (beam of) light pulses and particles**, such as strong-field induced ionization processes, high-harmonic generation and others. For these responses, almost no detailed atomic structure has been considered in the past, although these details will become relevant as more elaborate and accurate measurements are to be carried out. Only a rather restricted number of such response computations are supported so far. See section 10 for all further details.
- **Time evolution of statistical tensors in (intense) light pulses:** In JAC, a time evolution of statistical tensors always proceeds within a pre-specified set of sublevels  $\{|\alpha JM\rangle\}$ , i.e. within a pre-defined subspace of the many-electron Hilbert space; all further (decay) processes that lead the system eventually *out of this subspace* must be treated by loss rates. Although such a time evolution can deal with pulses of different shape, strength and duration, it is assumed that they are **weak enough in order not to disturb the level structure and level sequence of the atoms substantially in their neutral or ionic stage**, i.e. that every selected sublevel can still be characterized by its (total)

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energy and symmetry. However, such time-evolutions of statistical tensors has not yet been implemented in detail so far. Note that no attempt is made (nor planned) in JAC in order to solve the time-dependent (many-electron) Schrödinger equation explicitly.

- **Symbolic simplification of expressions from Racah's algebra:** Such expressions can often be simplified by applying well-selected algebraic transformation from the theory of angular momentum. These transformations may generally include any number of Wigner  $n$ - $j$  symbols of different kind as well as (various integrals over) the spherical harmonics, the Wigner rotation matrices and the Kronecker and triangular deltas. In practice, the complexity of Racah expressions increases very rapidly as more Wigner symbols, spherical harmonics and/or rotation matrices are involved. In JAC, a symbolic evaluation of these expressions can be performed, based on a sizeable set of special values, orthogonality relations and sum rules, including rules with a (multiple) summation over dummy indices, cf. the monography by Varshalovich et al (1988) and section 15 for further details about such symbolic simplifications.
- **Atomic descriptors:** In building models for machine learning, the definition of proper (atomic) descriptors or feature transformations is central for predicting the physical properties and behaviour of atoms and ions; here, we shall provide various of such descriptors useful for atomic physics. See section 12 for further details about atomic descriptors.
- **Semi-empirical estimates of atomic properties, cross sections, asymptotic behaviour, etc.:** A semi-empirical 'estimate' of atomic data refers either to some simplified model computation or to the evaluation of fit functions in order to **provide those atomic data which cannot be generated so easily by *ab-initio* computations**. These semi-empirical estimates are typically built on — more or less — sophisticated models and external parameter optimizations. However, only a very few of such estimates have been implemented so far, and no attempt is made to extend this type if computation, if such data are not essential for other applications of JAC. See section 13 for further details.

## 1.3. Frequent terms and notations in using JAC

### Glossary:

- **Angular coefficient:** Reduced many-electron matrix elements (amplitudes) can usually be decomposed into a sum of *angular coefficient*  $\times$  *interaction strength*, and where latter refers to standard one- and two-particle due to the character of the (many-electron) operator. The (pure) angular coefficients are presently calculated by means of the ANCO program (Gaigalas *et al.*, 2001); cf. section 3.7.
- **Atomic shell model:** This model, in which electrons fill a (more or less) regular list of atomic shells or make transitions (quantum jumps) between different shells, is **key and guidance for calculating the electronic structure of atoms, ions and molecules, and most of their properties**.

- **Atomic-state function (ASF):** In the multiconfiguration Dirac-Hartree-Fock method, an atomic state function is written as linear combination of configuration state functions (CSF) with well adapted symmetry, cf. section 4. This is analogue to the non-relativistic Hartree-Fock method with symmetry-adapted functions.
- **Basis:** In JAC, a many-electron basis is specified in terms of a CSF list and the radial orbitals of all (equivalent) electrons that occur in this list. Moreover, each CSF is specified uniquely by a proper set of quantum numbers. In JAC, the (so-called) **seniority scheme** is applied for the unique classification of the CSF and the evaluation of all matrix elements.
- **Cascade:** A cascade typically includes ions of an element in three or more charge states that are connected to each other by different atomic processes, such as photoionization, Auger emission or radiative transitions. A quantum modelling of a cascade requires to follow all possible *pathways* that the ions leads eventually into some stable ground state. In JAC, we distinguish between different *cascade scheme* (photoionization cascades, decay cascades) and *cascade approaches* to account for different computational models in dealing with the pathways.
- **Cascade simulation:** A cascade simulation makes use of a pre-calculated list of (many-electron) amplitudes, rates and/or cross sections in order to derive different ion, photon and/or electron distributions and spectra, and which can be compared directly to experiment. In JAC, cascade computations and cascade simulations are always handled independently.
- **Channel:** For most atomic lines, different (quantum) channels need to be distinguished due to the symmetry properties of the multipoles or of partial waves in the decomposition of the many-electron levels and/or matrix elements.
- **Configuration interaction (CI) expansion:** Refers to a CI representation of ASF.
- **Electron configuration:** Describes the occupation of shells within the atomic shell model, for instance,  $1s^2 2s^2 2p^6 3s^2$ . In JAC, closed-shell configurations can be abbreviated by using the noble gases or selected close-shell atoms with a closed ground-state configuration. For example, the valence-shell excited configurations of aluminium-like atoms can be given as  $[\text{Ne}] 3s^2 3p$ ,  $[\text{Ne}] 3s 3p^2$ , or  $[\text{Mg}] 3d$ .
- **Configuration-state function (CSF):** These symmetry-adapted many-electron (basis) states are constructed as antisymmetrized product of one-particle states but coupled to well-defined total angular momentum and parity. In JAC, CSF are typically abbreviated by  $|\gamma JM\rangle \equiv |\gamma J^P M\rangle$ .
- **Electro-magnetic property (EmProperty):** A (data) **struct** of JAC to maintain internally the same property (rates, cross sections) in Coulomb and Babushkin gauge for the coupling of the radiation field.
- **Envelope:** A (data) **struct** of JAC to deal with an (externally-defined) pulse-shape function  $f(t)$  in the time-evolution of statistical tensors. The user can select from a (small) library of such pulse-shape function due to different parametrization, and where an integer number of optical cycles is ensured for the sake of numerical stability.

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- **Green function expansion:** A (data) **struct** of JAC to compute an approximate (many-electron) Green function representation of an atom or ion, based on a user-specified set of reference configuration. Such a representation is provided by JAC by a list of Green function `channels::ArrayAtomicState.GreenChannel`, 1; cf. section 4.1.d.
- **Hyperfine level:** Analogon to an ASF but with well-defined total angular momentum and parity  $F = F^P: \alpha F$ , and where  $\alpha$  refers to all further quantum numbers that are needed for a unique specification. These hyperfine levels are typically expanded in terms of electronic ASF and not directly in CSF.
- **Hyperfine multiplet:** Analogon to a level multiplet but taken as group of hyperfine level. Such a hyperfine multiplet can refer to either a single electronic level or to one or several electron configurations.
- **Level (notation):**  $|\alpha \mathbb{J}\rangle \equiv |\alpha J^P\rangle; |\alpha \mathbb{J}M\rangle \equiv |\alpha J^P M\rangle$ .

Here, the multi-index  $\alpha$  formally refers to all additional quantum numbers that are needed for the unique specification of any given many-electron level or state. — In this User Guide, for instance, we shall often use  $(\alpha_i \mathbb{J}_i)$  and  $(\alpha_f \mathbb{J}_f)$  below in order to refer to the initial and final-ionic bound levels of some atomic amplitude and process.

- **Level key:** A (data) **struct** of JAC that help identifying a level by its symmetry, energy and some further property. These level keys facilitate the implementation of cascade simulations.
- **Level symmetry:** A (data) **struct** of JAC to represent  $\mathbb{J} = J^P$  in terms of its total angular momentum  $J$  and parity  $P$ .
- **Line:** A (transition) line refers to an atomic transition that is characterized in terms of a well-defined initial and final level; these lines frequently occur in the computation of atomic properties, such as cross sections or rates, angular distribution parameters. Typically, a line contains various channels (sublines), for instance, due to occurrence of multipoles or of partial waves in the decomposition of the many-electron levels and/or matrix elements.
- **Line key:** A (data) **struct** of JAC that help identifying a (transition) line by the keys of the initial and final level, its transition energy, decay strength, etc. These line keys facilitate the implementation of cascade simulations.
- **Mean field:** A (data) **struct** of JAC to compute a mean-field basis for an atom or ion, by starting from a set of user-specified reference configurations.
- **Multi-photon process:** Non-linear multi-photon absorption and emission processes occur in sufficiently intense field, including two-photon absorption and emission as well as higher-order processes; cf. section `refMultiPhotonDeExcitation`.
- **Multiplet:** Atomic levels are naturally *grouped together* into (so-called fine-structure) multiplets; most often, this term just refers to all fine-structure levels of one or a few given configurations. More generally, a multiplet can refer to any group of atomic levels, for instance, in

order to groups levels with the same total angular momentum  $J$  and/or parity  $P$ , the fine-structure levels of nearby-in-energy or overlapping configurations, etc.

- **Multipole:** In JAC, the standard notations is used for the E1 (electric-dipole), M1 (magnetic-dipole), E2 (electric-quadrupole), etc. (field) components; they are briefly referred to a *multipoles*  $\mathbb{M}$  of the radiation field. A multipole  $\mathbb{M}$  is internally characterized by its multipolarity  $L$  and its (boolean) character *electric* (= `true/false`).
- **Multipole components (fields) of the radiation field:** These multipole fields occur at many different places in atomic theory due to the electron-photon interaction, though often within slightly different contexts.
- **Multipole transition operator  $\mathbb{O}^{(\mathbb{M})}$ :** Transition operator in absorption and emission processes due to the interaction with the specified multipole component of the radiation field; these operators frequently occurs in summations  $\sum_{\mathbb{M}} \dots$  over such operators and/or the associated transition amplitudes (matrix elements).
- **Multipole moment operator  $\mathbb{Q}^{(\mathbb{M})}$ :** These operators describe the frequency-independent (part of the) interaction with a multipole component of the radiation field.
- **Nuclear model:** The nuclear charge distribution can be modelled by different – more or less – realistic models, including a point-like, uniform or Fermi-distributed nuclear charge.
- **Orbital:** In atomic physics, an orbital typically refers to a one-electron function in some radial-spherical representation and, often, only the radial function is meant (radial orbital). In the relativistic theory, moreover, one needs to distinguish between the large and small components of the orbital, as the occur for Dirac's equation in a central-field potential.
- **Pathway:** In contrast to an (atomic) line, that is characterized by an initial- and a final-level (from the corresponding multiplets), a pathway describe a sequence of three or more levels, and which are often connected via different atomic processes. These levels are usually referred to as initial, (one or several) intermediate as well as the final level of the pathway. Pathways occur naturally in dielectronic recombination of ions, in various excitation-ionization or excitation-autoionization processes and in photoionization and decay cascades.
- **Plasma model:** In JAC support is provided for a number of simple plasma models (Debye-Hückel, ion-sphere, ...) that can be applied in order to determine plasma shifts of atomic energies and rates.
- **Polarization:** Several atomic properties and processes depend on the polarization of the incident radiation field, which often need to be specified in terms of Stokes parameters.
- **Potential:** A (data) `struct` of JAC to represent a (spherically-symmetric) atomic potential.

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- **Probability propagation:** Process to propagate the occupation of the initial levels through some – photoionization or decay – cascade in order to determine final, photon and/or electron distribution. Such a probability propagation can be done either stepwise or by means of Monte-Carlo techniques.
- **QED model:** In JAC, two simplified models can be applied to estimate the dominant QED contributions to atomic level energies and wave functions: (1) **QedPetersburg** to apply a self-energy model operator from the St. Petersburg group; (2) **QedSydney** to make use of a *radiative* potential of the Sydney group.
- **Racah expression:** Such (Racah) expressions may generally include any number of Wigner  $n-j$  symbols of different kind as well as (various integrals over) the spherical harmonics, the Wigner rotation matrices and the Kronecker and triangular deltas. Obviously, the complexity of a Racah expression increases very rapidly as more Wigner symbols are involved.
- **Radial grid:** In JAC, all radial orbital functions are always represented on a (radial) grid, i.e. only the grid representation of these functions is eventually applied in the evaluation of all (single- and many-electron) matrix elements. In JAC, either an *exponential* grid, suitable for bound-state computations, or a *logarithmic-linear* grid, that still increases exponentially in the inner part and linearly in the outer part, can be selected by the user. A logarithmic-linear grid is suitable especially for collision processes and for dealing with electrons within the continuum.
- **RAS expansion:** An expansion of an ASF for a given restricted-active space of orbitals (and symmetries).
- **Relativistic angular-momentum quantum number:**  $\kappa = \pm(j + 1/2)$  for  $\ell = j \pm 1/2$  carries information about both, the total angular momentum  $j$  and the parity  $(-1)^\ell$  of the (single-electron) wavefunction.
- **Representation:** A (data) **struct** of JAC to specify an atomic state representation, i.e. a representation of atomic state vectors; different representations are supported by the program.
- **Resonances or scattering (atomic) states with a single free electron:**  $|(\alpha \mathbb{J}, \varepsilon \kappa) \mathbb{J}_t\rangle \equiv |(\alpha J^P, \varepsilon \kappa) J_t^{P_t}\rangle$   
describes a many-electron scattering wave with a single free electron in the partial wave  $|\varepsilon \kappa\rangle$ , and where  $\mathbb{J}_t$  denotes the overall symmetry of the many-electron scattering state (level).
- **Settings:** In JAC, the control of most, if not all, computations is made by specially-designed **Settings**, and which are associated with particular amplitudes, properties and processes. These settings are used in JAC in order to specify all details about the requested computation; these settings also enable one, for instance, to select individual levels or lines as well as various physical and technical parameters, such as the multipoles, gauges, etc.
- **Sharing:** A particular energy ratio of two photons (and/or electron) in multi-photon or multi-electron processes. Such sharings are given as percentages, while the energies themselves usually depend on the particular transitions.

- **Shells and subshells:** Shells and subshells are the building blocks of the atomic shell model. In the relativistic theory, each non-relativistic  $n\ell$ -shell (apart from the  $ns$ -shells) splits into two relativistic subshells due to  $j = \ell \pm 1/2$ . In JAC, the shell and subshell notations are therefore used in order to refer to electron configurations, configuration state functions (CSF), or to the orbitals of equivalent electrons. In JAC, there are special data struct's available to easily deal with and communicate the (sub-) shell occupation of levels and wave functions.
- **Statistical tensor:** Spherical tensors  $\rho_{kq}(\alpha\mathbb{J})$  that are associated with atomic levels and that help characterize the *polarization* and *alignment* of atoms and ions; these statistical tensor have well-defined symmetry properties.
- **Stokes parameter (EmStokes):** A (data) **struct** of JAC to describe the Stokes parameter for the polarization of emitted photons or electrons.
- **Target model:** A (abstract data) **struct** of JAC to represent an atomic target (cloud), for instance, for high-harmonic generation processes.
- **Tensor component:** Individual component of a statistical tensor, applied for the time-evolution of many-electron density matrices.
- **Transition amplitude:** Transition amplitudes refer to the many-electron matrix elements that provide access to all observables. The atomic structure and collision theory of many-electron atoms and ions is most naturally built upon such transition amplitudes (matrix elements).
- **Wigner  $n-j$  symbol:** The Wigner symbols are all related to the recoupling of angular momenta; they occur very frequently in the recoupling of matrix elements as well as the decomposition of angular distributions and the polarization of emitted photons and electrons.



## 1.4. A quick overview about the amplitudes, level properties and processes handled by JAC

### In JAC (partly) implemented amplitudes:

- In JAC, several many-electron (reduced) amplitudes are readily accessible. Further details about the call of these amplitudes can be found below in this User Guide or interactively by `?<module>.amplitude`.

Amplitude	Call within JAC	Brief explanation
$\langle \alpha \mathbb{J} \parallel \mathbb{T}^{(1)} \parallel \beta \mathbb{J}' \rangle$ , $\langle \alpha \mathbb{J} \parallel \mathbb{T}^{(2)} \parallel \beta \mathbb{J}' \rangle$	Hfs.amplitude	Amplitude for the hyperfine interaction with the magnetic-dipole and electric-quadrupole field of the nucleus.
$\langle \alpha \mathbb{J} \parallel \mathbb{N}^{(1)} \parallel \beta \mathbb{J}' \rangle$	LandeZeeman.amplitude	Amplitude for the interaction with an external magnetic field.
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{emission})} \parallel \alpha_i \mathbb{J}_i \rangle$	PhotonEmission.amplitude	Transition amplitude for the emission of a multipole ( $\mathbb{M}$ ) photon.
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle$	PhotonEmission.amplitude	Transition amplitude for the absorption of a multipole ( $\mathbb{M}$ ) photon.
$\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \parallel \alpha_i \mathbb{J}_i \rangle$	PhotoIonization.amplitude	Photoionization amplitude for the absorption of a multipole ( $\mathbb{M}$ ) photon and the release of an electron into the partial wave $ \varepsilon \kappa\rangle$ .
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J}_t \rangle$	PhotoRecombination.amplitude	Photorecombination amplitude for the emission of a multipole ( $\mathbb{M}$ ) photon and the capture of an electron that comes <i>in</i> the partial wave $ \varepsilon \kappa\rangle$ .
$\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle$	Auger.amplitude	Auger transition amplitude due to the electron-electron interaction and the release of an electron into the partial wave $ \varepsilon \kappa\rangle$ .
$\langle \alpha_f \mathbb{J}_f \parallel \sum \exp i \mathbf{q} \cdot \mathbf{r}_i \parallel \alpha_i \mathbb{J}_i \rangle$	FormFactor.amplitude	Amplitude for a momentum transfer $\mathbf{q}$ with an external particle or photon field.
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{weak} - \text{charge})} \parallel \alpha_i \mathbb{J}_i \rangle$	PNC.weakChargeAmplitude	Amplitude for the nuclear-spin independent Hamiltonian of the ( $P$ -odd, $T$ -even) interaction; here PNC stand for ParityNonConservation.
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{Schiff} - \text{moment})} \parallel \alpha_i \mathbb{J}_i \rangle$	PNC.schiffMomentAmplitude	Amplitude for the nuclear Schiff moment of the ( $P$ -odd, $T$ -odd) interaction.
$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{scalar} - \text{pseudo} - \text{scalar})} \parallel \alpha_i \mathbb{J}_i \rangle$	PNC.scalarPseudoScalarAmplitude	Amplitude for the scalar-pseudo-scalar ( $P$ -odd, $T$ -odd) interaction.



## In JAC (partly) implemented atomic level properties:

- In JAC implemented or partly-implemented atomic properties. For these properties, different parameters (observables) can usually be obtained by performing an `Atomic.Computation(..., properties=[id1, id2, ...])`, and if one or more of the given identifiers below are specified for this computation. For each of these properties, moreover, the corresponding (default) **Settings** can be readily overwritten by the user in order to control the computations.

Property	id	Brief explanation.
$ \alpha\mathbb{J}\rangle \longrightarrow  \alpha(J)\mathbb{F}\rangle$	HFS	Hyperfine splitting of an atomic level into hyperfine (sub-) levels with total angular momentum $F =  I - J , \dots, I + J - 1, I + J$ ; hyperfine $A$ and $B$ coefficients; hyperfine energies and interaction constants; representation of atomic hyperfine levels in a $IJF$ -coupled basis.
$ \alpha\mathbb{J}\rangle \longrightarrow  \alpha\mathbb{J}M\rangle$	LandeJ	Zeeman splitting of an atomic level into Zeeman (sub-) levels; Lande $g_J \equiv g(\alpha\mathbb{J})$ and $g_F \equiv g(\alpha\mathbb{F})$ factors for the atomic and hyperfine levels.
$K^{(\text{MS})}, F$	Isotope	Isotope shift of an atomic level for two isotopes with mass numbers $A, A'$ : $\Delta E^{AA'} = E(\alpha\mathbb{J}; A) - E(\alpha\mathbb{J}; A')$ ; mass-shift parameter $K^{(\text{MS})}(\alpha\mathbb{J})$ and field-shift parameter $F(\alpha\mathbb{J}; A)$ .
$\alpha$ -variations	AlphaX	Differential sensitivity of an atomic level $(\beta\mathbb{J})$ with regard to variation of the fine-structure constant; $\Delta E(\delta\alpha; \beta\mathbb{J}), \Delta q(\delta\alpha; \beta\mathbb{J}), K(\beta\mathbb{J})$ .
$F(q; \alpha\mathbb{J})$	FormF	Standard and modified atomic form factor of an atomic level $(\alpha\mathbb{J})$ with a spherical-symmetric charge distribution.
$\omega(\alpha\mathbb{J}) + a(\alpha\mathbb{J}) = 1$	Yields	Fluorescence & Auger decay yields of an atomic level, or averaged over an electron configuration.
$\alpha^{(\text{K}, \text{acStark})}(\omega; \beta\mathbb{J}) \dots$		Static (dc) and frequency-dependent (ac Stark) polarizabilities.
$E(\alpha\mathbb{J}; \text{plasma model})$	Plasma	Plasma shift of an atomic level as obtained for different but commonly-applied plasma models.
$ \alpha_i\mathbb{J}_i\rangle \longrightarrow  \alpha_f\mathbb{J}_f\rangle + \hbar\omega$	EinsteinX <sup>a</sup>	Photon emission from an atom or ion; Einstein $A$ and $B$ coefficients and oscillator strength between levels $ \alpha_i\mathbb{J}_i\rangle \rightarrow  \alpha_f\mathbb{J}_f\rangle$ that belong to a single multiplet (representation).

<sup>a</sup> Although the Einstein coefficients are not the property of a single level, we here still support a quick computation of these coefficients by means of the **Einstein** module for pairs of levels that are part of the same multiplet, i.e. given within a single CSF basis.

## In JAC (partly) implemented atomic processes:

- In JAC implemented or partly-implemented atomic processes. For just *one* of the listed process at a given time, different parameters (observables) can usually be obtained by performing an `Atomic.Computation(..., process=id)`, and if the corresponding identifier is specified. For this selected process, moreover, the corresponding (default) `Settings` can be overwritten by the user in order to control the computations.

Process	id	Brief explanation
$A^* \rightarrow A^{(*)} + \hbar\omega$	Radiative	Photon emission from an atom or ion; transition probabilities; oscillator strengths; angular distributions.
$A + \hbar\omega \rightarrow A^*$	PhotoExc	Photoexcitation of an atom or ion; alignment parameters; statistical tensors.
$A + \hbar\omega \rightarrow A^{+*} + e_p^-$	PhotoIon	Photoionization of an atom or ion; cross sections; angular parameters; statistical tensors.
$A^{q+} + e^- \rightarrow A^{(q-1)+} + \hbar\omega$	Rec	Photorecombination of an atom or ion; recombination cross sections; angular parameters.
$A^{q+*} \rightarrow A^{(q+1)+(*)} + e_a^-$	Auger	Auger emission (autoionization) of an atom or ion; rates; angular and polarization parameters.
$A^{q+} + e^- \rightarrow A^{(q-1)+*} \rightarrow A^{(q-1)+(*)} + \hbar\omega$	Dierec	Dielectronic recombination (DR) of an atom or ion; resonance strengths.
$A + \hbar\omega_i \rightarrow A^* \rightarrow A^{(*)} + \hbar\omega_f$	PhotoExcFluor	Photoexcitation of an atom or ion with subsequent fluorescence emission.
$A + \hbar\omega \rightarrow A^* \rightarrow A^{(*)} + e_a^-$	PhotoExcAuto	Photoexcitation & subsequent autoionization of an atom or ion.
$A + \hbar\omega_i \rightarrow A^{(*)} + \hbar\omega_f$	Compton	Rayleigh or Compton scattering of photons at an atom or ion; angle-differential and total cross sections.
$A + n\hbar\omega \rightarrow A^*$ or $A^* \rightarrow A^* + n\hbar\omega$	MultiPhotonDE	Multi-photon (de-) excitation of an atom or ion, including two-photon absorption and emission, bi-color two-photon absorption, etc.
$A + Z_p \rightarrow A^* + Z_p$	CoulExc	Coulomb excitation of an atom or ion by fast, heavy ions; energy-differential, partial and total Coulomb excitation cross sections.
$A + \hbar\omega \rightarrow A^* + e_p^- \rightarrow A^{(*)} + e_p^- + \hbar\omega'$	PhotoIonFluor	Photoionization of an atom or ion with subsequent fluorescence emission.
$A + \hbar\omega \rightarrow A^* + e_p^- \rightarrow A^{(*)} + e_p^- + e_a^-$	PhotoIonAuto	Photoionization of an atom or ion with subsequent autoionization.
$A^{q+} + e^- \rightarrow A^{(q-1)+*} \rightarrow A^{(q-1)+(*)} + \hbar\omega$ $\rightarrow A^{(q-1)+} + \hbar\omega + \hbar\omega'$	DierecFluor	Dielectronic recombination of an atom or ion with subsequent fluorescence.

Process	id	Brief explanation
$e_s^- + A \longrightarrow A^* + e_s^{-'}$	Eimex	Electron-impact excitation of an atom or ion; collision strength.
$A + e_s^- \rightarrow A^* + e_s^{-'} \rightarrow A^{+(*)} + e_s^{-'} + e_a^-$	EimexAuto	Electron-impact excitation and subsequent autoionization of an atom or ion.
$A^{q+*} \longrightarrow A^{(q+1)+(*)} + (e_a^- + \hbar\omega)$	RadAuger	Radiative-Auger (autoionization) of an atom or ion.
$A + n\hbar\omega \longrightarrow A^{(*)} + e_p^-$	MultiIon	Multi-photon ionization of an atom or ion.
$A + n\hbar\omega \longrightarrow A^{(*)} + e_{p_1}^- + e_{p_1}^-$	MultiDoubleIon	Multi-photon double ionization of an atom or ion.
$A^{q+}[\text{nucleus}^*] \longrightarrow A^{(q+1)+*} + e_c^-$	Conversion	Internal conversion, i.e. electron emission due to nuclear de-excitation.

## 1.5. Remarks on the implementation

### Why Julia ?

- Here, we just recall some of our own experiences as well as a few remarks from the literature [why JULIA have been found very helpful for developing the JAC program](#). Some of these arguments are directly adapted from the work of Bezanson *et al.* (2017, 2018).
- **Productivity:** [JULIA is a language for scientific computing that offers many of the features of productivity languages](#), namely rapid development cycles; exploratory programming without having to worry about types or memory management; reflective and meta-programming; and language extensibility via multiple dispatch (Bezanson *et al.*, 2018).
- **Productivity versus performance:** JULIA is often said to stand for the [combination of productivity and performance](#) through a careful language design and carefully chosen technologies; it never enforces the user to resort to C or Fortran for fast computations. — Moreover, JULIA’s design allows for gradual learning of modern concepts in scientific computing; from a manner familiar to many users and towards well-structured and high-performance code.
- **Productivity versus performance:** JULIA’s productivity features include: dynamic typing, automatic memory management, rich type annotations, and multiple dispatch. JULIA also supports some control of the memory layout and just-in-time compilation in order to eliminate much of the overhead of these features above (Bezanson *et al.*, 2018).
- **Productivity versus performance:** Julia promises scientific programmers the ease of a productivity language at the speed of a performance language.

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- **Productivity *versus* performance:** JULIA aims to decrease the natural gap that usually occurs between productivity and performance languages by providing **productivity features like dynamic typing, garbage collection, and multiple dispatch** but with a type-specializing just-in-time compiler and good control of the the layout of data structure in memory.
- **Productivity & language design:** Julia includes a number of (modern) features that are common to many productivity languages, namely dynamic types, optional type annotations, reflection, dynamic code loading as well as garbage collection (Bezanson *et al.*, 2018).
- **Productivity:** In JULIA, it is sometimes believed that **class-based methods are not scientifically powerful enough in order to express full abstraction in scientific computing.**
- **Performance:** A key to performance in JULIA refers to the synergy between language design, implementation techniques and programming style so that a rather small team of language implementers could create an efficient implementation/compiler (Bezanson *et al.*, 2018).
- **Performance:** There exist helpful **macros, such as `@timing function_call(parameters)` or `@benchmark function_call(parameters)` in order to analyze the performance** of the program and to find (and resolve) bottlenecks.
- **Performance & LAPACK:** All of LAPACK is available in JULIA, not just the most common functions. LAPACK wrappers are fully implemented by `ccall` and can be called directly from the Julia prompt.
- **Performance and parallelization:** One of the central motivation to build JULIA was the design of a parallel computing language. Therefore, JULIA provides different facilities for parallelism. **Two important concepts are *remote calls* and *remote references***; cf. `@parallel`. In contrast, vectorization is in JULIA NOT considered as a pre-requisite for performance.
- **High-level languages:** Most traditional high-level languages are hampered by the overhead from the interpreter, and which typically results into (much) more run-time processing of what is strictly necessary. One of these hindrances is **(missing) type information**, and which then results in the request for supporting vectorization. **JULIA is a 'verb'-based language in contrast to most object-oriented 'noun'-based language**, in which the generic functions play a more important role than the datatypes.
- **Multiple dispatch:** This concept refers to the dynamically selected implementation and to running the right code at the right time. This is achieved by overloading by means of multiple-argument function, a very powerful abstraction. Multiple dispatch makes it easier to structure the programs close to the underlying science.
- **Multiple dispatch:** **At run-time, a function call is dispatched to the most specific method applicable to the types of its arguments.** JULIA's type annotations can be attached also to datatype declarations and checked whenever typed fields are assigned to. Moreover, multiple dispatch help the programmers to extend the core languages functionalities to their particular needs.
- **Multiple dispatch** obviously reduces the needs for argument checking at the begin of a function. The overloading of functions by multiple dispatch is also called *ad-hoc polymorphism*. **Instead of encapsulating data-specific methods inside classes, JULIA's multiple dispatch is a**

paradigm in which methods are defined on combinations of data types (classes). JULIA demonstrates that this paradigm is remarkably well-suited for numerical computing.

- **Multiple dispatch** is perhaps the most prominent feature of JULIA's design and is crucial for the performance of the language and its ability to inline code efficiently. Another promise of multiple dispatch is that it can be used to extend existing behavior with new features.
- **JULIA's type system:** To a large extent, JULIA code can be implemented without any mentioning of types (in contrast to C and Fortran), and which are derived by data-flow interference. JULIA's expressive type system supports an **agressive code specialization against run-time types** and also allows the use of optional type annotations.
- **JULIA's type system:** **User's own types are also first class in JULIA**, that is there is no meaningful distinction between built-in and user-defined types. There are mutable and (default: immutable) composite types.
- **JULIA's type system:** JULIA distinguishes between concrete data types, that can be instantiated, and abstract types, that can (only) be extended by subtypes in order to built up an hierarchy of such types.
- **JULIA's type system *versus* object oriented programming:** **JULIA's design does not support the class-based object-oriented programming style**, that is familiar from Java, and it also **lacks the usual encapsulation** going back to Smalltalk: Instead, all fields of a (data) **struct** are public and can be accessed freely within the code.
- **Data type stability:** In JULIA, users are always encouraged to make their programs, whenever possible, **type stable**. Much of the efficiency of a JULIA code relies on being type stable and on devirtualization and inlining.
- **Name space and code selection:** JULIA name space allows for the use of the same vocabulary in different circumstances, and which makes programs easier to read. In particular, it uses the same mechanism of code selection at the lowest and highest levels and is therefore **able to select the right method, either already at compile time or later at run time**.
- **Use of macros:** **A macro is a function that runs at parse time**. It takes symbolic expressions in and returns transformed expressions out, which are inserted into the code for later compilation. The output of macros is often *inlined* into the code.
- **Optimization in JULIA:** **The JULIA compiler is built on three strategies that are still performed on a high-level intermediate representation of the code**, while all native code generation is later delegated to the LLVM compiler infrastructure. These optimization strategies are: (1) method inlining which devirtualizes multi-dispatched calls and inlines the call target; (2) object unboxing to avoid heap allocation; and (3) method specialization where code is special cased to its actual argument types (Bezanson *et al.*, 2018).

## Requests in building large software packages:

- The design and implementation of large software packages makes it advisable to follow some *common* rules and requests for those, who wish or need to contribute. For the design of good physics software, the following (and some further) requests were given by Post and Kendall (2004).
- **Physical models:** In general, better physics is more important than better computer science. It is recommended to use modern but well-proven computer-science techniques, and a 'physics code' should not be a computer-science research project. Instead, one should use best engineering practices to improve quality rather than processes. Emphasis should be given to improvements of useful physics capabilities. Do not use the latest computer-science features; let the new ideas mature first. *Better physics is the most important product of the code.*
- **Code development and evolution:** The scale of code-development can become truly immense; a good overview/quantitative database about (previously) successful software projects in some given field is typically required for good estimation for resources and schedules. *It is easy to loose motivation on a project that last years and which has few incremental deliveries. Continues replacement of code modules is recommended as better tools and techniques are developed.* Every code development typically proceeds in steps: First develop a core capability (with a small team) and let this small core be tested by users and, if successful, add further capabilities (so-called incremental delivery).
- **Success criteria:** One of the important success criteria is the costumer focus. — *What do the user really need ?*
- **Code specification:** Some flexibility in the requirement specification phase is essential because it is difficult to predict when (or if) a new algorithm/approach will be available. *There is a need to pursue multiple approaches for algorithms and modules near to the critical path.* If one approach is not feasible, another one can be used.
- **External users and developers:** The validation of physics models is a critical issue for all extended software packages and need to be done with regard to authoritative reference data.
- **Documentation** should be intended to cover all needs of the beginner through to the expert user, who wishes to expand the capabilities of some tools.
- **Demands on programs for electronic-structure calculations:** In practice, modern electronic structure calculations pose enormous challenges to create complex but yet robust software. In atomic physics, there is still an increasing demand for accurate large-scale computations of (atomic) processes and cascades. These demands comes along with an escalating size and complexity of the applied computational models, and they have been fueled by computers of moderate cost, on which large and complex simulations have become ever more possible.

- **Computational infrastructure:** Though various (highly) specialized language implementation are known in different research areas of physics, such as software tools from CERN, most scientific communities do not have the resources that are necessary to build and maintain their own computational infrastructure.

## 1.6. Brief comparison of JAC with other existing codes

We here compile some rather (incomplete) information about other existing atomic structure codes for the computation of level energies, transition rates, cross sections, etc. We just remind to some of their special features and briefly summarize how these codes differ from the implementation of the JAC toolbox. These codes are ordered chronologically how they first occurred (or were published) in the literature.

### CATS (Cowan: 'Theory of Atomic Spectra', 1980):

- CATS, the Cowan Atomic Structure code, relies on a semi-relativistic self-consistent potential and makes use of either a nonlocal Hartree-Fock (HF) or local Hartree-Fock-Slater (HFS) approach in order to deal with the exchange interaction.
- **Level energies & ASF:** Since the late 1960s, Cowan's HFX code has set some – well-approved – standard for many experimentalists and has, together with his well-known textbook, helped many (atomic) physicist to understand and make use of atomic structure theory. While these earlier developments are highly appreciated (and are still utilized for various applications), **CATS has several severe limitations in the layout and implementation of the code, which are hard to overcome.** The same applies also for the approximate computation of various atomic properties, such as transition probabilities, photo-excitation and ionization cross sections and Auger rates.
- Cowan's code has been found a mature tool for identifying new lines, especially if additional information is available from experimental observations in order to support further empirical adjustments of energies and ASF.
- **Display of data & spectra:** Several tools and facility-programs have been developed for CATS in order to display the computed data and to compare them with each other and with experiment. The success of some of these tools has or will motivate us for developing some graphical interfaces for the display of (radial) orbitals, line spectra, etc. also for the JAC toolbox.

## MCDFME (Desclaux *et al.*, 1975; Indelicato 2000 and later):

- **MCDFME code:** The Multi-configuration Dirac-Fock and General-Matrix-Element code by Desclaux and Indelicato includes one-electron one-loop corrections (self-energy and vacuum polarization) and two-loop one-electron corrections (two-loop self-energy, mixed self-energy as well as vacuum polarization diagrams, Källén-Sabry potential contributions).
- **MCDFME code:** This code also includes vacuum-polarization due to the electronic potential, retardation beyond the Breit interaction and the effect from the electron-electron interaction on the self-energy evaluated within the so-called **Welton method**. From the comparison with the model operator approach by Shabaev and co-workers, a relative difference of  $\leq 0.01\%$  was found for  $Z = 18$ .

## GRASP (Grant *et al.*, 1980; Jönsson *et al.*, 2013; Fischer *et al.*, 2018):

- **Level energies & ASF:** GRASP has originally been developed since the late 1960s in order to provide level energies and eigenvectors for quite general open-shell atoms. Much emphasis during the last two decades was placed upon the systematic improvement of these energies and representations. While we also provide such level energies and atomic state functions by the JAC toolbox, we *do not* intend (at present) to facilitate such extensive wave function expansions. Instead, **approximate level energies and ASF are mainly considered as the technical preposition in order to describe further atomic properties and processes**. With the computation of restricted-active space (RAS) representation of atomic ASF, however, we shall provide in JAC useful features for a (more or less) systematic improvement of such (*ab-initio*) ASF representations.
- **Transition probabilities & oscillator strength:** Apart from the level energies, GRASP has been extensively applied in order to compute and tabulate transition probabilities for many atoms, ions and isoelectronic sequences throughout the periodic table of elements. **With JAC, we provide analogue or even simpler tools for such computations**. Moreover, (the many-electron amplitudes that arise from) the coupling of the radiation field provides the natural *building blocks* for a large number of other atomic processes, cf. section 8 on atomic processes below.
- **Selected advantages of JAC:**
  - The use of the JULIA language clearly facilitates the coding and maintenance of the JAC code, when compared to previous Fortran codes.
  - JAC enables one to handle a much larger number of atomic properties and processes, the computation and simulation of atomic cascades as well as several other types of computation.
  - SCF fields can be generated in JAC at different levels of complexity, including several (local) mean-field potentials as well as, in the future, the average-level and extended average-level schemes.



- JAC supports a much larger flexibility in handling the output data and, in particular, does not know any relevant limitation with regard to the length of filenames (in contrast, for instance, to 24 letters in grasp2K).

### RMATRIX (Berrington *et al.*, 1995):

- The Belfast RMATRIX code is readily available and used by a (small) group of users, and with an updated version from 2020. Already the 1995 version was based on a number of previous versions and included various extensions by the Opacity Project and the Iron Project team.
- Various parallel R-matrix codes have been developed as well from modified versions of the serial RMATRIX code, the non-exchange R-matrix programs and the Dirac Atomic R-matrix Code (DARC).
- Calculations with the RMATRIX code can be either in *LS*-coupling, or in an intermediate-coupling scheme by including terms of the Breit-Pauli Hamiltonian.

### LADW (Los Alamos Atomic Physics, 2000 and later):

- **LADW:** The Los Alamos Distorted-Wave code, has been developed by Sampson and co-workers; it has been further utilized and partly incorporated into the (so-called) LASER code.
- Interface to Los Alamos Atomic Physics Codes is some gateway to the set of atomic physics codes developed at the Los Alamos National Laboratory. These codes include the well known Hartree-Fock method Cowan, developed at LANL, as well as electron-impact excitation cross sections by using the distorted wave approximation (DWA).

### HULLAC (Bar-Shalom *et al.*, 2001):

- **HULLAC:** The Hebrew University Lawrence Livermore Atomic Code (HULLAC, Bar-Shalom *et al.* 2001) is a computational platform for atomic structures and cross sections that help modelling emission spectra as well as atomic processes in plasma; this code is based on a parametric potential method and has been applied to many medium and heavy elements.
- **HULLAC:** This code applies fully relativistic orbitals to calculate atomic energy levels and radiative transition probabilities. These orbitals are obtained as solution of the **Dirac equation with a local and parametrized central-field potential  $U(r)$**  to represent the nucleus and the spherically averaged interaction with all other electrons in the atom. The central-field potential is optimized such that energy levels of the ground state and a few low-lying excited states agree with the NIST (or related) tables. Although such a semi-empirical optimization procedure requires less computational resources, it hampers a systematic improvement of the results.

## 1. Overview about JAC. Structure of this User Guide

- **HULLAC** has been developed as an integrated code for calculating the atomic structure and cross sections for collisional and radiative atomic processes, based on the relativistic configuration interaction method.
- In HULLAC, all collisional cross sections are calculated in the distorted wave approximation with special emphasis on efficiency.

### RATIP (Fritzsche, 2001 and 2012):

- **Relativistic CI (RELCI):** While RATIP has always used the SCF computations and orbitals from the GRASP code, it also supports relativistic configuration-interaction (CI) computations. For several years, it also helped define a new standard for performing the angular intergration (angular coefficients; cf. Gaigalas *et al.*, 2002). These angular coefficients are presently utilized in JAC by an interface to the Fortran modules of RATIP.
- **Atomic properties and processes:** RATIP was (one of) the first codes that made use of GRASP's systematically improved wave functions in order to compute a good number of atomic properties and processes, such as relaxed-orbital transition probabilities (REOS; Fritzsche and Froese Fischer 1999), Auger rates, photoionization cross sections and angular parameters, radiative and dielectronic recombination rates, electron-impact excitation cross sections, and several others. **The experience with RATIP has been found central for the development of JAC and has find its continuation here.**

### ELSEPA (Salvat *et al.*, 2005):

- **ELSEPA:** facilitates the computation of differential cross sections, total cross sections and transport cross sections for the (single) elastic scattering of electrons and positrons by neutral atoms, positive ions as well as randomly oriented molecules. Moreover, this code help compute scattering amplitudes and spin-polarization functions for projectiles with kinetic energies  $E_{\text{kin}} \lesssim 5$  MeV by means of a conventional relativistic Dirac partial-wave analysis.
- The calculations are performed by means of relativistic (Dirac) partial wave analysis for an effective local central-interaction potential. The scattering by molecules is described by making use of an *independent-atom* approximation, i.e. by adding coherently the waves scattered from all the atoms in the molecule as well as by performing an average over random orientations of the molecule.
- For high kinetic energies, however, the convergence of the partial-wave series becomes slow and is then replaced by some approximate factorization method. ELSEPA has been found useful to explore the sensitivity of differential cross sections for different choices of the (static) interaction potential.

### GEANT4 (Amako *et al.*, 2005):

- **GEANT4** is an object-oriented toolkit for analyzing and simulating the passage of particles through matter; this toolbox provides a **variety of semi-empirical models in order to simulate the underlying electromagnetic and hadronic interactions**. GEANT4 combines theoretical models with experimental data or parameterizations of such data.
- **GEANT4** is especially based on a number of separate packages in order to deal with the electromagnetic interactions of (either) electrons, muons, positrons, photons, hadrons and ions as well as for dealing with specific energy ranges of the processes that are taken into account by this toolbox.
- **Implemented processes:** The electro-magnetic packages of the GEANT4 toolbox include: multiple scattering, ionization, Bremsstrahlung, positron annihilation, photo-electric effect, Compton and Rayleigh scattering, pair production, synchrotron and transition radiation, Cherenkov effect, refraction, reflection, absorption, scintillation, fluorescence as well as Auger electron emission (Amako *et al.*, 2005). **Less attention has been placed however on the electronic structure of atoms and ions**. However, it is not obvious how easily this toolbox can be applied in order to predict the spectra and behaviour of individual atoms and ions.
- **GEANT4** mainly covers the energy range from 1 keV to 10 PeV; for these energies, the **atomic electrons are treated as quasi-free particles which, apart from photoelectrons, is often a really crude approximation**. For all these processes, moreover, GEANT4 always considers *fixed* atomic nuclei with no recoil momentum.

### BSR (Zatsarinny 2006):

- **BSR code:** The B-spline R-matrix (BSR) method and the accompanying code was developed by Zatsarinny and coworkers; this code computes **photoionization and electron-impact excitation amplitudes**. From these many-electron amplitudes, the cross sections and other experimentally observable parameters can be obtained. Apart from these amplitudes, the BSR code also support simple bound-state computations for the energies and oscillator strengths.
- The BSR code solves the close-coupling equations in coordinate space and, thus, is complementary to the usual convergent close-coupling (CCC) computations for electron-ion collisions in momentum space. The BSR code applies a finite-element (B-spline) rather than a finite-difference approach in order to compute the Hamiltonian matrix elements in the inner region.
- The BSR code supports the **use of non-orthogonal sets of one-electron orbitals** in order to account for the term-dependence of the valence orbitals. This enables one to apply an economical and flexible construction of both, bound-state wave functions and scattering states and, hence, the treatment of electron-impact single-ionization as well as photon-driven double ionization processes. Still, setting up the

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Hamiltonian matrix can be (very) expensive for complex targets, and the large number of resonances may require to deal with many thousands of collision energies separately; this makes it difficult to include details from the asymptotic region.

- The (published) BSR code is a serial non-relativistic version that can be applied also for (semi-relativistic) Breit-Pauli computations. A relativistic DBSR as well as MPI-parallelized versions exists and has been applied by a small group of people (Zatsarinny, 2020; <https://github.com/zatsaroi>).

### FAC (Gu 2008):

- **FAC** is a well-known relativistic atomic structure code based on the (standard) Dirac-Fock-Slater method and on some fit of free parameters in order to define the atomic potentials.
- **Level energies & wave functions:** When compared to GRASP, the simplified and more object-oriented treatment of wave functions in the FAC code has partly stimulated us in developing the JAC program. While JAC enable the user to perform also systematically improved computational models, the support of some first and perhaps rather simple approximation has been found crucial and need to be supported, for example, for dealing with cascades and time-evolutions. **Angular integration:** FAC makes use of the angular coefficients by Gaigalas *et al.* (2001), which is based on quasi-spin space and the coupling of second-quantized operators.
- **Single-multipole approximation:** Although FAC supports different multipoles in the computation of decay rates and (photoionization) cross sections, it does not support interference contributions from different multipoles, i.e. the summation of amplitudes from different multipoles. Moreover, it remains unclear how easily the contributions from different multipole fields could be added together due to different phases (phase conventions) and prefactors.
- **Simulation of atomic processes:** Several features of the FAC code have stimulated and have been adapted to the JAC program. Many atomic processes, which are supported by FAC, can now be handled, and often more readily, within JAC
- **Electron-impact excitation and ionization:** In FAC, the implemented (first-Born) distorted-wave approximation for the electron-impact excitation and ionization cross sections is very similar to a number of previous implementation used in astro- and plasma physics.
- **Selected advantages of JAC:**
  - JAC is (almost) completely programmed within the Julia language, and this simplifies the further extension of the code;
  - JAC always applies a relativistic representation of all one-electron orbitals in terms of their large and small components;
  - JAC also supports both, the Dirac-Coulomb and well as Dirac-Coulomb-Breit Hamiltonians.

### tRecX (Scrinzi 2010):

- **tRECX code:** This code provides a general framework for solving initial-value problems of the form

$$\frac{\partial}{\partial t} \Psi = \mathbb{L}[\Psi, t] + \Phi(t)$$

for any number of spatial dimensions and for different coordinate systems. While the main emphasis was placed on some *linear* evolution operators  $\mathbb{L}$ , non-linear operators can be used as well.

### AUTOSTRUCTURE (Badnell, 2011):

- AUTOSTRUCTURE is a rather general atomic code for the description of free-bound electron and photon collision processes, based on the original SUPERSTRUCTURE code bei Eissner and coworkers.
- AUTOSTRUCTURE supports efficient computations of dielectronic recombination cross sections and rates, especially if large numbers of highly-excited states are involed in the radiative stabilization of an atom or ion.
- The code applies the Breit-Pauli distorted wave method for the electron-impact excitation of atomic ions in order to support problems that are impractical or even impossible for more sophisticated methods.
- AUTOSTRUCTURE mainly computes (Maxwell-averaged) effective collision strengths at temperatures with a broad ionic abundance, rather than the detailed collision strengths at all the energies.
- **AUTOSTRUCTURE:** This code applies Slater determinants and an explicit coupling of angular momenta (without the concept of parentage). In this code, therefore, first an uncoupled Slater basis is formed before further transformations are to either *LS* or *LSJ* coupling.

### LASER (Fontes *et al.*, 2015):

- **LASER:** The Los Alamos Suite of Relativistic atomic physics code, comprises various codes for fundamental atomic structure calculations as well as for various processes, such as photoexcitation, electron-impact excitation and ionization, photoionization and autoionization, within a consistent framework. It may help develop atomic physics models in either configuration-average and fine-structure modes, and by including a proper self-consistency. This suite of code has been developed for more than 20 years.

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- **Applications of the code:** The LASER code has been applied to the collisional-radiative modeling of plasma, for line identifications in plasma spectroscopy and for testing relativistic atomic and quantum electro-dynamics (QED) theories. The code also has been utilized for feasibility studies of collisional-radiative modeling of non-LTE (optically thin) gold plasmas for and to questions from inertial confinement fusion.
- **Approximations:** LASER mainly employs the semi-relativistic theory, similar to or by directly applying Cowan's atomic structure code (CATS). All bound-electron wavefunctions are obtained from the semi-relativistic approach in CATS, while the continuum-electron orbitals are obtained as solutions of Schrödinger's equation from some specialized routines. In the LASER code, the bound and continuum radial wave functions are typically single-component orbital functions associated with the Schrödinger equation, rather than two- or four-component spinors associated with the Dirac equation.
- **Features:** Cross sections and other properties can be calculated with the LASER code for five fundamental processes: photo-excitation, photo-ionization, electron-impact excitation and ionization and autoionization. The code supports the IPCRESS (Independent of Platform and Can be Read by Existing Software Subroutines) random-access binary file format that is used to store large amounts of data, and which can be ported to almost any platform.

## QEDMOD (Shabaev *et al.*, 2015):

- **Self-energy model operator,  $\mathfrak{h}^{(\text{QED})}$ :** Computes the matrix elements of a model QED operator  $\mathfrak{h}^{(\text{QED})}$  that accounts for the Lamb shift in accurate atomic-structure calculations. However, there arises various technical difficulties with QEDMOD, which make a direct application of the code and its combination with GRASP or JAC rather cumbersome.
- **Effective QED Hamiltonian:** The QEDMOD code provides one-electron matrix elements that, in principle, can be added directly to any CI matrix and, hence, to the computation of level energies and multiplets. For the vacuum polarization, it includes automatically both, the Uehling and Wichmann-Kroll terms.
- **Selected advantages of JAC:** A simplified version of the effective QED Hamiltonian from QEDMOD has been implemented also in JAC.

## QUANTICS (Worth, 2019):

- **QUANTICS toolbox:** For small molecules, this code help solve the time-independent Schrödinger equation as well as the (time-dependent) Liouville-von Neumann equation by propagating density matrices. The package comprises various auxiliary programs to set-up calculations and to analyse different outputs.

- QUANTICS has been promoted as a community code of the UK Collaborative Computational Project for Quantum Dynamics (CCPQ) and of the European E-CAM project, an e-infrastructure for software development by the Centre European de Calcul Atomique et Molculaire (CECAM).

## 1.7. To-do's, next steps & desired features of the JAC program

### Encouragement for external users and developers:

- While we (will further) develop JAC for applications that are requested explicitly by selected users, here I shall compile a number of **desired features which will make JAC even more powerful and/or easy to use**. For these *additional features*, I wish to encourage collaboration with external developers. In particular, I welcome all help from outside if the overall style of the program is maintained and if some prior consensus exist how to add and implement additional features.
- New code developments may concern incremental improvements but also multiple approaches for selected algorithms and modules in order to provide well-defined alternatives, for instance, if some particular approach does not work properly under certain circumstances.
- Emphasis will first be placed upon those applications that receive good attention by the community.

### 1.7.a. To-do lists

#### Urgent to-do's:

- Design and development of a robust continuum solver.
- Design and development of a module for the computation of electron-impact excitation cross sections.
- Design and implementation of a DHF self-consistent-field that include the full exchange interaction into the MCDHF equations.
- **Use of JAC on remote clusters:** Work out some prototype example how 'job scripts' (similar to those from examples) can be exported and handled at remote cluster computers and how to re-import the results later on.

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- `Documenter.jl`: How to establish an alternative and web-based documentation of JAC.

### Short-term to-do's:

- Implement ... `Jac.modify("level energies: interactive", multiplet::Multiplet)`
- Implement ... `Jac.display("level energies: HFS", multiplets::HFSMultiplet[..])`
- Implement ... `Jac.display("level energies", multiplets::Multiplet[..])`
- Implement ... `Jac.display("configuration list: from basis", basis::Basis)`
- **Alternative diagonalization procedures:** We shall look for and establish 1-2 further diagonalization procedures that work with the same input/output data or very similar as `Jac.diagonalize("matrix: Julia, eigfact", matrix::ArrayFloat64,2)` ... but allows to just find certain low-lying eigenstates or certain bands of eigenstates.

### Medium- and long-term to-do's:

- Implement ... `Jac.apply("restrictions: CSF list", csfs::Csfr[..], basis::Basis)` ... to apply a number of restrictions interactively to a list of CSF. The procedure might proceed in three steps: (i) by taking and applying a restriction to a given CSF list; (ii) showing the number of CSF to be deleted from the given list; and (iii) making this restrictions explicit. The user would then be requested to enter one restriction after the other, and until the reduction process is terminated by the user. A `csfList::ArrayCsfr,1` is returned. — Here we might adopt especially the form of restrictions from the RATIP program.
- Implement ... `Jac.apply("biorthogonal transformation", mpltb::Multiplet, mpltb::Multiplet, grid::Radial.Grid)`
- Compute and extract the Fano parameters and line-shapes for a given set of autoionizing resonances.
- **Atoms in plasma environments:** Implement 2-3 plasma models in order to deal with atoms in a few (averaged but) different plasma environments. This usually works via some effective `Jac.InteractionStrength.XL_plasma_ionSphere(L::Int64, a::Orbital, b::Orbital, c::Orbital, d::Orbital, lambda::Float64)` that depends on some particular model and plasma parameters; cf. Saha and Fritzsche, PRE (2004). This will likely require also the set-up of a corresponding Hamiltonian matrix: `Jac.compute("matrix: plasma, ion-sphere model", settings::Plasma.Settings, basis::Basis)`.



## 1.7.b. Discussion about (further) implementations

### Issues that need to be discussed:

- **Parallelization and performance of the code:** How can one make the code parallel without that the user need to know and provide much information about the cluster that is used for the computations.
- **Modern input forms in scientific computing:** Which modern formats do exist ?? Which simple graphical (applet) features exist ? How useful can be tomel.jl ??

## 1.7.c. Desired medium- and long-term features of the JAC program

### Plotting and visualization:

- Implement ... `Jac.plot("spectrum: oscillator strength over energy, emission", lines::RadiativeLine[..]; widths=value::Float64)` and `Jac.plot("spectrum: oscillator strength over energy, absorption", lines::RadiativeLine[..]; widths=value::Float64)`
- Implement ... `Jac.plot("spectrum: transition rates over energy, Gaussian", lines::RadiativeLine[..]; widths=value::Float64)` and `Jac.plot("spectrum: transition rates over energy, Lorentzian", lines::RadiativeLine[..]; widths=value::Float64)`
- Visualize the convergence of energies or other results as function of the size of the computation and/or model space.
- Visualize the level structure of a given multiplet, for instance, by displaying the level energies in different colors for different (leading) configurations or groups of such configurations.
- Plot energy diagrams for an atomic cascade together with its major decay pathes; here, it would be highly desirable to be able to 'zoom' into such a energy diagram in order to easily understand how the levels form different configurations *group* together.

### More physics in Jac ?

- **Atomic spectra:** Evaluate and display the photoabsorption spectra from calculated photoexcitation and photoionization cross sections.

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### ➤ Computation of approximate single-electron properties:

- Subshell-dependent differential and total photoionization cross sections; cf. Eichler and Meyerhof (1995, Eqs. 9.34 and 9.47).
- Non-relativistic total K-shell or subshell radiative recombination cross sections by using the Stobbe cross section; cf. Eichler & Meyerhof (1995, Eqs. 9.49–9.50)

### ➤ Collisional-radiative models: Such collisional-radiative models have been frequently applied to describe the evolution of plasma and to derive information for plasma diagnostics. JAC can provide many (if not all) of the rates and cross sections that are needed in order to built-up such models for selected (plasma) environments.

### ➤ Electron-momentum distributions: Provide the expectation values $\langle p^k \rangle$ , $k = -2, \dots, 4$ of the single-electron radial momentals, i.e. the radial orbitals in momentum space. These expectation values are frequently applied in crystallography and in studying Compton profiles; cf. Koga and Thakkar (1996), Eq. (10-11). In the first instance, these expectation values could be readily provided as semi-empirical values by following the work above.

## 2. Dirac's hydrogenic atom

### 2.1. Energies and wave functions

#### Notations & application in Jac:

- In JAC, non-relativistic hydrogenic orbitals can be easily generated by a call to `JAC.HydrogenicIon.radialOrbital()`.
- JAC also provides approximate radial (relativistic bound-state) orbitals by just applying the kinetic-balance condition to the corresponding non-relativistic radial orbital and by re-normalizing it afterwards.

#### Dirac's (one-electron) energies:

- **Relativistic bound-state energy spectrum:** For electrons with principal quantum number  $n$  and angular-momentum quantum number  $\kappa$ , the relativistic bound-state energy spectrum is given by

$$\varepsilon_{n\kappa} = mc^2 W_{n\kappa} = \frac{mc^2}{\sqrt{1 + \left(\frac{\alpha Z}{n' + s}\right)^2}}$$

where  $\alpha$  is the fine-structure constant,  $n' = n - |\kappa| = 0, 1, 2, \dots$  is the number of nodes, and  $s = \sqrt{\kappa^2 - (\alpha Z)^2}$ , respectively.

- Since  $W_{n\kappa} < 1$ , it can be expanded in terms of  $(\alpha Z)$  and written as

$$W_{n\kappa} = 1 - \frac{1}{2} \frac{(\alpha Z)^2}{n^2} - \frac{1}{2} \frac{(\alpha Z)^4}{n^3} \left( \frac{1}{j + 1/2} - \frac{3}{4n} \right) - \dots$$

where the second term, multiplied with  $mc^2$ , represents the nonrelativistic binding energy of a hydrogenic atom.

## 2. Dirac's hydrogenic atom

- For a given (principal) shell  $n$ , the eigenvalues are the same for equal values of  $j$  but are different for equal values of  $\ell$ . For a given value of  $\ell$ , the spin-orbit splitting between states with  $j = \ell + 1/2$  and  $j = \ell - 1/2$  gives rise to the fine-structure in the spectrum of hydrogen-like atoms. The equation above shows that the relativistic corrections to the one-electron energies decreases rapidly with  $n$ . The relativistic correction to the non-relativistic energy is therefore important, especially for highly-charged ions with rather large  $Z$ .
- Number of nodes in relativistic orbitals: The large component  $P_{n\kappa}(r)$  has  $n - \ell - 1$  nodes, as in the non-relativistic case, while the small component  $Q_{n\kappa}(r)$  has  $n - \ell - 1$  nodes for  $\kappa < 0$  but  $n - \ell$  nodes for  $\kappa > 0$ , respectively.

### Non-relativistic radial orbitals:

- Radial orbital functions  $P(r)$ : These functions in the non-relativistic orbital  $\psi(r, \vartheta, \varphi) = \frac{P(r)}{r} Y_{\ell m}(\vartheta, \varphi)$  is known to obey the radial Schrödinger equation and belongs to either the discrete part of the spectrum with the (negative) energies  $E_n = -\frac{Z^2}{2n^2}$  a.u.  $< 0$  (bound states), or to the continuous part for all energies  $E > 0$  (the so-called free-electron or continuum states).
- Radial orbital functions  $P(r)$ : An analytic solution of the radial functions  $P(r)$  in terms of the confluent hypergeometric function  $F(\alpha, \beta; x)$  are known for both, the bound-states

$$P_{n\ell}(r) = r^{\ell+1} \frac{1}{(2\ell+1)!} \sqrt{\frac{(n+\ell)!}{(n-\ell-1)! 2n}} \left(\frac{2Z}{n}\right)^{3/2+\ell} e^{(-\frac{Zr}{n})} F\left(-(n-\ell-1), 2\ell+2; \frac{2Zr}{n}\right)$$

as well as for the continuum ( $E > 0$ ) with  $k = \sqrt{2E}$  and  $n' = Z/k$

$$P_{E\ell}(r) = \frac{2\sqrt{Z}}{\sqrt{1-e^{-2\pi n'}}} \left[ \prod_{s=1}^{\ell} \sqrt{s^2 + n'^2} \right] \frac{(2kr)^{\ell}}{(2\ell+1)!} e^{-ikr} F(in' + \ell + 1, 2\ell + 2, 2ikr).$$

### Non-relativistic orbitals in momentum representation:

- **Wave function in momentum representation:** These wave functions are often written in terms of the wave vector  $\mathbf{k} = (k, \vartheta_k, \varphi_k) = \mathbf{p}/\hbar$  and the spherical Bessel functions  $j_\ell(z) = \sqrt{\pi/2z} J_{\ell+1/2}(z)$

$$G(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int d^3r \exp(-i \mathbf{k} \cdot \mathbf{r}) \psi(\mathbf{r})$$

$$G_{n\ell m}(\mathbf{k}) = g_{n\ell}(k) Y_{\ell m}(\vartheta_k, \varphi_k), \quad g_{n\ell}(k) = (-i)^\ell \sqrt{\frac{2}{\pi}} \int_0^\infty dr r P_{n\ell}(r) j_\ell(kr), \quad \int_0^\infty dk k^2 g_{n'\ell}^*(k) g_{n\ell}(k) = \delta_{n'n}.$$

- **Hydrogenic orbitals in momentum representation:** The hydrogenic orbitals in momentum representation can be written in terms of the Gegenbauer polynomials  $C_n^\ell$  and the reduced momentum coordinate  $x = n k a_o/Z$  as

$$g_{n\ell}(k) = \left(\frac{a_o}{Z}\right)^{3/2} \left[ \frac{2}{\pi} \frac{(n-\ell-1)!}{(n+\ell)!} \right]^{1/2} n^2 2^{2(\ell+1)} \ell! \frac{(-ix)^\ell}{(x^2+1)^{\ell+2}} C_{n-\ell-1}^{\ell+1} \left( \frac{x^2-1}{x^2+1} \right)$$

$$C_{n-\ell-1}^{\ell+1} \left( \frac{x^2-1}{x^2+1} \right) = \frac{(2n+\ell+n)!}{n! (2\ell+1)!} F \left( -n; n+2\ell+2; \ell+3/2; \frac{1}{x^2+1} \right).$$

### Relativistic radial orbitals:

- **Radial orbital functions  $P(r)$ ,  $Q(r)$ :** Analogue to the non-relativistic case, the solution  $\psi(\mathbf{r})$  of the Dirac equation can be separated for a spherical potential into a radial and angular part

$$\psi_{\kappa m}(r, \vartheta, \varphi) = \frac{1}{r} \begin{pmatrix} P(r) \Omega_{\kappa m}(\vartheta, \varphi) \\ i Q(r) \Omega_{-\kappa m}(\vartheta, \varphi) \end{pmatrix},$$

where  $\Omega_{\kappa m}(\vartheta, \varphi)$  denotes a standard Dirac spin-orbital function, and where  $\kappa = \pm(j+1/2)$  for  $\ell = j \pm 1/2$  is called the *relativistic* angular-momentum quantum number.

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- **Relativistic angular-momentum quantum number:** Owing to the definition of  $\kappa = \pm 1, \pm 2, \dots$ , this relativistic quantum number carries information about both, the total angular momentum  $j$  and the parity  $(-1)^\ell$  of the orbital function.
- **Angular-momentum operator with eigenvalues  $\kappa$ :** In the spherical spinors, there occur generally two values of  $\ell$  for each  $j$ :  $\ell = j \pm 1/2$ , and for spinors with different parity. Instead of the quantum numbers  $j, \ell$ , it is possible to introduce the (relativistic) angular momentum operator

$$k = -2\mathbf{l} \cdot \mathbf{s} - 1, \quad k \Omega_{\kappa m}(\vartheta, \varphi) = k \Omega_{j\ell m}(\vartheta, \varphi) = \kappa \Omega_{\kappa m}(\vartheta, \varphi).$$

- **Large & small component:** The radial part of a relativistic wavefunctions is given by the two functions  $P(r)$  and  $Q(r)$ , and which are often called the *large* and *small* components.
- **Dirac spin-orbital:** As usual, the Dirac spin-orbitals can be written in terms of the spin-1/2 Pauli spinors  $\chi_\pm$  and the spherical harmonics by

$$\Omega_{\kappa m}(\vartheta, \varphi) = \sum_{m_\ell} \langle \ell m_\ell, 1/2, m - m_\ell | jm \rangle Y_{\ell m_\ell}(\vartheta, \varphi) \chi_{m - m_\ell}, \quad \int d\Omega \Omega_{\kappa m}^*(\vartheta, \varphi) \Omega_{\kappa' m'}(\vartheta, \varphi) = \delta_{\kappa, \kappa'} \delta_{mm'}.$$

$$Q(r) = \frac{1}{2mc} \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P(r).$$

The two-component angular-momentum function  $\Omega_{\kappa m}(\vartheta, \varphi)$  are often also referred to as **spherical spinors**.

## 2.2. Coulomb-Green function

### Relativistic radial Coulomb-Greens function:

- **Radial Green function of the Dirac equation:** Following Yerokhin and Shabaev (1999, appendix D), the radial Green function of the Dirac equation for electrons with the angular-momentum symmetry  $\kappa$  can be written in the form:

$$G_\kappa(\omega, r_1, r_2) = -\frac{1}{W_\kappa(\omega)} \left[ \phi_\kappa^\infty(\omega, r_1) \phi_\kappa^{0T}(\omega, r_2) \Theta(r_1 - r_2) + \phi_\kappa^0(\omega, r_1) \phi_\kappa^{\infty T}(\omega, r_2) \Theta(r_2 - r_1) \right]$$

where  $\phi_\kappa^0(\omega, r)$  and  $\phi_\kappa^\infty(\omega, r)$  are solutions of the radial Dirac equation, bounded at the origin and at the infinity, and where  $W_\kappa(\omega)$  is the Wronskian.

- The functions  $\phi_\kappa^0(\omega, r)$  and  $\phi_\kappa^\infty(\omega, r)$  can be calculated in terms of the Whittaker functions of the first and second kind, although special care has to be taken.

## 2.3. Matrix elements with Dirac orbitals

### 2.3.a. Matrix elements with radial orbitals

#### Matrix elements with non-relativistic radial orbitals:

- **Special non-relativistic  $r^k$  expectation values:** The following expectation values are displayed by Marxer (1991)

$$\langle r^{-1} \rangle = \frac{Z}{a_o n^2}, \quad \langle r^{-2} \rangle = \frac{2 Z^2}{2 (\ell + 1) n^3}$$

$$\langle r^{-4} \rangle = \frac{16 Z^4}{n^5} \left[ 3n^2 - \ell(\ell + 1) \frac{(2\ell - 2)!}{(2\ell + 3)!} \right]$$

$$\langle r^{-6} \rangle = \left[ \frac{Z}{a_o} \right]^6 \frac{35n^4 - n^2 [30\ell(\ell + 1) - 25] + 3(\ell - 1)\ell(\ell + 1)(\ell + 2)}{8n^7 (\ell - 3/2)(\ell - 1)(\ell - 1/2)\ell(\ell + 1/2)(\ell + 1)(\ell + 3/2)(\ell + 2)(\ell + 5/2)}$$

$$\langle r^{-k-2} \rangle = \left[ \frac{Z}{a_o} \right]^{k+2} \frac{1}{n^{k+3} \ell^{k+1}} \mathcal{P}_{k,\ell} \left( \frac{n}{\ell} \right), \quad \mathcal{P}_{k,\ell}(x) = \frac{(2\ell)^{k+1} (2\ell - k)!}{(2\ell + 1)!} {}_3F_2(-k, k + 1, \ell + 1 - \ell x; 1, 2\ell + 2; 1)$$

- **Pasternack-Kramers rekursion relation:** For  $k \leq 0$ , the  $r^{-k}$  expectation values of any  $(n\ell)$  level fulfill the relation (Marxer 1991)

$$\langle r^{-k-2} \rangle = \frac{4}{(2\ell + 1)^2 - k^2} \left[ \left( \frac{2k - 1}{k} \right) \frac{Z}{a_o} \langle r^{-k-1} \rangle - \left( \frac{k - 1}{k} \right) \frac{Z^2}{n^2 a_o^2} \langle r^{-k} \rangle \right]$$

$$\langle r^k \rangle = \frac{(2\ell + k + 2)!}{(2\ell - k - 1)!} \left[ \frac{n a_o}{2Z} \right]^{2k+3} \langle r^{-k-3} \rangle$$

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From this relation, explicit formulas for low principal quantum number  $n$  can be computed rather easily.

### Matrix elements with relativistic Dirac wavefunctions:

- An analytical expression of the matrix elements with operators  $r^k e^{-\sigma r}$  can be found (also) for Dirac's relativistic wavefunctions. In order to derive such expressions, it is typically more convenient first to re-write the standard representation of the hydrogenic functions in terms of a series expansion in  $r$  as it was suggested originally by Rose (1961).
- An expression for the corresponding matrix element is given by:

$$\begin{aligned}
 \langle n \kappa | r^k e^{-\sigma r} | n' \kappa' \rangle &= \int_0^\infty dr e^{-\sigma r} (P_{n\kappa}(r) P_{n'\kappa'}(r) + Q_{n\kappa}(r) Q_{n'\kappa'}(r)) \\
 &= N_{n\kappa} N_{n'\kappa'} \sum_{\nu=0}^{n-|\kappa|} \sum_{\nu'=0}^{n'-|\kappa'|} (c_{n\kappa,\nu}^+ c_{n'\kappa',\nu'}^+ + c_{n\kappa,\nu}^- c_{n'\kappa',\nu'}^-) \frac{q^{s+\nu-1} q'^{s'+\nu'-1}}{(q+q'+\sigma)^{1+\nu+\nu'+s+s'+k}} \Gamma(\nu+\nu'+k+s+s'+1), \\
 c_{n\kappa,\nu}^\pm &= \left(1 \pm \sqrt{1-q^2}\right)^{1/2} \frac{((-n+|\kappa|)_\nu 2^\nu)}{\nu! (2s+1)_\nu} [(\nu-n+|\kappa|) \pm (\alpha Z/q - \kappa)]
 \end{aligned}$$

with  $(a)_\nu$  being the Pochhammer symbol and where the parameters  $q$ ,  $s$  and the normalization factor  $N_{n\kappa}$  were defined above.

### 2.3.b. Matrix elements including the angular part of Dirac orbitals

#### Matrix elements of spherical tensors:

- **Matrix elements of the  $\mathbb{C}^K$  tensors:** In the nonrelativistic theory, we have

$$\langle \ell_a || \mathbb{C}^{(K)} || \ell_b \rangle = (-1)^{\ell_a} [\ell_a, \ell_b]^{1/2} \begin{pmatrix} \ell_a & K & \ell_b \\ 0 & 0 & 0 \end{pmatrix}, \quad (\mathbb{C}^{(k_1)} \mathbb{C}^{(k_2)})^{(K)} = (-1)^K [K]^{1/2} \begin{pmatrix} k_1 & K & k_2 \\ 0 & 0 & 0 \end{pmatrix} \mathbb{C}^{(K)},$$

where, in the last expression,  $\mathbb{C}^{(k_1)}$ ,  $\mathbb{C}^{(k_2)}$  must act upon the same electron (coordinates).



➤ **Matrix elements of the  $\mathbb{C}^K$  tensors:** Gaidamauskas *et al.* (2011) use the following definition:

$$\langle \kappa_a || \mathbb{C}^{(K)} || \kappa_b \rangle = (-1)^{j_a + 1/2} [j_a, j_b]^{1/2} \begin{pmatrix} j_a & K & j_b \\ 1/2 & 0 & -1/2 \end{pmatrix} \delta_{\ell_a + \ell_b + 1, \text{even}}$$

## 2.4. Frequently applied expansions, transformations and identities in atomic theory

### 2.4.a. Partial-wave expansions of free electrons

#### Partial-wave expansion:

- **Partial-wave components of a plane-wave electron:** The computation of partial (and total) ionization cross sections often requires an integration over all possible angles  $\Omega_p = (\vartheta_p, \varphi_p)$  of the photoelectrons, emitted in  $4\pi$ . In practice, this integration over  $\Omega_p$  can be carried out rather easily by making use of the *decomposition* of the free-electron wavefunction  $|\mathbf{p} m_s\rangle$  into *partial-wave* components.
- In practice, however, this expansion generally depends on the choice of the quantization axis.
- **If the quantization axis is taken along  $\mathbf{e}_z$ ,** this expansion is given by

$$|\mathbf{p} m_s\rangle = \sum_{\kappa m} i^\ell e^{-i\Delta_\kappa} \langle l m_\ell, 1/2 m_s | j m \rangle Y_{\ell m_\ell}^*(\vartheta_p, \varphi_p) |\varepsilon \kappa m\rangle ,$$

and where the summation runs over all partial waves,  $\kappa = \pm 1, \pm 2, \dots$  as well as  $m = -j, \dots, j$ . In this expansion, moreover,  $\Delta_\kappa$  is the **Coulomb phase shift**, and the (nonrelativistic orbital angular momentum) quantum number  $\ell$  just distinguishes the parity of the partial waves.

## 2.4.b. Expansions including spherical harmonis

### Expansions including the spherical harmonics:

➤ Expansion of a plane-wave in terms of spherical Bessel functions:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell m} i^\ell j_\ell(kr) Y_{\ell m}^*(\hat{k}) Y_{\ell m}^*(\hat{r}) .$$

➤ Multipole expansion of the (transverse-gauge) plane-wave vector potential:

$$\mathbf{A}^{(\text{transverse})}(\mathbf{r}, \omega) = 4\pi \sum_{LM} i^{L-p} \left( \mathbf{Y}_{LM}^{(p)}(\hat{k}) \cdot \boldsymbol{\epsilon} \right) \mathbf{a}_{LM}^{(p)}(\mathbf{r}),$$

where the vector functions  $\mathbf{a}_{LM}^{(p)}(\mathbf{r})$  are referred to as **multipole potentials**, and where only terms with  $p = 0$  (magnetic) and  $p = 1$  (electric) contribute, since  $\mathbf{Y}_{LM}^{(-1)}(\hat{k})$  is orthogonal to  $\boldsymbol{\epsilon}$ .

➤ Multipole expansion with two vectors  $\mathbf{r}, \mathbf{r}' \ll R$ : For this expansion, one finds (Patil and Tang, 2000)

$$\frac{1}{|\mathbf{R} - \mathbf{r} + \mathbf{r}'|} = \sum_{\ell \ell' m} a(\ell, \ell', m) \frac{r^\ell r'^{\ell'}}{R^{\ell+\ell'+1}} Y_{\ell m}(\vartheta, \varphi) Y_{\ell', -m}(\vartheta', \varphi')$$

$$a(\ell, \ell', m) = \frac{4\pi (-1)^{\ell'} (\ell + \ell')!}{[(2\ell + 1)(2\ell' + 1)(\ell + m)!(\ell - m)!(\ell' + m)!(\ell' - m)!]^{1/2}}$$

$$\frac{1}{|\mathbf{R} - \mathbf{r} + \mathbf{r}'|} = \sum_{\ell \ell'} \left( \frac{r^\ell r'^{\ell'}}{R^{\ell+\ell'+1}} \right) \frac{4\pi (-1)^{\ell'} (\ell + \ell')!}{[(2\ell + 1)(2\ell' + 1)]^{1/2}} \sum_m \frac{Y_{\ell m}(\vartheta, \varphi) Y_{\ell', -m}(\vartheta', \varphi')}{[(\ell + m)!(\ell - m)!(\ell' + m)!(\ell' - m)!]}$$

$$\Delta \left( \frac{1}{|\mathbf{R} - \mathbf{r} + \mathbf{r}'|} \right) = \Delta' \left( \frac{1}{|\mathbf{R} - \mathbf{r} + \mathbf{r}'|} \right) = 0, \quad R \gg r, r'.$$

➤ Addition theorem for Legendre polynomials:

$$\begin{aligned}
 P_\ell(\cos \vartheta) &= \left( \frac{4\pi}{2\ell+1} \right)^{1/2} Y_{\ell 0}(\vartheta, \varphi) \\
 P_{\ell+\ell'}(\cos \vartheta) &= \left( \frac{4\pi}{2\ell+2\ell'+1} \right)^{1/2} \left[ \frac{1}{(2\ell+2\ell')!} \right]^{1/2} \left[ \frac{4\pi (2\ell+2\ell'+1)!}{(2\ell+1)! (2\ell'+1)!} \right]^{1/2} \frac{\ell! \ell'}{(\ell+\ell')!} \\
 &\quad \times \sum_m \frac{(\ell+\ell')!}{(\ell-m)! (\ell'+m)!} \left[ \frac{(2\ell)! (\ell-m)! (2\ell')! (\ell'+m)!}{(\ell+m)! (\ell'-m)!} \right]^{1/2} Y_{\ell m}(\vartheta, \varphi) Y_{\ell', -m}(\vartheta', \varphi').
 \end{aligned}$$

### 2.4.c. Radial grid transformations

#### Radial grids:

➤ **Radial grids for atomic computations:** Various types of (radial) grid transformation  $t = t(r)$  have been applied in the literature in order to adapt the physics, that need to be described, to an *equi-distant* grid. For bound-state (SCF) computations, one often applies a **logarithmic transformation**  $t(r) \propto \ln(r)$  to account for the singularity of the potential at the origin. In a **logarithmic-linear transformation**  $t(r) = c_1 \ln(r) + c_2 r$ , one combines a exponential increase of the step-size near to the origin with a (nearly) linear behavior for large  $r$ . In the HULLAC and FAC codes, moreover, a **logarithmic-square-root transformation**  $t(r) = c_1 \ln(r) + c_2 \sqrt{r}$  has been applied, which ensures that approximately the same number of grid points occurs for each oscillation of the continuum waves. When compared to the logarithmic-linear transformation, the logarithmic-square-root transformation covers for a given number of points a larger radial extent. This may have advantages for multiply- and highly-charged ions, though no detailed analysis has been made in the literature.

### 2.4.d. Useful identities

#### Useful identities:

➤ Derivative of the spherical Bessel functions:

$$j_{n-1}(z) = \frac{n+1}{z} j_n(z) + j'_n(z), \quad j_{n+1}(z) = \frac{n}{z} j_n(z) - j'_n(z)$$

## 2.5. Frequently occuring radial integrals

### Notation & applications in Jac:

➤ In JAC, all these radial integrals can be directly computed by a call to some function from the `RadialIntegrals` module.

### Functions $Y^k(r; ab)$ and $Z^k(r; ab)$ :

➤ **Nonrelativistic functions  $Y^k(r; ab)$  and  $Z^k(r; ab)$ :** These two function naturally arises from the derivative of the (two-electron) Slater integrals and appear very frequently in all atomic structure calculations. For radial orbitals with quantum numbers  $a = (n_a, \kappa_a)$ ,  $b = \dots$ , these functions are given by

$$Y^k(r; ab) = r \int_0^\infty ds \frac{r_{<}^k}{r_{>}^{k+1}} P_a(s) P_b(s) = \int_0^r ds \left(\frac{s}{r}\right)^k P_a(s) P_b(s) + \int_r^\infty ds \left(\frac{r}{s}\right)^{k+1} P_a(s) P_b(s)$$
$$Z^k(r; ab) = \int_0^r ds \left(\frac{s}{r}\right)^k P_a(s) P_b(s).$$

Indeed, the fast and accurate calculation of  $Y^k(r; ab)$  depends on  $Z^k(r; ab)$ , i.e. the first part in the definition above.

- **Solutions of the  $Y^k(r; ab)$  and  $Z^k(r; ab)$  functions:** It was originally suggested by Hartree that the  $Y^k(r; ab)$  and  $Z^k(r; ab)$  integrals can be determined by simultaneously solving a pair of differential equations with boundary conditions

$$\begin{aligned} \frac{d}{dr} Z^k(r; ab) &= P_a(r) P_b(r) - \frac{k}{r} Z^k(r; ab), & Z^k(0; ab) &= 0 \\ \frac{d}{dr} Y^k(r; ab) &= \frac{1}{r} [(k+1) Y^k(r; ab) - (2k+1) Z^k(r; ab)], & Y^k(r \rightarrow \infty; ab) &= Z^k(r \rightarrow \infty; ab) \end{aligned}$$

### Grant's radial integrals for the coupling of the radiation field:

- Grant (1988) defines the following radial integrals that frequently occur in the coupling of the radiation field

$$\begin{aligned} I_L^o(q; ab) &= \int_0^\infty dr j_L(qr) [P_a Q_b] = \int_0^\infty dr j_L(qr) [P_a(r) Q_b(r)] \\ I_L^\pm(q; ab) &= \int_0^\infty dr j_L(qr) [P_a Q_b \pm Q_a P_b] \\ J_L(q; ab) &= \int_0^\infty dr j_L(qr) [P_a P_b + Q_a Q_b] \end{aligned}$$

- These integrals are useful also if the spherical Bessel function occurs in the integrant as  $j_L(qr)/qr$ , and where the following recursion relations can be used:

$$\frac{j_L(x)}{x} = \frac{1}{2L+1} [j_{L-1}(x) + j_{L+1}(x)].$$

### Further radial integrals for different one-electron spherical tensor operators:

- In the treatment of the electron nucleus (hyperfine) interaction and the interaction with an external magnetic field, some radial integrals occur frequently:

$$I_L^{[r]}(ab) \equiv [r^L]_{ab} = \int_0^\infty dr r^L [P_a Q_b + Q_a P_b]$$

$$J_L^{<r>}(ab) = \langle r^L \rangle_{ab} \equiv \int_0^\infty dr r^L [P_a P_b + Q_a Q_b]$$

- **Vinti-Integral:** In the treatment of the (relativistic) mass shift, the (so-called) Vinti-Integrals occur

$$R^{(\text{Vinti})}(a, b) = \int_0^\infty dr P_a \left[ \frac{d}{dr} - \frac{\kappa_a(\kappa_a + 1) - \kappa_b(\kappa_b + 1)}{2r} \right] P_b + \int_0^\infty dr Q_a \left[ \frac{d}{dr} - \frac{-\kappa_a(-\kappa_a + 1) + \kappa_b(-\kappa_b + 1)}{2r} \right] Q_b .$$

## 2.6. B-splines

### Properties of B-splines:

- A B-spline (basis spline) is a spline function with a minimal support and which can be used to express all spline function of any given as a finite linear combination.
- In physics, B-splines are often utilized for curve-fitting and in order to fit derivatives to experimental data.
- **Knot sequence:** A sequence of (radial) grid points  $\{t_1, t_2, \dots, t_m\}$  with  $t_1 \leq t_2 \leq \dots \leq t_m$ .
- **Set of B-splines:** Set of piecewise polynomial functions of order  $k$ , the so-called B-splines:

$$\left\{ B_1^{(k)}(x), B_2^{(k)}(x), \dots, B_n^{(k)}(x) \right\}, \quad B_i^{(1)}(x) = \begin{cases} 1 & \text{for } t_i \leq x \leq t_{i+1} \\ 0 & \text{otherwise,} \end{cases} \quad i = 1, 2, \dots, m-1.$$

- **Recursion relation for the generation of B-splines:**

$$B_i^{(k)}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_i^{(k-1)}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1}^{(k-1)}(x) \quad i = 1, 2, \dots, m - k$$

The number of B-splines  $n = m - k$  ( $k < m$ ) is determined by the order  $k$  and the number of knots  $m$ . For B-splines of a given order, it is therefore sufficient to use the notation  $B_i^{(k)}(x)$

- Each B-spline is non-negative and is non-zero only for:  $B_i(x) > 0$  for  $t_i < x < t_{i+k}$  and  $B_i(x) = 0$  for  $x < t_i$ ,  $x > t_{i+k}$ . — Essentially, the B-spline  $B_i(x)$  starts at  $t_i$  and ends at  $t_{i+k}$  with only positive values in between.
- **Use of B-splines in pseudo-code summations:** The first and last B-spline are often omitted in bound- and pseudo-state computations in order to fulfill the proper boundary conditions:  $Q_{n\kappa}(0) = 0$  ( $\kappa < 0$ ) and  $P_{n\kappa}(0) = 0$  ( $\kappa > 0$ ) as well as  $P_{n\kappa}(r_{\max}) = P_{n\kappa}(r_{\max}) = 0$ . Such a construction avoids the appearance of non-physical (*spurious*) states that may hamper the computations.

## Application of B-splines:

- Application of B splines for constructing single- and many-electron basis sets are nowadays widely employed in computational atomic and molecular physics.
- **B-splines:** For a B-spline representation of single-electron orbitals, only the low-lying orbitals will usually contribute significantly to the many-electron wave function. More generally, the configuration mixing between two configuration states is inversely proportional to the energy interval between them. It is therefore said sometimes that a B-spline representation of the single-electron orbitals provide an effective and natural way in order to adopt the basis to the problem of interest.
- **B-splines in relativistic theory:** In contrast to the nonrelativistic theory, the use of B-splines in relativistic computations is often accompanied by the occurrence of spurious states (Shabaev *et al.*, 2004). In a Coulomb potential, spurious states appear especially for  $\kappa > 0$  as the lowest bound states but with rather nonphysical energies.

## 2.7. Generation of continuum orbitals

### Simple approximations in Jac:

- For a first estimate of continuum processes, we have implemented a number of (rather) simple approximations/methods for the continuum orbitals that occur frequently at various places in the program. In JAC, the particular method can be selected by (re-) defining the global variable `JAC_CONT_SOLUTION` by a proper call to `Jac.define("method: continuum; ...")`.
- Approximations implemented in JAC:
  - (a) spherical Bessel functions;
  - (b) non-relativistic Coulomb waves for the large component of the continuum orbital, together with the kinetic-balance condition to obtain a small component;
  - (c) asymptotically correct, relativistic Coulomb orbital;
  - (d) Galerkin method to solve for continuum orbitals within a B-spline basis and for a given atomic potential.
- In JAC, spherical Bessel orbitals are generated if the global constant `JAC_CONT_SOLUTION = ContBessel`; cf. `JAC.define()` and section 2.7.a.
- In JAC, a free nonrelativistic Coulomb orbitals are generated if the global constant is `JAC_CONT_SOLUTION = NonrelativisticCoulomb`; cf. `JAC.define()` and section 2.7.b. Not available at present.
- In JAC, asymptotically-correct relativistic Coulomb orbitals are generated for a potential with a Coulombic tail, if the global constant `JAC_CONT_SOLUTION = AsymptoticCoulomb`; cf. `JAC.define()` and section 2.7.c.
- In JAC, a B-spline representation of the relativistic orbital  $\varepsilon\kappa$  in a given local potential are generated if the global constant `JAC_CONT_SOLUTION = BsplineGalerkin`; cf. `JAC.define()` and section 2.7.d.
- In JAC, different normalization methods can be selected for all continuum orbitals; a pure-sine normalization for `JAC_CONT_NORMALIZATION = PureSine`, an asymptotic Coulomb normalization for `JAC_CONT_NORMALIZATION = CoulombSine`, or a WKB-type normalization for multiply and highly-charged ions for `JAC_CONT_NORMALIZATION = OngRussek`; cf. `JAC.define()`.
- At present, no attempt has yet been made to incorporate the exchange interaction of the continuum and bound-state orbitals.



### 2.7.a. Spherical Bessel orbitals

#### Implementation and numerical details:

- **Generating equation and solutions:** The spherical Bessel functions  $j_\ell(|\mathbf{k}|r)$  obey the (non-relativistic) *free* radial Schrödinger equation for positive energies  $\varepsilon > 0$ , and the corresponding wave number  $k = \sqrt{2\varepsilon}$ ,  $\rho = kr$  and for well-defined orbital angular momentum  $\ell$

$$R_{\varepsilon\ell}(r) = \frac{P_{\varepsilon\ell}}{r} = N j_\ell(|\mathbf{k}|r) = N j_\ell(\sqrt{2\varepsilon} r) \quad \Longleftrightarrow \quad j_\ell''(\rho) + 2 \frac{j_\ell'(\rho)}{\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2}\right) j_\ell(\rho) = 0.$$

- While the large component of such a continuum (Bessel) orbital  $|\varepsilon\kappa\rangle$  are represented by the Bessel function  $P = N r j_\ell(|\mathbf{k}|r)$  above, the **small components are here obtained from the kinetic-balance condition**.

### 2.7.b. Non-relativistic Coulomb orbitals

#### Implementation and numerical details:

- The non-relativistic Coulomb orbitals  $|\varepsilon\ell\rangle$  are known analytically for  $\varepsilon > 0$  and can be utilized to represent the large components of a relativistic orbital with this (given kinetic) energy, while the **small components are here obtained again from the kinetic-balance condition**.
- **Non-relativistic free Coulomb waves:** The free solutions with  $\varepsilon > 0$  to the radial Schrödinger equation with a central-field potential  $V(r)$  with Coulombic tail satisfy the boundary condition:

$$P_{\varepsilon\ell}(0) = 0; \quad P_{\varepsilon\ell}(r \rightarrow \infty) \simeq \sqrt{\frac{2}{\pi k}} \sin \left( kr + \frac{\bar{Z}}{k} \ln(2kr) - \frac{\ell\pi}{2} + \sigma_\ell^{(\text{Coulomb})} + \delta_\ell \right),$$

where  $k^2 = 2\varepsilon$ ,  $\bar{Z} = Z - N$  is the effective charge as seen by the free electron at large distance and  $\sigma_\ell^{(\text{Coulomb})} = \arg \Gamma(\ell + 1 - i\bar{Z}/k)$  is the (well-known) **Coulomb phase**. Note that this solution is normalized on the energy scale.

- See section 2.1 for a representation of a non-relativistic Coulomb orbital with positive energy  $\varepsilon > 0$ . **This approach does not yet work properly since there is no hypergeometric function with complex arguments available in JULIA.**

### 2.7.c. Asymptotically-correct relativistic Coulomb orbitals

#### Implementation and numerical details:

- **Relativistic free-Coulomb waves:** The free solutions to the radial Dirac equation in a spherical potential with Coulombic tail satisfy the boundary conditions (Åberg and Howat, 1982; Eqs. (19.29-30))

$$\begin{aligned}
 P_{\varepsilon\kappa}(0) &= Q_{\varepsilon\kappa}(0) = 0 \\
 P_{\varepsilon\kappa}(r \rightarrow \infty) &\simeq \sqrt{\frac{\varepsilon + 2c^2}{\pi c^2 k}} \cos [\theta_\kappa(\varepsilon) + \delta_\kappa(\varepsilon)], & Q_{\varepsilon\kappa}(r \rightarrow \infty) &\simeq -\sqrt{\frac{\varepsilon}{\pi c^2 k}} \sin [\theta_\kappa(\varepsilon) + \delta_\kappa(\varepsilon)] \\
 \theta_\kappa(\varepsilon) &= k r + y \ln(2k r) - \arg \Gamma(\bar{\gamma} + i y) - \frac{1}{2} \pi \bar{\gamma} + \eta, & k^2 &= 2\varepsilon + \frac{\varepsilon}{c^2} \\
 \bar{\gamma} &= + \left( \kappa^2 - \frac{\bar{Z}^2}{c^2} \right)^{1/2}, & y &= \frac{\bar{Z}(\varepsilon + c^2)}{c^2 k} & \exp(2i\eta) &= -\frac{\kappa - i y / (\varepsilon + c^2)}{\bar{\gamma} + i y}.
 \end{aligned}$$

- The phase-shift  $\delta_\kappa$  is the non-Coulombic phase shift and is set to  $\delta_\kappa = 0$  for a pure Coulombic potential.

### 2.7.d. Continuum orbitals in an atomic potential: Galerkin method

#### Implementation and numerical details:

- One advantage of using B-splines is that solutions of the Schrödinger or Dirac equation can be found for any energy  $\varepsilon > 0$  by properly adopting  $r_{\max}$ .
- While both the Schrödinger and Dirac equations have formally a solution for any positive energy  $\varepsilon > 0$ , a diagonalization in a B-spline representation provides only a discrete set of solutions due to the boundary condition  $P(r_{\max}) = Q(r_{\max}) = 0$ , and where  $r_{\max}$  here denotes the size of the *numerical box*.

- **Galerkin method:** This method determines an approximate solution of the generalized eigenvalue equations

$$\sum_i \langle B_i | (\mathbb{H} - \varepsilon) | B_j \rangle c_j = \sum_i A_{ij} c_j = 0, \quad A_{ij} = \langle B_i | (\mathbb{H} - \varepsilon) | B_j \rangle = H_{ij} - \varepsilon S_{ij}.$$

- **Galerkin method:** A possible approximation to this generalized eigenvalue problem is to compute the smallest eigenvalue of  $\mathbf{A} \cdot \mathbf{c} = \lambda \mathbf{c}$ , a more accurate solution follows from a minimization of  $|A\psi|^2$  under the constraint  $|\psi|^2 = 1$ . This variational problem is mathematically equivalent to find the smallest eigenvalue of the matrix  $A^+ A$ :  $\mathbf{A}^+ \mathbf{A} \cdot \mathbf{c} = a \mathbf{c}$ . — The eigenvector of the smallest eigenvalue  $a_i > 0$  is then the requested (approximate) solution of the eigenvalue problem above.

### 2.7.e. Normalization and phase of continuum orbitals

#### Pure sine behaviour at large $r$ :

- **Pure sine behaviour:** The free radial Schrödinger equation without an external potential always satisfies the asymptotic pure sine behaviour  $\sim \sin(kr + \varphi)$ . A very similar asymptotic form  $\sim \sin(kr - \ell\pi/2 + \varphi)$  also applies for all partial-wave solutions  $\ell \geq 0$  and positive energy  $\varepsilon > 0$  for the standard radial Schrödinger equation with just a centrifugal potential  $\sim 1/r^2$ .
- **Normalization for a pure sine behaviour:** For this normalization, the large component is assumed to be given with  $k = \sqrt{2\varepsilon}$  by

$$P(r \approx r_{\max}) = \sqrt{\frac{2}{\pi k}} \begin{cases} \sin(kr + \varphi) & \text{for } \ell = 0 \\ \sin(kr - \frac{\ell\pi}{2} + \varphi) & \text{for } \ell > 0. \end{cases}$$

With this behaviour, the normalization constant  $N$  and the phase  $\varphi$  can be obtained by means of the logarithmic derivative  $P/P'$ .

#### Asymptotic Coulomb behaviour at large $r$ :

- **Normalization for an asymptotic Coulomb behaviour:** For this normalization, the large and small components are assumed to be described for all  $r$ -values by the asymptotic behaviour as shown in subsection 2.7.c. With this assumption, the normalization constant  $N$  and the phase  $\varphi$  can again be obtained by means of the logarithmic derivative  $P'/P$ .
- Instead of the logarithmic derivative  $P'/P$ , one can of course also apply the ratio  $Q/P$ ; this option is currently hard-coded in JAC but need to be further tested.

## Normalization for multiply-charged ions due to Ong and Russek (1973):

- This normalization scheme has not yet been implemented and tested so far.
- **Normalization on energy scale:** Continuum orbital functions are often **normalized on an energy scale**,  $\langle \varepsilon \kappa | \varepsilon' \kappa' \rangle = \delta(\varepsilon - \varepsilon') = \delta(E - E')$ , and where  $E, E'$  are the free-electron energies *inclusive* the rest mass energy, i.e.  $E > mc^2$ .
- **WKB ansatz for the large component  $P_{\varepsilon\kappa}(r)$ :** If  $V(r)$  is an atomic central-field potential of the ionic core and if we make use of the ansatz below for the large component in the Dirac equation, a second-order ODE can be derived for the function  $\phi(r)$ , cf. Ong and Russek (1978)

$$P_{\varepsilon\kappa}(r) = A \sqrt{\frac{E - V(r) + c^2}{c (d\phi/dr)}} \cos \phi(r),$$

$$-\left(\frac{d\phi}{dr}\right)^2 + \frac{(E - V)^2 - c^4}{c^2} - \frac{\kappa(\kappa + 1)}{r^2} + \left(\frac{d\phi}{dr}\right)^{1/2} \frac{d^2}{dr^2} \left(\frac{d\phi}{dr}\right)^{-1/2} - (E - V + c^2)^{1/2} \frac{d^2}{dr^2} (E - V + c^2)^{-1/2} + \frac{\kappa}{r} \frac{dV/dr}{E - V + c^2} = 0.$$

- **WKB approximation:** If the last three terms are neglected in the equation above, an approximate solution to this ODE is given by

$$\left(\frac{d\phi}{dr}\right)^2 \approx \frac{(E - V)^2 - c^4}{c^2} - \frac{\kappa(\kappa + 1)}{r^2}, \quad P_{\varepsilon\kappa}(r) \approx \frac{A \sqrt{E - V + c^2}}{[(E - V)^2 - c^4 - c^2 \kappa(\kappa + 1)/r^2]^{1/4}} \cos \phi(r).$$

- **Normalization and phase of the WKB solution at some finite value  $r_o$ :** Following Ong and Russek (1978, Eq. 12), one can introduce an auxiliary potential  $U(r)$ , from which the normalization constant  $A(r_o)$  and the phase  $\phi(r_o)$  at some finite radius  $r_o$  is obtained by

$$U(r) = \frac{c}{2} \frac{(E - V) \frac{dV}{dr} - c^2 \kappa(\kappa + 1)/r^3}{[(E - V)^2 - c^4 - c^2 \kappa(\kappa + 1)/r^2]^{3/2}} P_{\varepsilon\kappa}(r) - c \frac{\frac{dP_{\varepsilon\kappa}}{dr} + \frac{dV/dr}{2(E - V + 2c^2)} P_{\varepsilon\kappa}(r)}{[(E - V)^2 - c^4 - c^2 \kappa(\kappa + 1)/r^2]^{1/2}}$$

$$A(r_o) = \sqrt{\frac{[(E - V)^2 - c^4 - c^2 \kappa(\kappa + 1)/r^2]^{1/2}}{E - V + c^2}} (P_{\varepsilon\kappa}^2 + U^2) |_{r=r_o}, \quad \phi(r_o) = \text{atan2}(U, P_{\varepsilon\kappa}) |_{r=r_o}.$$

- **Normalization and phase of the asymptotic wave function  $P_{\varepsilon\kappa}(r)$ :** The normalization of  $A(r_o)$  can be used to normalize also the large (and small) component  $P_{\varepsilon\kappa}(r)$ . For  $V(r_o) \approx 0$  and  $\phi(r) \approx kr + \delta_\kappa(\varepsilon)$  and if  $C$  is the normalization constant so that  $CP_{\varepsilon\kappa}$  has the correct asymptotic amplitude, one finally obtains

$$C = \frac{1}{A} \sqrt{\frac{(E + c^2) c d\phi/dr}{\pi c^2 k (E - V + c^2)}} \approx \frac{1}{A \sqrt{\pi c}}, \quad \delta_\kappa(\varepsilon) \approx \phi(r) - kr.$$

## 2.8. Nuclear models and potentials

### 2.8.a. Uniform nuclear model

#### Uniform charge distribution and potential:

- **Uniform nuclear-charge distribution:** For a nucleus with radius  $R$ , charge  $Z$  and mass number  $A$ , the nuclear charge distribution and potential is given for  $r \leq R$  by

$$\rho^{(\text{uniform})}(r) = \frac{3Z}{4\pi R^3}, \quad \phi^{(\text{uniform})}(r) = \begin{cases} \frac{Ze}{2R} \left[ 3 - \left(\frac{r}{R}\right)^2 \right] & \text{if } r \leq R \\ \frac{Ze}{R} & \text{if } r > R \end{cases}$$

$$R = R_n \sqrt{\frac{1 + (5s^2/2 R_n^2)}{1 + (3s^2/4 R_n^2)}}, \quad R_n = 1.07 \times 10^{-15} A^{1/3} \text{ m}, \quad s = 2.0 \times 10^{-15} \text{ m}.$$

- **Form factor for nuclei with uniform nuclear-charge distribution:**

$$F^{(\text{uniform})}(q; R) \equiv 4\pi \int_0^\infty dr r^2 \frac{\sin(qr)}{qr} \rho^{(\text{uniform})}(r) = \frac{3Z}{(qR)^3} [\sin(qR) - qR \cos(qR)].$$

### 2.8.b. Helm's uniform-uniform nuclear model

#### Uniform-uniform charge distribution and potential:

- **Helm's uniform-uniform nuclear-charge distribution:** An alternative realistic nuclear-charge distribution can be expressed as convolution of two uniform distributions  $\rho_1^{(\text{uniform})}$ ,  $\rho_2^{(\text{uniform})}$  with nuclear radii  $R_1 > R_2$  and normalization constant  $N$  (Salvat *et al.*, 2005)

$$\rho^{(\text{Helm})} = Z N \int d^3 \mathbf{r}' \rho_1^{(\text{uniform})}(\mathbf{r}') \rho_2^{(\text{uniform})}(\mathbf{r} - \mathbf{r}')$$

$$\phi^{(\text{Helm})} = \begin{cases} N & \text{if } r \leq R_1 - R_2 \\ N \frac{[(r + R_1)^2 - R_2^2 + 2r R_1][(r - R_1)^2 - R_2^2]^2}{32 r^3 R_1 - 2^3} + \frac{[(r + R_2)^2 - R_1^2 + 2r R_2][(r - R_2)^2 - R_1^2]^2}{32 r^3 R_2 - 2^3} & \text{if } R_1 - R_2 \leq r \leq R_1 + R_2 \\ 0 & \text{if } r > R_1 + R_2 \end{cases}$$

- The normalization constant  $N$  of Helm's uniform-uniform nuclear-charge distribution and the corresponding electrostatic potential  $\phi^{(\text{Helm})}$  need to be determined numerically.

### 2.8.c. Helm's nuclear-depression model

#### Distribution and potential for central nuclear depression:

- **Central depression of the nuclear density:** In (super-) heavy nuclei with  $Z \gtrsim 100$ , a central depression of the nuclear density is caused by the Coulomb repulsion of the  $Z$  protons, i.e. the **nuclear charge distribution slightly rise from the centre towards the surface region**. Although this nuclear suppression is further affected by the (detailed) nuclear shell structure, it leads to an estimated decrease of up to 7.5 % of the nuclear matter density at the center of the nucleus (Friedrich *et al.*, 1986).
- **Helm model:** A quantitative relation between the nuclear electromagnetic form factor and the nuclear charge distribution has been established by means of the **folding (Helm) model**. In this Helm model, the nuclear charge density is described by means of a convolution of a square-well distribution  $\rho^{(\text{square-well})} = \rho_o \Theta(R_d - r)$ , with **diffraction radius  $R_d$** , and a Gaussian distribution  $\rho^{(\text{Gaussian})} = \rho(r, \sigma)$ .
- **Nuclear charge distribution:**

$$\rho^{(\text{Helm})} = \rho^{(\text{square-well})} \rho^{(\text{Gaussian})} = (1 + w r^2) \rho^{(\text{homogeneous})} \exp\left(-\frac{r^2}{2\sigma^2}\right)$$

- **Modified Helm model:** Since the rise of the nuclear density near to the origin is proportional to  $r^2$ , a modified modified Helm model has been suggested by Friedrich *et al.* (1986) in terms of the weight  $w$  whose value follows from the normalization  $\int dr \rho^{(\text{Helm})} = 1$ . With this weight parameter, the nuclear charge distribution is often written as:

$$\rho^{(\text{modified Helm})} = \frac{(1 + w r^2)}{1 + w \langle r^2 \rangle^{(\text{homogeneous})}} \rho^{(\text{homogeneous})} \exp\left(-\frac{r^2}{2\sigma^2}\right).$$

## 2.8.d. Fermi nuclear model

### Fermi charge distribution and potential:

- **Fermi model:** For a nucleus with *root-mean-square* (rms) radius  $R = \sqrt{\langle r^2 \rangle}$

$$\rho(r, R) = \frac{N}{1 + \exp[(r - c)/a]}, \quad \int dr r^2 \rho(r, R) = 1$$

where the **thickness parameter**  $a$  is often chosen as  $a = 2.3/4 \ln 3$ .

- **Fermi nuclear-charge distribution:** For a nucleus with *half-density* density  $R_n$ , the Fermi distribution is uniform in the center and falls off smoothly at the surface of the nucleus from 0.9 to 0.1 of the central density within a skin of thickness  $t$

$$\rho^{(\text{Fermi})} = \frac{\rho_o}{\exp[(r - R_n)/z] + 1}, \quad z = \frac{t}{(4 \ln 3)} = 0.546 \times 10^{-15} \text{ m}$$

- The normalization constant  $\rho_o$  of the Fermi nuclear-charge distribution and the corresponding electrostatic potential  $\phi^{(\text{Fermi})}$  need to be determined numerically.
- With high accuracy, the parameters  $N$  and  $c$  can be obtained from the analytical formulas

$$N = \frac{3}{4\pi c^3} \left(1 + \frac{\pi^2 a^2}{c^2}\right)^{-1}, \quad c = \sqrt{\frac{5}{3} \langle r^2 \rangle - \frac{7}{3} \pi^2 a^2}.$$

## Nuclear potential:

➤ Potential of extended nucleus:

$$\mathbb{V}^{(\text{nuc})}(r; R) = -4\pi \alpha Z \int_0^\infty dr' r'^2 \frac{\rho(r', R)}{r_{>}} = -\frac{4\pi \alpha Z}{r} \int_0^r dr' r'^2 \rho(r', R) - 4\pi \alpha Z \int_r^\infty dr' r' \rho(r', R), \quad r_{>} = \max(r, r').$$

### 2.8.e. $Z$ -scaling of atomic energies, rates and properties

#### Simple $Z$ -scaling:

➤  $Z$ -scaling of atomic energies, energy splittings and rates for hydrogenic ions: The analytical treatment of hydrogenic ions readily allows to extract the  $Z$ -scaling of energies, energy splittings and rates. These scalings enable one to quickly check for the relevance of interactions and processes under quite different circumstances. A few of such scalings are given by:

Observable	scaling	observable	scaling
Transition energy	$(\alpha Z)^2$	Fine-structure splitting	$(\alpha Z)^4$
Lamb shift	$\alpha (\alpha Z)^4$	Hyperfine-structure splitting	$\alpha (\alpha Z)^3 m/m_p$



# 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

## 3.1. Electron-electron interaction

### Background & notations:

- In the (non-relativistic) limit of a rather slow motion of the electrons, each electron pair just interact by the instantaneous Coulomb repulsion

$$\frac{1}{r_{12}} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Already this quite simple (interaction) operator results mathematically in various complications and is generally the major source of electron-electron correlations in all many-electron computations.

- For moving charges, Maxwell's theory also predicts both, current-current and retarded interactions, to which we briefly refer as Breit interactions in atomic physics. — These relativistic contributions to the electron-electron interactions must be added to the electro-static Coulomb repulsion.
- An effective (relativistic) operator for the electron-electron interaction can be formally derived from QED in perturbation theory with regard to the number of virtually exchanged photons (Sapirstein 1987, Grant und Quiney 1988), while the same expressions can be obtained also from heuristic arguments as given, for example, by Bethe and Salpeter (1957) und Johnson (1995).
- In practice, the computation of the electron-electron interaction usually requires the largest effort in all electronic-structure codes and, therefore, deserves special consideration. In atomic physics, a considerable simplification is usually achieved if all electron-electron interaction operators are represented as spherical tensors.

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

- For two electrons in orbitals  $a, b$  and with energies  $\varepsilon_a, \varepsilon_b$ , the **interaction energy** can be written as difference of a direct and exchange **matrix element** of the potential

$$\mathbb{V}^{(\text{tr})} = -\frac{1}{2\pi} \int \frac{d^3k}{k^2 - \omega^2} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \sum_{i,j=1}^3 \left[ \delta_{ij} - \frac{k_i k_j}{k^2} \right] \alpha_{1i} \alpha_{2j}$$

where  $\alpha_{1i}$  is the  $i$ -th component of the  $\boldsymbol{\alpha}$  matrix (vector) of the electron at position  $\mathbf{r}_1$  and

$$\omega = \begin{cases} 0 & \text{direct matrix element} \\ \frac{|\varepsilon_a - \varepsilon_b|}{c} & \text{exchange matrix element} \end{cases}$$

refers to the momentum of the exchanged photon.

- **The exchange matrix elements of the potential  $\mathbb{V}^{(\text{tr})}$  is generally complex**; while the *real* part describes an energy shift due to this transverse interaction, the *imaginary* part represents a rate for the decay  $a \rightarrow b$  for  $\varepsilon_a > \varepsilon_b$  or  $b \rightarrow a$  *vice versa*.
- **Frequency-independent Breit interaction**: For  $\omega \rightarrow 0$ , the transversal Breit interaction gives rise to the **frequency-independent Breit interaction**

$$b_{12}^o = -\frac{1}{2r_{12}} \left[ \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right],$$

which neglects all contributions  $\sim \alpha^4 Z^3$  (as well as of higher order in  $\alpha Z$ ).

- Typically, the explicit energy-dependence of the transverse interaction [upon the energy difference of the two electrons] gives rather tiny corrections, so that, in practice, **often no difference is made between the transversal and zero-frequency Breit interaction**.
- **Gaunt interaction**: The first term of the zero-frequency Breit interaction (operator) is known also as Gaunt interaction (Gaunt 1929). This term describes the current-current interaction due to the motion of the electrons and contributes about 90 % of the total Breit interaction for closed-shell atoms.
- For many elements of the periodic table, the corrections due to the Breit interaction are usually small, when compared with the dominant Coulomb repulsion. This applies especially for the Breit contributions to the electron-electron correlation.
- For describing most processes, it is **sufficient, if at all, to include the Breit interaction perturbatively in lowest order**. Formally, however, both terms

$$v_{12} = \frac{1}{r_{12}} + b_{12} \quad \Longleftrightarrow \quad \mathbb{V}^{(\text{e-e})} = \mathbb{V}^{(\text{Coulomb})} + \mathbb{V}^{(\text{Breit})}$$

are equivalent, and they should be treated simply together for all (super-) heavy elements.

➤ In JAC, only the frequency-independent Breit interaction is currently implemented.

### Effective interaction strength $X^{(L)}(abcd)$ of scalar electron-electron interactions:

➤ All operators of the (scalar) electron-electron interaction can be generally represented as spherical tensors in the form:

$$g_{12} \equiv g(\mathbf{r}_1, \mathbf{r}_2) = \sum_L g_L(r_1, r_2) (\mathbb{T}^{(L)}(\vartheta_1, \varphi_1) \cdot \mathbb{T}^{(L)}(\vartheta_2, \varphi_2))$$

$$\langle n_a \kappa_a m_a(1) n_b \kappa_b m_b(2) | \mathbb{G}_{12} | n_c \kappa_c m_c(1) n_d \kappa_d m_d(2) \rangle = \sum_{LM} (-1)^{L-M+j_a-m_a+j_b-m_b} \begin{pmatrix} j_a & L & j_c \\ -m_a & M & m_c \end{pmatrix} \begin{pmatrix} j_b & L & j_d \\ -m_b & -M & m_d \end{pmatrix} X^{(L)}(abcd),$$

leading to a simple **factorization of the two-electron matrix elements**, and where the magnetic quantum numbers (i.e. the angular dependence) of the matrix elements only occurs in the phase and the Wigner 3-j symbols.

➤ **Effective interaction strength  $X^{(L)}(abcd)$  of order  $L$ :** The strengths  $X^{(L)}(abcd)$  describe the physical interaction and are specific for every operator. They are often used as the **building blocks in order to handle the electron-electron interactions efficiently in electronic structure computations**.

### Effective interaction strength $X^{(L, \text{Coulomb})}(abcd)$ of the Coulomb repulsion:

➤ **Coulomb repulsion:** The decomposition of the Coulomb operator is given by:

$$\frac{1}{r_{12}} = \sum_{L=0}^{\infty} U_L(r, s) P_L(\cos(\vartheta)) = \sum_{L=0}^{\infty} U_L(r, s) (\mathbb{C}^{(L)}(\vartheta_1, \varphi_1) \cdot \mathbb{C}^{(L)}(\vartheta_2, \varphi_2)), \quad U_L(r, s) = \begin{cases} \frac{r^L}{s^{L+1}} & r < s \\ \frac{s^L}{r^{L+1}} & r > s. \end{cases}$$

In this expansion,  $P_L(x)$  denotes a Legendre-polynomial and  $\vartheta = \mathbf{r} \cdot \mathbf{s}/rs$  the angle between the two electron coordinates.

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

#### ➤ Effective interaction strength of the Coulomb repulsion:

$$X^{(L, \text{Coulomb})}(abcd) = \delta(j_a, j_c, L) \delta(j_b, j_d, L) \Pi^e(\kappa_a, \kappa_c, L) \Pi^e(\kappa_b, \kappa_d, L) (-1)^L \langle \kappa_a \parallel \mathbb{C}^{(L)} \parallel \kappa_c \rangle \langle \kappa_b \parallel \mathbb{C}^{(L)} \parallel \kappa_d \rangle R^L(abcd),$$

$$\delta(j_a, j_b, j_c) = \begin{cases} 1 & |j_a - j_b| \leq j_c \leq |j_a + j_b| \text{ and cyclic interchanged} \\ 0 & \text{otherwise,} \end{cases}$$

and where  $\Pi^e(\kappa, \kappa', L)$  represent the angular momentum and parity selection rules.

#### Effective interaction strength $X^{(L, \text{Breit})}(abcd)$ of the Breit interaction:

#### ➤ Effective interaction strength of the zero-frequency Breit: For the zero-frequency interaction, we find

$$X^{(L, \text{Breit})}(abcd) = (-1)^L \langle \kappa_a \parallel \mathbb{C}^{(L)} \parallel \kappa_c \rangle \langle \kappa_b \parallel \mathbb{C}^{(L)} \parallel \kappa_d \rangle \left[ \Pi^o(\kappa_a, \kappa_c, L-1) \Pi^o(\kappa_b, \kappa_d, L+1) \sum_{\mu=1}^8 s_{\mu}^L(abcd) S_{\mu}^L(abcd) + \right. \\ \left. + \sum_{\nu=L-1}^{L+1} \Pi^o(\kappa_a, \kappa_c, \nu) \Pi^o(\kappa_b, \kappa_d, \nu) \sum_{\mu=1}^4 t_{\mu}^{\nu, L}(abcd) T_{\mu}^{\nu}(abcd) \right].$$

$$\Pi^o(\kappa_a, \kappa_b, L) = \begin{cases} 1 & \text{if } l_a + l_b + L \text{ odd} \\ 0 & \text{otherwise.} \end{cases}$$

#### ➤ The constant coefficients $s_{\mu}^L$ and $t_{\mu}^{\nu, L}$ just depend on the angular quantum numbers $\{\kappa_a, \kappa_b, \kappa_c, \kappa_d, \nu, L\}$ and are displayed, for example, by Grant (1988; tables 3 and 4, and where we here use $t_{\mu}^{\nu, L} \equiv r_{\mu}^{\nu, L}$ ).

Table 3.1.: Definition of the integrales  $S_\mu^\nu(abcd)$  und  $T_\mu^\nu(abcd)$ 

$S_1^\nu(abcd) = S^\nu[ac    bd]$	$S_2^\nu(abcd) = S^\nu[bd    ac]$	$T_1^\nu(abcd) = T^\nu[ac    bd]$
$S_3^\nu(abcd) = S^\nu[ca    db]$	$S_4^\nu(abcd) = S^\nu[db    ca]$	$T_2^\nu(abcd) = T^\nu[ca    db]$
$S_5^\nu(abcd) = S^\nu[ac    db]$	$S_6^\nu(abcd) = S^\nu[db    ac]$	$T_3^\nu(abcd) = T^\nu[ac    db]$
$S_7^\nu(abcd) = S^\nu[ca    bd]$	$S_8^\nu(abcd) = S^\nu[bd    ca]$	$T_4^\nu(abcd) = T^\nu[ca    bd]$

➤ The radial integrals  $S_\mu^\nu(abcd)$  and  $T_\mu^\nu(abcd)$  are different (linear) combinations of the two integrals [cf. table 3.1]

$$S^\nu[ac | bd] = \int_0^\infty dr \int_0^\infty ds P_a(r) Q_c(r) \frac{1}{2} [W_{\nu-1, \nu+1, \nu}(r, s; \omega_{ac}) + W_{\nu-1, \nu+1, \nu}(r, s; \omega_{bd})] P_b(s) Q_d(s)$$

$$T^\nu[ac | bd] = \int_0^\infty dr \int_0^\infty ds P_a(r) Q_c(r) \frac{1}{2} [V_\nu(r, s; \omega_{ac}) + V_\nu(r, s; \omega_{bd})] P_b(s) Q_d(s)$$

$$V_\nu(r, s; \omega) = \begin{cases} -(2\nu+1) j_\nu(\omega r) n_\nu(\omega s) & r < s \\ -(2\nu+1) j_\nu(\omega s) n_\nu(\omega r) & r > s \end{cases}$$

$$W_{\nu-1, \nu+1, \nu}(r, s; \omega) = \begin{cases} -(2\nu+1) j_{\nu-1}(\omega r) n_{\nu+1}(\omega s) + \left(\frac{2\nu+1}{\omega}\right)^2 \frac{r^{\nu-1}}{s^{\nu+2}} & r < s \\ -(2\nu+1) \omega j_{\nu-1}(\omega s) n_{\nu+1}(\omega r) & r > s \end{cases}.$$

➤ In these expressions,  $j_\nu(\omega r)$  and  $n_\nu(\omega r)$  denote the spherical Bessel functions, and  $\omega_{ac} = |\epsilon_a - \epsilon_c|$  the difference of the corresponding single-particle energies.

## 3.2. Atomic potentials

### Parametrized many-electron densities:

- **Thomas-Fermi-Moliere (TFM) electron density:** A useful analytical model for the spherical symmetric electron density follows from a simple parametrization of the Thomas-Fermi (TF) screening function  $\chi^{(\text{TFM})}(r)$  and its substitution into the Poisson equation (Salvat *et al.*, 2005)

$$\chi^{(\text{TFM})}(r) = \sum_{i=1}^3 A_i \exp\left(\frac{a_i r}{b}\right), \quad A_1 = 0.1, \quad A_2 = 0.55, \quad A_3 = 0.35, \quad a_1 = 6, \quad a_2 = 1.2, \quad a_3 = 0.3$$

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}} \frac{\hbar^2}{m e^2 Z^{1/3}} = \frac{0.88534 a_o}{Z^{1/3}}$$

$$\rho^{(\text{TFM, electrons})}(r) = \frac{Z}{4\pi r} \sum_{i=1}^3 A_i a_i^2 \exp(a_i r).$$

- **Thomas-Fermi-Dirac (TFD) electron density:** The TFD theory also accounts for the exchange term of the electron gas and leads again to a differential equation that need to be solved numerically for each individual atom or ion. A parametrized form for an approximated TFD screening function  $\chi^{(\text{TFD})}$  has been suggested in the literature but results in a rather lengthy and cumbersome expansion.

### 3.2.a. In JAC implemented potentials

#### Atomic potentials:

- **Core-Hartree potential:**

$$V^{(\text{core-Hartree})}(r) = \int_0^\infty dr' \frac{\rho_c(r')}{r_{>}}, \quad r_{>} = \max(r, r'), \quad \rho_c(r) = \sum_a (P_a^2(r) + Q_a^2(r)),$$

and where the summation runs over all *core* orbitals of electron configurations. This potential is applied if just a single valence electron occurs (alkali atoms). In JAC, this potential can be obtained for a given level from `Jac.computePotentialCoreHartree(grid::Radial.Grid, level::Level)`.

➤ Dirac-Fock-Slater potential:

$$V^{(\text{DFS})}(r) = \int_0^\infty dr' \frac{\rho_t(r')}{r_{>}} - \left( \frac{3}{4\pi^2 r^2} \rho_t(r) \right)^{1/3}, \quad r_{>} = \max(r, r'), \quad \rho_t(r) = \sum_a (P_a^2(r) + Q_a^2(r)),$$

and where the summation runs over *all* orbitals (electrons). In JAC, this potential can be obtained for a given level from `Jac.computePotentialDFS(grid::Radial.Grid, level::Level)`.

➤ Hartree potential:

$$V^{(\text{Hartree})}(r) = - \sum_a \bar{q}_a r Y_{aa}^0(r)$$

where  $\bar{q}_a$  is the generalized occupation number, and where the summation runs over all orbitals here. In JAC, this potential can be obtained for a given level from `Jac.computePotentialHartree(grid::Radial.Grid, level::Level)`.

➤ Hartree-Slater potential:

$$V^{(\text{HS})}(r) = - \sum_a \bar{q}_a Y_{aa}^0(r) + \frac{3}{2} \left( \frac{3}{4\pi^2 r^2} \rho(r) \right)^{1/3} \frac{r}{2}, \quad \rho(r) = \sum_a \bar{q}_a (P_a^2(r) + Q_a^2(r)),$$

and where the summation runs over *all* orbitals. In JAC, this potential can be obtained for a given level from `Jac.computePotentialDFS(grid::Radial.Grid, level::Level)`.

➤ Kohn-Sham potential:

$$V^{(\text{Kohn-Sham})}(r) = \int_0^\infty dr' \frac{\rho_t(r')}{r_{>}} - \frac{2}{3r} \left( \frac{81}{32\pi^2} r \rho_t(r) \right)^{1/3}, \quad r_{>} = \max(r, r'), \quad \rho_t(r) = \sum_a (P_a^2(r) + Q_a^2(r)),$$

and where the summation runs over *all* orbitals (electrons). In JAC, this potential can be obtained for a given level from `Jac.computePotentialKohnSham(grid::Radial.Grid, level::Level)`.

### 3.2.b. Further atomic potentials, not yet considered in JAC

#### Atomic potentials:

- **Modified Dirac-Fock potential:** For a closed-shell  $N$ -electron atom, a modified Dirac-Fock potential has been defined for the (outgoing) electron by Derevianko *et al.* (1999) as

$$V(r) = \sum_b (2j_b + 1) \frac{Y_0(r, bb)}{r} - V^{(\text{exchange})}(r), \quad V^{(\text{exchange})}(r) = \frac{V^{(\text{direct})}(r)}{N}.$$

In this potential, the function  $Y_0(r, bb)/r$  is the Hartree screening potential for an electron in subshell  $b$ , and all generated orbitals are orthonormal to each other if the bound electrons are generated self-consistently in this potential. All continuum orbitals can then be generated in the same potential.

- **Tietz (1954) potential:**

$$V^{(\text{Tietz})}(r) = -\frac{\alpha Z}{r} \phi(x), \quad \phi(x) = \frac{1}{(1 + (\pi/8)^{2/3} x)^2}, \quad x = \frac{r Z^{1/3}}{\mu}, \quad \mu = \left(\frac{3\pi}{4}\right)^{2/3} \approx 0.8853.$$

- **Modified-Tietz potential:** (Neuffer and Commins, 1977)

$$V^{(\text{modified-Tietz})}(r) = -\frac{\alpha}{r} \left(1 + \frac{(Z-1)}{(1+tr)^2} e^{-\gamma r}\right)$$

where  $\gamma$  and  $t$  are parameters adjusted to fit the low-lying spectra of the atoms under consideration. Johnson *et al.* (1985) tabulate these parameters for rubidium, cesium, gold and thallium.

- **extended-Hartree potential:** The extended-Hartree potential has been defined by Gu (2008) and is based on the  $Y^k(r, ab)$  function as



well as various direct and exchange coefficients, as they arise from the energy average of a given (non-relativistic) configuration.

$$\begin{aligned}
 V^{(\text{extended-Hartree})}(r) &= \frac{1}{r \sum_a q_a \rho_a(r)} \left\{ \sum_{ab} q_a (q_b - \delta_{ab}) Y^0(r; bb) \rho_a(r) + \sum_a q_a (q_a - 1) \sum_{k>0} f_k(a, a) Y^k(r; aa) \rho_a(r) \right. \\
 &\quad \left. + \sum_{a \neq b} \sum_k q_a q_b g_k(a, b) Y^k(r; ab) \rho_{ab}(r) \right\} \\
 E^{(\text{extended-Hartree})} &= \frac{1}{2} \sum_a q_a \langle a | V^{(\text{extended-Hartree})} | a \rangle = \frac{1}{2} \sum_a q_a \int dr V^{(\text{extended-Hartree})}(r) \rho_{aa}(r)
 \end{aligned}$$

$$f_k(a, b) = - \left( 1 + \frac{1}{2j_a} \right) \begin{pmatrix} j_a & k & j_b \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2, \quad g_k(a, b) = - \begin{pmatrix} j_a & k & j_b \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2, \quad \rho_{ab} = P_a(r), P_b(r) + Q_a(r), Q_b(r).$$

For a single configuration, this potential is chosen so that it just contributes with  $E^{(\text{extended-Hartree})}$  as electron-electron part to the averaged DHF energy; here, the factor 1/2 occurs due to the double counting of electron pairs in the summation over electron shells in the potential  $V^{(\text{extended-Hartree})}(r)$  and which has the correct asymptotic behavior for  $r \rightarrow \infty$ .

➤ **Green-potential:** (Green *et al.*, 1969)

$$V^{(\text{Green})}(r) = -\frac{\alpha}{r} \left( 1 + \frac{(Z-1)}{[H (e^{r/d} - 1) + 1]} \right)$$

where  $H = d(Z-1)^{1/3}$  and  $d$  is an adjustable parameter. Johnson *et al.* (1985) apply this type of potential but leave  $d$  and  $H$  adjustable; they also tabulate these parameters for rubidium, cesium, gold and thallium.

➤ **Norcross (1973) potential:**

$$V^{(\text{Norcross})}(r) = V^{(\text{Thomas-Fermi})}(\lambda, r) - \frac{\alpha}{2r^4} \alpha_d \left( 1 - e^{-(r/r_c)^6} \right) - \frac{\alpha}{2r^6} (\alpha_q - 6\beta a_o) \left( 1 - e^{-(r/r_c)^{10}} \right)$$

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where  $V^{(\text{Thomas-Fermi})}(\lambda, r)$  is a Thomas-Fermi type potential with an adjustable parameter  $\lambda$ . The second and third terms correct for the polarization of the core;  $\alpha_d$  is the electric-dipole polarizability of the core,  $\alpha_q$  is the electric-quadrupole polarizability of the core and  $\beta a_o$  a dynamical correction to the quadrupole polarizability. Johnson *et al.* (1985) tabulate these parameters for rubidium, cesium, gold and thallium.

- **Variationally-optimized spherical potential for given Hamiltonian:** Talman and Shadwick (1976) derived a formal expression for a spherical potential that is variationally optimal for a given Hamiltonian. For this, they considered a given spherical potential  $V(r)$ , for which (1) the single-electron Schrödinger is solved equation and (2) an associated  $N$ -electron Hamiltonian is formed. The potential  $V_H(r)$  is then varied to minimize the ground-state energy of the Hamiltonian. These derivations give rise to a **formal integral equation for the difference  $V(r) - V_H(r)$** , and which can be interpreted as an equation for an effective central exchange potential. Overall, however, this equation seem to be of **little practical use**, since no explicit expression for the optimized spherical potential is obtained. It is shown only that such an optimized potential behaves like  $-e/r$  (for neutral atoms), i.e. that any electron of the atom moves asymptotically ( $r \rightarrow \infty$ ) in the Coulomb potential of the residual ion — likely, as expected by most atomic physicists.

#### Thomas-Fermi theory:

- **Thomas-Fermi density and equation:** The TF model of atoms and ions assumes that the electronic charge density  $\rho(r)$  [in atomic units] is continuous and finite in the interval  $[0, r_o]$ ; this charge density is related to the (dimensionless) **Thomas-Fermi potential  $\psi(x)$**  with the **ion boundary  $x_o = x_o(r_o)$**  by (Dmitrieva *et al.*, 1982)

$$\rho^{(\text{Thomas-Fermi})}(x) = \frac{32 Z^2}{9 \pi^3} \left[ \frac{\psi(x)}{x} \right]^{3/2} = \frac{32 Z^2}{9 \pi^3} \frac{\psi''(x)}{x}, \quad x = \left( \frac{128 Z}{9 \pi^2} \right)^{1/3} r = \frac{r}{\mu}$$

$$\psi''(x) = \frac{\psi^{3/2}(x)}{\sqrt{x}}, \quad \psi(0) = 1, \quad \psi(x_o) = 0, \quad x_o \psi'(x_o) = -1 + \frac{N}{Z}.$$

For neutral atoms, we have  $x_o \rightarrow \infty$ , and both  $\psi(x)$  and the ion boundary  $x_o$  just depend on the parameter  $N/Z \leq 1$ .

- **Multipole moments of the Thomas-Fermi density:** The multipole moments of the charge density can then be expressed as

$$\langle r^k \rangle^{(\text{Thomas-Fermi})} = \int d^3r r^k \rho^{(\text{Thomas-Fermi})}(r) = \left( \frac{9 \pi^2}{128} \right)^{k/3} Z^{\frac{3-k}{3}} \int_0^{x_o} dx \psi^{3/2}(x) x^{k+1/2}$$

- **Thomas-Fermi expectation value  $\langle 1/r \rangle^{(\text{Thomas-Fermi})}$  for neutral atoms:** An expansion of the Thomas-Fermi density can be utilized to express the  $\langle r^{-1} \rangle$  expectation value (multipole moment) by three just three terms (Dmitrieva *et al.*, 1982)

$$\langle r^{-1} \rangle^{(\text{Thomas-Fermi})} = 1.7937 Z^{4/3} - Z + 0.44983 Z^{2/3}.$$

In comparison with Hartree-Fock calculations, it was shown that this expectation value provides a reliable estimate within a few percent for all neutral atoms with  $Z \gtrsim 10$ .

### 3.3. Construction of symmetry-adapted CSF basis

#### Definition of symmetry-adapted CSF:

- **Coefficients of fractional parentage (CFP):** A set of CFP is defined for each subshell occupation  $(n\kappa)^w$ ; these coefficients are defined in order to ensure that all shell-state functions are antisymmetric and, hence, satisfy the Pauli exclusion principle. The CFP coefficients play an crucial role in the theory of many-electron atoms but are not needed in the quasi-spin formalism.
- **Factorization of CSF:** For a single subshell  $(n\kappa)$ , aCSF simply factorizes into a radial and a spin-angular part with well-defined seniority  $\nu$  and (subshell) total angular momentum  $\mathbb{J}M$

$$|(n\kappa)^w \alpha \nu \mathbb{J}M\rangle = \Pi_{j=1}^w R_{n\kappa}(r_i) |\kappa^w \alpha \nu \mathbb{J}M\rangle, \quad R_{n\kappa}(r) = \frac{1}{r} \begin{pmatrix} P(r) \\ Q(r) \end{pmatrix},$$

and where  $|\kappa^w \alpha \nu \mathbb{J}M\rangle$  refers to a spin-angular subshell state that only involves angular variables of all  $w$  equivalent electrons in this subshell.

- **Quasispin of relativistic subshell states:** Analogue to the construction of non-relativistic shell states, a quasi-spin quantum number and its projection can be assigned to each relativistic subshell state  $|\kappa^w \alpha \nu \mathbb{J}M\rangle$  by

$$Q = \left( \frac{2j+1}{2} - \nu \right), \quad M_Q = \frac{1}{2} \left( w - \frac{2j+1}{2} \right)$$

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With this notation, a relativistic subshell state of  $w$  equivalent electrons can be written in either seniority or quasi-spin notation:  
 $|(n\kappa)^w \alpha \nu \mathbb{J} M\rangle = |(n\kappa) \alpha Q M_Q \mathbb{J} M\rangle$ .

#### Excitation schemes for the constructing a many-electron CSF basis:

- Several (de-) excitation schemes for the construction of non-relativistic configuration lists are defined within JAC in order to facilitate the set-up of (lists of) CSF bases with selected total symmetry  $\mathbb{J}$ . These bases are required specially for the computation of cascades and/or approximate many-electron Green functions.
- In JAC, various excitation schemes are distinguished by the (abstract) `scheme::Basics.AbstractExcitationScheme`, and which is used for the construction of systematically enlarged basis sets, the computation of approximate Green functions as well as for the generation of atomic cascades.
- (De-) excitation of a single electron from a given set of (non-relativistic) configurations (`DeExciteSingleElectron`): This scheme includes all excitations and de-excitations of a single electron from a given list of (nonrelativistic bound-electron) configurations. Here, of course, the number of electrons of the newly generated configurations is the *same* as given by the configuration, while up to *one* free electron occur in each CSF for representing  $N$ -electron scattering levels.

Example:  $1s^2 2s^2 2p^6 \longrightarrow \left\{ \begin{array}{l} 1s 2s^2 2p^6 (ns + np + nd + \dots) \\ 1s^2 2s 2p^6 (ns + np + nd + \dots) \\ 1s^2 2s^2 2p^5 (ns + np + nd + \dots) \end{array} \right\}$

- (De-) excitation of two electrons from a given set of (non-relativistic) configurations (`DeExciteTwoElectrons`): Similar as above, this scheme includes all excitations and de-excitations of up to *two* electrons from the given list of (bound-electron) configurations and, hence, allows up to *two* free electrons for representing the  $N$ -electron scattering levels.

Example:  $1s^2 2s^2 2p^6 \longrightarrow \left\{ \begin{array}{l} 1s 2s^2 2p^6 (ns + np + nd + \dots) + 2s^2 2p^6 nl n'l' \\ 1s^2 2s 2p^6 (ns + np + nd + \dots) + 1s^2 2p^6 nl n'l' \\ 1s 2s 2p^6 nl n'l' \\ \dots \end{array} \right\}$

- Add a single electron to a given set of configurations (`AddSingleElectronWithoutHoles`): This scheme generates all configurations with one additional electron to the given set of configurations but without any replacement from the occupied orbitals.

Example:  $1s^2 2s^2 2p^6 \longrightarrow \{ 1s^2 2s^2 2p^6 (ns + np + nd + \dots) \}$

## 3.4. Dirac-Hartree-Fock method

### Remarks:

- **DHF equations:** The solutions of the DHF equations are often not unique because the DHF equations are *invariant* with regard to orbital rotations, i.e. unique only up to some unitary transformation. These unitary transformation changes the radial functions, but leaves the (total) wave function and energy invariant. This non-uniqueness of the DHF method can often be resolved by either placing some additional constraints upon the occupation numbers of the orbitals, or by minimizing the energy of the lowest orbital of each single-electron symmetry  $\kappa$ . Moreover, Koopman's theorem enables one to construct a symmetric energy matrix  $(\varepsilon_{n\kappa, n'\kappa'})$  and to separately optimize the extreme values of this matrix (Froese Fischer *et al.*, 2016).
- **DHF equations:** Various methods have been worked out to solve the set of coupled DHF equations (coupled integro-differential equations). Instead of solving these integro-differential equations directly, an **iterative procedure is often applied in which the exchange interaction and the off-diagonal energy parameters are treated as non-homogeneous terms** (and obtained from the last iteration), and where the equations are simply solved as a boundary-value problem. In finite-difference methods, moreover, all the radial functions are typically described on either a logarithmic or logarithmic-linear mesh.
- **Hartree-Dirac-Fock potential:** A very particular choice of a central-field potential in all many-electron computations refer to the Hartree-Fock potential for closed-shell atoms or ions. This is a non-local potential that can be defined by its action upon any orbital as

$$V^{(\text{HF})} \phi_a(\mathbf{r}) = \sum_b \int d^3\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} [\phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}') \phi_a(\mathbf{r}) - \phi_b^*(\mathbf{r}') \phi_a(\mathbf{r}') \phi_b(\mathbf{r})]$$

and where the summation over  $b = (n_b, \kappa_b, m_b)$  runs over all occupied orbitals in the closed-shell core.

- **Hartree-Dirac-Fock potential for a spherical-symmetric atom:** For a spherical-symmetric core, the radial part of an orbital function  $R_a(r) = \begin{pmatrix} P_a(r) \\ Q_a(r) \end{pmatrix}$  can be expressed in terms of its *large* and *small* component, and the integration over all spherical coordinates can

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be performed analytically. In this representation, the Hartree-Fock potential can be written also in terms of the **Hartree screening function**  $v_L(r; a, b)$  as

$$V^{(\text{HF})} R_a(r) = \sum_{n_b \kappa_b} [j_b] \left\{ v_o(r; b, b) R_a(r) - \sum_L \frac{\langle \kappa_b \| C^{(L)} \| \kappa_a \rangle}{[j_a, j_b]} v_L(r; b, a) R_b(r) \right\}.$$

➤ **Hartree screening function**  $v_L(r; a, b)$ :

$$v_k(r; a, b) = e^2 \int_0^\infty dr' \frac{r_{<}^k}{r_{>}^{k+1}} [P_a(r') P_b(r') + Q_a(r') Q_b(r')], \quad r_{<} = \min(r, r'), \quad r_{>} = \max(r, r')$$

## 3.5. Atomic estimates of quantum-electrodynamic (QED) corrections

### 3.5.a. QED model operators & model potentials

#### Background & notations:

- Various proposals have been made in the literature to incorporate the (radiative) quantum-electrodynamic corrections by different model potentials into correlated many-electron methods, such as the MCDHF, many-body perturbation or coupled-cluster theories.
- **Effective single-electron QED Hamiltonian:** To a good approximation, **these QED corrections can be incorporated into the (many-electron) representation  $\{c_r(\alpha \mathbb{J})\}$  of some level  $(\alpha \mathbb{J})$  by means of a local single-electron QED Hamiltonian.** This Hamiltonian can be separated into two parts

$$\mathbb{h}^{(\text{QED})} = \mathbb{h}^{(\text{SE})} + \mathbb{h}^{(\text{VP})},$$

the self-energy (SE) and vacuum-polarization (VP) Hamiltonians, and which are often written in terms of (effective) potentials.

- **Vacuum-polarization:** The vacuum-polarization is given by a *local* potential and **can be further splitted into an Uehling and a Wichmann-Kroll potential**; this local potential is rather straightforward to calculate and has already been applied in many applications in the past.

- **Self-energy Hamiltonian  $\mathfrak{h}^{(\text{SE})}$**  : Such a Hamiltonian can be generally represented as sum of a local and non-local potential. These potentials are typically based on *ab initio* calculations of the diagonal and nondiagonal matrix elements of the one-loop QED operator with H-like wave functions (Shabaev *et al.*, 2013).
- Shabaev and coworkers (2013) have shown that the **QED corrections can be systematically incorporated into an effective Hamiltonian that acts in the space of Slater determinants**, if these determinants are built from one-electron positive-energy states only and if the total (many-electron binding) energies of the system are smaller than the pair-creation energy. This effective QED Hamiltonian can then be added to the Dirac-Coulomb-Breit Hamiltonian.
- **Beyond QED model Hamiltonians**: Explicit calculations of radiative corrections are extremely sophisticated and time-consuming for many-electron systems, if the standard QED perturbation theory is to be applied. **Until the present, such detailed QED computations can be carried out only for highly-charged, few-electron ions and by still making use of an effective screening potential** (instead of the complete perturbation expansion for all electron-electron pairs).

### Vacuum polarization potentials:

- **Uehling potential**: This potential is the dominant part of the VP and can be obtained from the direct numerical integration of the well-known formula

$$V^{(\text{Uehling})}(r) = -\alpha Z \frac{2\alpha}{3\pi} \int_0^\infty dr' 4\pi r' \rho(r') \int_1^\infty dt \left(1 + \frac{1}{2t^2}\right) \frac{\sqrt{t^2 - 1}}{t^2} \frac{e^{-2m|r-r'|t} - e^{-2m(r+r')t}}{4mrt},$$

and where  $Z\rho(r)$  denotes the density of the nuclear charge distribution, if normalized to  $\int dV \rho(r) = 1$ .

- **Approximate Uehling potential**: The Uehling potential can be calculated also by an approximate formula for a point-like nucleus (Flambaum and Ginges, 2005)

$$V^{(\text{simplified Uehling})}(r) = \frac{2\alpha}{3\pi} V_{\text{nuc}}(r) \int_1^\infty dt \left(1 + \frac{1}{2t^2}\right) \frac{\sqrt{t^2 - 1}}{t^2} e^{-2mrt}.$$

- **Wichmann-Kroll potential**: A detailed evaluation of the Wichmann-Kroll potential is (much) more sophisticated but can be estimated again to a rather good accuracy by the approximate formula for a point-like nucleus and with the classical radius  $r_c$  (Flambaum and Ginges,

2005)

$$V^{(\text{simplified WK})}(r) = -\frac{2\alpha}{3\pi} V(r) \frac{0.092 Z^2 \alpha^2}{1 + (1.62 r/r_c)^4}.$$

- The Wichmann-Kroll correction is generally small and gives a  $\sim 1\%$  contribution to the VP shifts only for  $Z \gtrsim 80$  (Flaumbaum and Ginges, 2005).

### Local self-energy potentials:

- Shabaev *et al.* (2013) suggest a **local but independent part of the self-energy potential for each symmetry block  $\kappa$**  of the one-electron orbitals of the form

$$V_{\kappa}^{(\text{local SE})}(r) = A_{\kappa} \exp\left(-\frac{2\pi r}{\lambda_C}\right) = A_{\kappa} \exp\left(-\frac{r}{\alpha}\right),$$

where the constants  $A_{\kappa}$  are chosen to reproduce the SE shift for the lowest (one-electron, H-like) energy of each given  $\kappa$  symmetry, and where  $\lambda_C = h/mc$  is the Compton wavelength of the electron.

- These local contributions can also be cast be into the form

$$V^{(\text{local SE})}(r) = \sum_{\kappa} A_{\kappa} P_{\kappa} \exp\left(-\frac{2\pi r}{\lambda_C}\right), \quad \langle a | P_{\kappa} | b \rangle = \delta_{\kappa, \kappa_a} \delta_{\kappa, \kappa_b}.$$

- **Self-energy interaction strength:** Following the discussion with Volotka (2019), a (single-electron) **local self-energy interaction strength** for the (local) potential above can be written

$$\langle a || \mathbb{h}^{(\text{local SE})} || a \rangle = \left[ \frac{\langle n_g \kappa || \mathbb{h}^{(\text{local SE})} || n_g \kappa \rangle}{\langle n_g \kappa || \exp\left(-\frac{r}{\alpha}\right) || n_g \kappa \rangle} \right]_{\text{hydrogenic}} \langle a || \exp\left(-\frac{r}{\alpha}\right) || a \rangle, \quad \langle a || \mathbb{h}^{(\text{local SE})} || b \rangle = 0 \quad \text{for } a \neq b,$$

where  $|n_g \kappa\rangle = \{1s_{1/2}, 2p_{1/2}, 2p_{3/2}, 3d_{3/2}, \dots\}$  refers to the lowest hydrogenic orbitals of symmetry  $\kappa$  and nuclear charge  $Z$ . For a non-diagonal self-energy potential, the representation of the one-electron matrix elements will be more difficult and are presently not considered in JAC.



- **Self-energy interaction strength:** Shabaev *et al.* (2013) have tabulated values for  $\langle n_g \kappa \| \mathbb{h}^{(\text{local SE})} \| n_g \kappa \rangle_{\text{hydrogenic}}$  for selected nuclear charges, which can be readily applied in order to compute the self-energy interactions strengths for general many-electron atoms and ions.

### Radiative potentials:

- **Radiative potential:** Flambaum and Ginges (2005) suggest an approximate expression for a (so-called) **radiative potential** which can be utilized in order to estimate the radiative corrections in strong Coulomb fields to the energies and electric-dipole transition amplitudes in atomic (many-electron) computation. This (alternative) potential is said to give good QED estimates with an accuracy of just a few percent but has been mainly tested and applied to (neutral) cesium only.
- **Radiative potential:** Flambaum and Ginges (2005) decompose this radiative potential into five terms which are explained either above or below:

$$V^{(\text{total QED})} = V^{(\text{simplified Uehling})} + V^{(\text{magnetic form})} + V^{(\text{electric form})} + V^{(\text{low frequency})} + V^{(\text{simplified WK})}.$$

- **Magnetic form-factor potential:** For the magnetic form-factor contribution, Flambaum and Ginges (2005) give

$$V^{(\text{magnetic form})} = \frac{\alpha}{4\pi m} i \boldsymbol{\gamma} \cdot \boldsymbol{\nabla} \left[ V(r) \left( \int_1^\infty dt \frac{\exp(-2m r t)}{t^2 \sqrt{t^2 - 1}} - 1 \right) \right],$$

and where  $\boldsymbol{\gamma} = (\gamma_1, \gamma_2, \gamma_3)$  is the vector of gamma matrices.

- **Low-frequency potential to the electric form-factor:** Flambaum and Ginges (2005) suggest the (low-frequency) expression

$$V^{(\text{low frequency})} = -\frac{B(Z)}{e} Z^4 \alpha^5 m c^2 \exp\left(\frac{Z r}{a_o}\right), \quad B(Z) = 0.074 + 0.35 Z \alpha,$$

with the Bohr radius  $a_o$  and where the function  $B(Z)$  has been fitted in order to reproduce the radiative energy shifts for  $p$ -levels of selected heavy elements. This term should be used with some care however.

- **Electric form-factor potential (including high-frequency contributions):** Flambaum and Ginges (2005) display a final expression for the electric form-factor contribution

$$V^{(\text{electric form})}(r) = -A(Z, r) \frac{\alpha}{\pi} V(r) \int_1^\infty dt \frac{\exp(-2m r t)}{\sqrt{t^2 - 1}} \left[ \left(1 - \frac{1}{2t^2}\right) [\ln(t^2 - 1) + 4 \ln(1/Z\alpha + 0.5)] - \frac{3}{2} + \frac{1}{t^2} \right].$$

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Here, the function  $A(Z, r) = (1.071 - 1.976 x^2 - 2.128 x^3 + 0.169 x^4) m r / (m r + 0.07 Z^2 \alpha^2)$ , has been suggested with  $x = (Z - 80) \alpha$ . The detailed form of  $A(Z, r)$  was found by fitting the radiative shifts for the high Coulomb  $s$  levels from the literature. **This term should be used with good care again.**

- Note that this local potential by Flambaum and Ginges (2005) was optimized for weakly bound valence states of heavy neutral atoms and may be less accurate for strongly bound ionic or even core-hole states.

### 3.5.b. In JAC implemented QED estimates

#### Models & applications:

- In JAC, the radiative QED corrections can be incorporated into the computation and representation of the wave functions if `AsfSettings(..)` is initialized with `qedModel = QedPetersburg()` or `qedModel = QedSydney()`. This singleton datatype tells JAC how the estimates for the vacuum polarization and the (local) self-energy contributions are incorporated into the Hamiltonian matrix, cf. below.
- In JAC, use `qedModel = NoneQed()` in `AsfSettings(..)` if no QED estimates are to be included; this is also the default.

#### Implementation:

- **QedPetersburg model:** Here, we simply add to all matrix elements  $\langle a || \mathbb{h}^{(1\text{-particle})} || b \rangle$  in the many-electron Hamiltonian matrix the (single-electron) matrix elements

$$\langle a || \mathbb{h}^{(\text{QED})} || b \rangle = \langle a || \mathbb{h}^{(\text{local SE})} || b \rangle + \langle a || \mathbb{h}^{(\text{simplified Uehling})} || b \rangle.$$

- **QedSydney model:** Analogous, here we add to all matrix elements  $\langle a || \mathbb{h}^{(1\text{-particle})} || b \rangle$  in the many-electron Hamiltonian matrix the (single-electron) matrix elements

$$\langle a || \mathbb{h}^{(\text{QED})} || b \rangle = \langle a || \mathbb{h}^{(\text{magnetic form})} || b \rangle + \langle a || \mathbb{h}^{(\text{electric form})} || b \rangle + \langle a || \mathbb{h}^{(\text{low frequency})} || b \rangle + \langle a || \mathbb{h}^{(\text{simplified Uehling})} || b \rangle.$$

- **Effective QED operator** With the definitions from above, the total QED operator for a many-electron atom includes of course a summation over all atomic electrons:

$$\mathbb{H}^{(\text{QED})} = \mathbb{H}^{(\text{SE})} + \mathbb{H}^{(\text{VP})} = \sum_j \mathbb{h}_j^{(\text{QED})} = \sum_j \left( \mathbb{h}_j^{(\text{SE})} + \mathbb{h}_j^{(\text{VP})} \right),$$

where the  $\mathbb{h}_j^{(\text{SE})}$  and  $\mathbb{h}_j^{(\text{VP})}$  refers to the one-electron operators for electron  $j$ .

## 3.6. Unitary $jjJ - LSJ$ transformation of atomic states

### 3.6.a. Transformation matrices from $jjJ$ - to $LSJ$ -coupling

#### Atomic coupling schemes:

- **Coupling schemes:** Atomic and ionic levels are usually identified and labeled by means of quantum numbers of an appropriate coupling scheme. However, these quantum numbers are well-conserved only for a pure coupling of symmetry-adapted many-electron state, and which is realized only (rather) approximately in Nature.
- **$LSJ$ - and  $jjJ$ -coupling** are nowadays the two most frequently applied coupling schemes in atomic theory.
- As usual in quantum mechanics, the transformation from one to another orthonormal basis (i.e. the representation of atomic levels in a particular coupling scheme) is simply given by a unitary matrix, although it is generally not easy to evaluate this transformation matrix for arbitrary shell structures of atoms and ions.
- **$LSJ$ -notation:** In atomic spectroscopy, the standard  $LSJ$ -notation of the levels is frequently applied for classifying the low-lying level structures of atoms or ions.
- **Labeling of levels:** Atomic energy levels are often labeled by means of their leading  $LSJ$ -coupled CSF in a wave function expansion. However, special care need to be taken, if the same CSF occurs largest in the expansion of two levels, since then, the classification is no longer unique.
- The lack of providing a fast and proper spectroscopic notation in relativistic computations may hamper the spectroscopic level classification of medium and heavy elements as well as the interpretation and analysis of inner-shell processes.

### $jjJ - LSJ$ transformation of subshell states:

- **Unique subshell order:** Since each non-relativistic  $n\ell$ -shell (apart from the  $ns$  shells) split into two relativistic subshells with  $j = \ell \pm 1/2$ , the order of these subshell is relevant for the transformation of the many-electron basis and is always fixed in JAC to  $n\ell_{j=\ell-1/2}$ ,  $n\ell_{j=\ell+1/2}$ . For the  $np$ - and  $nd$ -shells, for example, we always assume the sequence  $np_{1/2}$ ,  $np_{3/2}$  and  $nd_{3/2}$ ,  $nd_{5/2}$  in all formulas below.
- **Non-relativistic subshell states:** In the transformation of the non-relativistic shell states  $|n\ell^N \alpha\nu LS\rangle$ , we generally have to consider the product of two (relativistic) subshell states  $\left| n\bar{\kappa}^{\bar{N}} \bar{\nu} \bar{J}, n\kappa^{\dagger N} \dagger \nu \dagger J \right\rangle$ , and with  $\bar{N} + \dagger N = N$ . Here, the  $+$  and  $-$  on top of the quantum numbers just refer to the relativistic subshells with  $j = \ell \pm 1/2$ .
- The transformation between the (sub-) shell states in  $jjJ$ - and  $LSJ$ -coupling can be expressed with real Fourier coefficients as

$$\left| (n\bar{\kappa}^{\bar{N}} \bar{\nu} \bar{J}, n\kappa^{\dagger N} \dagger \nu \dagger J) J \right\rangle = \sum_{\alpha\nu LS} |n\ell^N \alpha\nu LSJ\rangle \left\langle n\ell^N \alpha\nu LSJ \left| (n\bar{\kappa}^{\bar{N}} \bar{\nu} \bar{J}, n\kappa^{\dagger N} \dagger \nu \dagger J) J \right. \right\rangle, \quad N \equiv \bar{N} + \dagger N$$

$$\left\langle n\ell^N \alpha\nu LSJ \left| (n\bar{\kappa}^{\bar{N}} \bar{\nu} \bar{J}, n\kappa^{\dagger N} \dagger \nu \dagger J) J \right. \right\rangle = \left\langle (n\bar{\kappa}^{\bar{N}} \bar{\nu} \bar{J}, n\kappa^{\dagger N} \dagger \nu \dagger J) J \left| n\ell^N \alpha\nu LSJ \right. \right\rangle.$$

- The evaluation of the (unitary) transformation does generally not involve the radial (orbital) functions but depends only on the spin-angular functions.
- Although the notation of the non-relativistic and relativistic (sub-) shell states is quite similar in  $jjJ$ - and  $LSJ$ -coupling, these states generally belong to different irreducible representations of the  $SO_3$  rotation group. This can be seen already from the splitting of each non-relativistic shell into two subshells as outlined above.

### Transformation of atomic states:

- **$LSJ$ -coupled, non-relativistic CSF:**

$$|\gamma^{(\text{NR})} LSJ\rangle = |((\cdot ((n_1 \ell_1^{N_1} \alpha_1 \nu_1 L_1 S_1), (n_2 \ell_2^{N_2} \alpha_2 \nu_2 L_2 S_2)) L_{12} S_{12}, (n_3 \ell_3^{N_3} \alpha_3 \nu_3 L_3 S_3)) L_{123} S_{123}, \dots) LS) J\rangle$$

➤  $jjJ$ -coupled, relativistic CSF:

$$|\gamma^{(R)} J\rangle = \left| \left( \left( \left( (n_1 \bar{\kappa}_1 \bar{\nu}_1 \bar{J}_1), (n_1 \bar{\kappa}_1 \bar{\nu}_1 \bar{J}_1) \right) \bar{X}_1, (n_2 \bar{\kappa}_2 \bar{\nu}_2 \bar{J}_2) \right) \bar{X}_2, \dots \right) J \right\rangle$$

➤ To determine the explicit transformation matrix for going from one to another (many-electron) basis, of course, all these quantum numbers above play an important role in practice. For the sake of simplicity, however, it is sufficient to just re-call that the  $jj$ -coupled CSF basis spans a (finite) part  $\mathcal{H}^{(\text{finite})}$  of the  $N$ -electron Hilbert space and that the matrix  $(\langle \gamma^{(\text{NR})} LSJ | \gamma^{(R)} J \rangle)$  just represent the (usual) Fourier coefficients for the expansion of an atomic state with respect to the basis  $\{|\gamma^{(\text{NR})} LSJ\rangle\}$  in  $\mathcal{H}^{(\text{finite})}$ .

➤ Representation of atomic state functions:

$$|\psi_\alpha\rangle = \sum_r c_r^{(R)}(\alpha) |\gamma_r^{(R)} \mathbb{J}\rangle = \sum_t c_t^{(\text{NR})}(\alpha) |\gamma_t^{(\text{NR})}(L_t, S_t) \mathbb{J}\rangle$$

➤ **Formal construction of the  $jjJ \rightarrow LSJ$  transformation matrix:** If we denote the basis states of the (standard) product basis of the (subshell) states in  $jjJ$ - and  $LSJ$ -coupling by the  $|\text{standard} - jjJ\rangle$  and  $|\text{standard} - LSJ\rangle$ , the transformation of a relativistic CSF can be formally written as

$$\begin{aligned} |\gamma_r^{(R)} \mathbb{J}\rangle &= \sum_{\text{standard} - jjJ} |\text{standard} - jjJ\rangle \langle \text{standard} - jjJ | \gamma_r^{(R)} \mathbb{J}\rangle \\ &= \sum_{\substack{\text{standard} - jjJ \\ \text{standard} - LSJ \\ \text{atomic} - LSJ}} |\gamma_t^{(\text{NR})}(L_t, S_t) JP\rangle \langle \gamma_t^{(\text{NR})}(L_t, S_t) JP | \text{standard} - LSJ\rangle \langle \text{standard} - LSJ | \text{standard} - jjJ\rangle \langle \text{standard} - jjJ | \gamma_r^{(R)} \mathbb{J}\rangle \\ &= \sum_{Q_p, Q_r} |\gamma_t^{(\text{NR})}(L_t, S_t) \mathbb{J}\rangle \times [\text{LSJ} - \text{recoupling}] \times [\text{product of LSJ} - jjJ \text{ matrix elements}] \times [jjJ - \text{recoupling}] \end{aligned}$$

Here, a summation over  $\text{standard} - jjJ$ ,  $\text{standard} - LSJ$ , ... implies a summation over all quantum numbers that are not bound due to given values at the left-hand-side of the expression. In the last line, in particular, the summation runs over the (product basis) quantum numbers  $Q_p = [(\alpha_1 \nu_1 L_1 S_1), (\alpha_2 \nu_2 L_2 S_2), \dots]$  as well as over the (re-coupling) quantum numbers as defined by the [LSJ-recoupling] and [jjJ-recoupling] recoupling coefficients,  $Q_p = [J_1, J_2, J_{12}, J_3, J_{123}, \dots, T_1, T_2, T_{12}, T_3, T_{123}, \dots]$  with  $\delta_{J_1, T_1} \delta_{J_2, T_2} \delta_{J_{12}, T_{12}} \dots$ .

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➤ Re-coupling from the  $LSJ$ -product to the  $(L_t, S_t)$   $J$ -coupled basis:

$$\begin{aligned} \left\langle \gamma_t^{(\text{NR})} (L_t S_t) \mathbb{J} \mid \text{standard} - \text{LS} \right\rangle &\equiv [\text{LSJ} - \text{recoupling}] \\ &= \left\langle \left( \left( \left( (L_1, L_2) L_{12}, (L_3) L_{123}, \dots \right) L_t, \left( (S_1, S_2) S_{12}, (S_3) S_{123}, \dots \right) S_t \right) J \mid \left( \left( (L_1, S_1) T_1, (L_2, S_2) T_2 \right) T_{12}, (L_3, S_3) T_3 \right) T_{123}, \dots \right) J \right\rangle \end{aligned}$$

➤ Re-coupling from the  $jjJ$ -product to the  $jXJ$ -coupled basis:

$$\begin{aligned} \left\langle \text{standard} - \text{jj} \mid \gamma_r^{(\text{R})} \mathbb{J} \right\rangle &\equiv [\text{jjJ} - \text{recoupling}] \\ &= \left\langle \left( \left( \left( \left( \bar{J}_1, \bar{J}_1^+ \right) J_1, \left( \bar{J}_2, \bar{J}_2^+ \right) J_2 \right) J_{12}, \left( \bar{J}_3, \bar{J}_3^+ \right) J_3 \right), J_{123}, \dots \right) J \mid \left( \left( \left( \left( \bar{J}_1, \bar{J}_1^+ \right) \bar{X}_1, \bar{J}_2 \bar{X}_2, \bar{J}_2^+ \right) \bar{X}_2, \bar{J}_3 \right) \bar{X}_3, \dots \right) J \right\rangle \end{aligned}$$

➤ In practice, the summation over such large sets of quantum numbers is often replaced by a (simpler or even single) summation over the allowed and predefined sets of quantum numbers.

### 3.6.b. Re-coupling coefficients

#### Zero open shell:

➤ CSF with *no* open shell are the same in the  $jjJ$ - and  $LSJ$ -coupling scheme,

$$\left| \gamma_r^{(\text{R, closed})} \mathbb{J} = 0^+ \right\rangle \equiv \left| \gamma_r^{(\text{NR, closed})} \mathbb{J} = 0^+ \right\rangle$$

and can be simply replaced with their (expansion) coefficients in the expansion of the wave function.

#### Single open shell:

➤ Re-coupling from the  $LSJ$ -product to the  $(L_t, S_t)$   $J$ -coupled basis:

$$[\text{LSJ} - \text{recoupling}] = \langle (L_1, S_1) J \mid (L_1, S_1) J \rangle = 1.$$

➤ Re-coupling from the  $jjJ$ -product to the  $jXJ$ -coupled basis:

$$[\text{jjJ} - \text{recoupling}] = \left\langle (\bar{J}_1, J_1^+) J \mid (\bar{J}_1, J_1^+) J \right\rangle = 1.$$

## Two open shells:

➤ Re-coupling from the  $LSJ$ -product to the  $(L_t, S_t)J$ -coupled basis:

$$\begin{aligned} [\text{LSJ} - \text{recoupling}] &= \langle ((L_1, L_2) L_{12}, (S_1, S_2) S_{12}) J \mid ((L_1, S_1) T_1, (L_2, S_2) T_2) J \rangle \\ &= (-1)^{L_1 + S_1 - T_1 + L_2 + S_2 - T_2 + L_{12} + S_{12} - J} \sqrt{[T_1, T_2, L_{12}, S_{12}]} \begin{Bmatrix} L_1 & S_1 & T_1 \\ L_2 & S_2 & T_2 \\ L_{12} & S_{12} & J \end{Bmatrix}, \quad Q_r = [T_1, T_2]. \end{aligned}$$

➤ Re-coupling from the  $jjJ$ -product to the  $jXJ$ -coupled basis:

$$\begin{aligned} [\text{jjJ} - \text{recoupling}] &= \left\langle \left( (\bar{J}_1, J_1^+) J_1, (\bar{J}_2, J_2^+) J_2 \right) J \mid \left( ((\bar{J}_1, J_1^+) \bar{X}_1, \bar{J}_2), \bar{X}_2, J_2 \right) J \right\rangle \\ &= (-1)^{\bar{J}_2 + J_2^+ + J_1 + J} \delta(\bar{J}_1, J_1^+, J_1) \delta_{J_1 \bar{X}_1} \sqrt{[J_2, \bar{X}_2]} \begin{Bmatrix} J_1 & \bar{J}_2 & \bar{X}_2 \\ J_2^+ & J & J_2 \end{Bmatrix}, \quad Q_r = [J_1, J_2]. \end{aligned}$$

➤ The summation over  $Q_r$  also implies all further quantum numbers that are needed in order to distinguish different subshell states in  $jjJ$  and to  $LSJ$  product basis, respectively. In JAC, this summation is performed by (1) applying the standard coupling  $L \oplus S = T_{\text{low}}, \dots, T_{\text{up}}$  and (2) by a summation over the corresponding subshell states from a internally (defined) list. An explicit summation over  $J_1, J_2$  can be omitted because of orthogonality, and which gives rise to the Kronecker factors  $\delta_{T_1, J_1}, \delta_{T_2, J_2}$ .

### Three open shells:

➤ Re-coupling from the  $LSJ$ -product to the  $(L_t, S_t)J$ -coupled basis: (Kosheleva 2020)

$$\begin{aligned}
 [\text{LSJ} - \text{recoupling}] &= \langle (((L_1, L_2) L_{12}, L_3) L_{123}, ((S_1, S_2) S_{12}, S_3) S_{123}) J | (((L_1, S_1) T_1, (L_2, S_2) T_2) T_{12}, (L_3, S_3) T_3) J \rangle \\
 &= (-1)^{L_1 + S_1 - T_1 + L_2 + S_2 + L_3 - L_{123} + S_3 - S_{123} - J - 2T_{12}} \sqrt{[L_{12}, L_{123}, S_{12}, S_{123}, T_1, T_2, T_2, T_{12}]} \\
 &\quad \times \begin{Bmatrix} L_2 & L_1 & L_{12} \\ S_2 & S_1 & S_{12} \\ T_2 & T_1 & T_{12} \end{Bmatrix} \begin{Bmatrix} J & L_{123} & S_{123} \\ T_3 & L_3 & S_3 \\ T_{12} & L_{12} & S_{12} \end{Bmatrix}, \quad Q_r = [T_1, T_2, T_{12}, T_3].
 \end{aligned}$$

➤ Re-coupling from the  $jjJ$ -product to the  $jXJ$ -coupled basis:

$$\begin{aligned}
 [\text{jjJ} - \text{recoupling}] &= \left\langle \left( ((\bar{J}_1, \bar{J}_1^+) J_1, (\bar{J}_2, \bar{J}_2^+) J_2) J_{12} (\bar{J}_3, \bar{J}_3^+) J_3 \right) J \mid \left( (((\bar{J}_1, \bar{J}_1^+) \bar{X}_1, \bar{J}_2) \bar{X}_2, \bar{J}_2^+) \bar{X}_2, \bar{J}_3) \bar{X}_3, \bar{J}_3^+) J \right) \right\rangle \\
 &= (-1)^{2\bar{X}_1 + \bar{J}_2 + \bar{J}_2^+ + J_2 + 2J_{12} + \bar{J}_3 + \bar{J}_3^+ + J_3} \sqrt{[J_2, \bar{X}_2, J_3, \bar{X}_3]} \begin{Bmatrix} \bar{J}_2 & \bar{J}_2^+ & J_2 \\ J_{12} & \bar{X}_1 & \bar{X}_2 \end{Bmatrix} \begin{Bmatrix} \bar{J}_3 & \bar{J}_3^+ & J_3 \\ J & J_{12} & \bar{X}_3 \end{Bmatrix}, \\
 &\quad Q_r = [J_1, J_2, J_{12}, J_3].
 \end{aligned}$$

➤ The summation over  $Q_r$  also implies all further quantum numbers that are needed in order to distinguish different subshell states in  $jjJ$  and to  $LSJ$  product basis, respectively. In JAC, this summation is performed by (1) applying the standard coupling  $L \oplus S = T_{\text{low}}, \dots, T_{\text{up}}$  and (2) by a summation over the corresponding subshell states from a internally (defined) list. An explicit summation over  $J_1, J_2, J_3$  can be omitted because of orthogonality, and which gives rise to the Kronecker factors  $\delta_{T_1, J_1}, \delta_{T_2, J_2}, \delta_{T_3, J_3}$



### 3.6.c. In JAC implemented $jjJ - LSJ$ transformation

#### Transformation, notations & application:

- Representation  $c_s^{(\text{NR})}(\alpha)$  of atomic states.

$$|\psi_\alpha\rangle = \sum_t c_t^{(\text{NR})}(\alpha) |\gamma_t^{(\text{NR})} LSJ\rangle = \sum_r c_r^{(\text{R})}(\alpha) |\gamma_r^{(\text{R})} J\rangle$$

- **Unique label:**  $\left( \dots \left( (n_1 \ell_1)^{N_1} {}^{2S_1+1}L_1; (n_2 \ell_2)^{N_2} {}^{2S_2+1}L_2 \right) {}^{2S_{12}+1}L_{12}, (n_3 \ell_3)^{N_3} {}^{2S_3+1}L_3 \dots \right) {}^{2S+1}L_J$

Such a label is assigned to each selected level, for instance, by printing

$$[(n_1 \ell_1)^{N_1} {}^{2S_1+1}L_1] {}^{2S_1+1}L_1 : [(n_2 \ell_2)^{N_2} {}^{2S_2+1}L_2] {}^{2S_{12}+1}L_{12} : [(n_3 \ell_3)^{N_3} {}^{2S_3+1}L_3] {}^{2S_{123}+1}L_{123} : \dots$$

- In JAC, a  $jjJ - LSJ$  transformation is performed for all selected levels if `jjLS = LSjjSettings(true, ...)` is set in `AsfSettings()`.
- In JAC, the  $LSJ$ -coupled expansion of selected levels is printed by default after the diagonalization of the (many-electron) Hamiltonian matrix.
- Apart from the  $LSJ$  assignment to atomic levels, JAC can rather easily support also the full transformation of the wave functions, if required for (nonrelativistic) computations. This is achieved by setting the cut-off parameter to *zero* in `LSjjSettings(...)`.
- A proper  $LSJ$  spectroscopic notation has been found useful in order to explain the excitation and decay properties of individual levels, at least qualitatively.
- The  $jjJ - LSJ$  transformation of the ( $jjJ$ -coupled) CSF is supported for all **shell structures with (up to) two open shells, including open *s*-, *p*-, *d*-shells**. Further work is required to fully implement also transformation of open *f*-shells.

#### Implementation of $jjJ - LSJ$ transformation:

- Internally, a  $jj - LS$  transformation of selected levels from a given multiplet is carried out by the following steps:
  - 1) Generation of a non-relativistic shell list for the given multiplet, based on a proper relativistic subshell list. The program terminates with an error message if the relativistic subshells of the given multiplet are ordered in *non-standard order*, for example, ...,  $2p_{3/2}$ ,  $2p_{1/2}$ , ... or similar.
  - 2) Extract all non-relativistic configurations that contribute to the given multiplet and generate a corresponding set of nonrelativistic CSF states; define an instance of a nonrelativistic basis.

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- 3) Expand (in turn) each relativistic CSF into the non-relativistic basis and add their contributions to the (nonrelativistic) eigenvectors. This expansion is made independently of CSF with zero-, one-, two-, ... open (nonrelativistic) shells.
- 4) Check and print the  $LSJ$  expansion of all selected levels in a neat format with respect to the (nonrelativistic) configurations as well as CSF.

```
"""
'struct LS_jj_qn' ... defines a struct for the generalized quantum numbers (qn) of a LS_jj matrix element.
+ NN      ::Int64    ... occupation w = NN
+ QQ      ::Int64    ... subshell total quasispin 2*Q = nu
+ LL      ::Int64    ... subshell total angular momentum 2*L
+ SS      ::Int64    ... subshell total angular momentum 2*S
+ JJ      ::Int64    ... subshell total angular momentum 2*J
+ Nm      ::Int64    ... subshell Nm
+ Qm      ::Int64    ... subshell quantum number 2*Qm = nu^-
+ Jm      ::Int64    ... subshell quantum number 2*Jm
+ Qp      ::Int64    ... subshell quantum number 2*Qp = nu^+
+ Jp      ::Int64    ... subshell quantum number 2*Jp
"""
```

## 3.7. Atomic interaction amplitudes

### Concept of interaction amplitudes:

- **Hamiltonian matrix:** The (scalar) Hamiltonian matrix elements in section ?? below describe the interaction energy between two ASF  $|\alpha \mathbb{J} M\rangle$  and  $|\alpha' \mathbb{J}' M'\rangle$ , and these Hamiltonian matrix elements are perhaps the most simplest (many-electron) **interaction amplitudes in atomic structure theory**:  $\langle \psi_\alpha | \mathbb{H} | \psi_{\alpha'} \rangle = \langle \alpha \mathbb{J} M || \mathbb{H} || \alpha' \mathbb{J}' M' \rangle = \sum_{rs} c_r^*(\alpha) H_{rs} c_s(\alpha') \delta_{JJ'} \delta_{MM'} \delta_{PP'}$ .
- In relativistic atomic structure theory, in particular,  $E_\alpha = \langle \alpha \mathbb{J} || \mathbb{H}^{(\text{DCB})} || \alpha \mathbb{J} \rangle \approx \langle \alpha \mathbb{J} || \mathbb{H}^{(\text{DC})} || \alpha \mathbb{J} \rangle$  is the total energy of a given level ( $\alpha \mathbb{J}$ ).
- **Many-electron interaction amplitudes:** Using time-dependent perturbation theory and Fermi's Golden rule, most atomic level and transition properties can be expressed rather **similarly as matrix elements of a (so-called) transition or interaction operator  $\mathbb{T}$** :

$$\langle \psi_\alpha | \mathbb{T} | \psi_\beta \rangle = \sum_{rs} c_r^*(\alpha) T_{rs} c_s(\beta).$$

- **Reduced matrix elements:** More often than not, the transition operator  $\mathbb{T}$  can be expressed in terms of **spherical tensor operators of rank  $K$** , and, perhaps, with magnetic projections  $Q = -K, -K+1, \dots, K$ , respectively. These spherical tensor operators transform under rotations like the spherical harmonics  $Y_{KQ}(\vartheta, \varphi)$ :  $\mathbb{T} = \sum_{KQ} a(K, Q) \mathbb{T}_Q^{(K)}$ . – Instead of the complete matrix elements, that include the magnetic projections  $M$  of the given atomic or configuration states as well as of the tensor operators, one often makes then use of the reduced matrix elements by applying the **Wigner-Eckart theorem**:

$$T_{Q,rs}^{(K)} \equiv \left\langle \alpha_r \mathbb{J}_r M_r \left| \mathbb{T}_Q^{(K)} \right| \alpha_s \mathbb{J}_s M_s \right\rangle = \langle J_r M_r, KQ | J_s M_s \rangle \langle \alpha_r \mathbb{J}_r || \mathbb{T}^{(K)} || \alpha_s \mathbb{J}_s \rangle.$$

- Although these reduced transition amplitudes are frequently utilized in the literature, for instance in order to discuss and analyze various atomic processes, **not many codes make explicit use of these amplitudes as the natural building blocks** for describing the level structure and properties of (open-shell) atoms and ions. – More often than not, a **prior decomposition of these transition amplitudes** into various types of one- and two-particle (reduced) matrix elements or even directly into radial integrals is made well before any implementation or coding is considered. **This prior decomposition has seriously hampered the modelling of complex processes** and is still the reason, why most atomic structure codes support the computation of just a few properties, cross sections and rates.
- Indeed, the different techniques, which are employed in the decomposition of the many-electron amplitudes, as well as the large number of definitions (and notations) of angular- or radial-type integrals in the literature has hampered not only the comparison of different codes

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during the last decades but made it difficult also to (re-) use these entities for other properties than those considered by the original program developers.

- In JAC, we attempt to overcome this situation and to make consequent use of the many-electron amplitudes  $\langle \alpha_r \mathbb{J}_r M_r \mid \mathbb{T}_Q^{(K)} \mid \alpha_s \mathbb{J}_s M_s \rangle$  and/or  $\langle \alpha_r \mathbb{J}_r \parallel \mathbb{T}^{(K)} \parallel \alpha_s \mathbb{J}_s \rangle$  as the central building blocks for describing the interaction among the electrons as well as with external particles and fields.
- The concept of these interaction amplitudes has helped to simplify and maintain the code. — Moreover, it (will hopefully) enable us to exploit the many-electron interaction and transition amplitudes also in second- and higher-order processes, once an appropriate (intermediate) basis  $\{\psi_\nu(PJM) \equiv |\alpha_\nu \mathbb{J}_\nu M_\nu\rangle, \nu = 1, \dots, n_\nu\}$  has been constructed for modelling some given process.

#### Reduced matrix elements of spherical tensor operators for two CSF:

- For two CSF of well-defined symmetry, the **reduced matrix elements of spherical tensor operators** take always the form

$$\langle \gamma_r P_r J_r \parallel \mathbb{T}^{(K)} \parallel \gamma_s P_s J_s \rangle = \sum_t u(a_t b_t; K) X(a_t b_t; K), \quad \mathbb{T}^{(K)} = \sum_j \mathbb{T}^{(K)}(j; \dots) \quad \dots \text{one part. operators}$$

$$\langle \gamma_r P_r J_r \parallel \mathbb{T}^{(K)} \parallel \gamma_s P_s J_s \rangle = \sum_t v(L_t; a_t b_t c_t d_t; K) X^{L_t}(a_t b_t c_t d_t; K), \quad \mathbb{T}^{(K)} = \sum_{i < j} \mathbb{T}^{(K)}(i, j; \dots) \quad \dots \text{symmetric two part. operators,}$$

and where  $X(a_t b_t; K)$  and  $X^{L_t}(a_t b_t c_t d_t; K)$  are **one- and two-particle (effective) interaction strengths**, cf. section 3.1. These interaction strengths are specific to the particular transition or interaction operator under consideration, and **special care has to be taken that the same phase convention applies, if different interaction amplitudes are to be combined with each other.**

- In practice, there are two steps in the computation of the transition amplitudes above for any pair of CSF, which need to be performed separately: The (pure) angular coefficients are usually calculated by means of some proper program, for instance ANCO (Gaigalas *et al.*, 2001), for either a pair or a whole set of CSF, and all the non-vanishing coefficients are then returned together to the calling routine. For these coefficients, the associated one- or two-particle interaction strengths are evaluated and summed up to form the requested matrix element  $T_{rs}$  of the transition matrix.
- To decrease the computational effort, these (one- and two-particle) interaction strength are often also *stored* and *re-utilized* in various applications, a feature which has not yet been considered in JAC.
- A similar decomposition of the many-electron matrix elements (amplitudes) as for the Hamiltonian matrix elements into a sum of *angular coefficient*  $\times$  *interaction strength* can be made for every physically relevant (interaction) amplitude, independent of the particular rank of

the corresponding interaction operator. Since most atomic processes can be traced back to just a (very) few of such interaction or transition amplitudes, we made use of them as the *building blocks in the design and implementation of the JAC tools*.

### Electron-electron interaction:

- The interaction among the electrons is described by the scalar operator that occurs in the Dirac-Coulomb-Breit Hamiltonian; cf. section 3.1

$$\mathbb{V}^{(\text{e-e})} = \mathbb{V}^{(\text{Coulomb})} + \mathbb{V}^{(\text{Breit})} = \sum_{i < j} \left( \frac{1}{r_{ij}} + b_{ij} \right).$$

- The Dirac-Coulomb-Breit Hamiltonian gives rise to the (reduced) interaction amplitudes

$$\langle \gamma_r P_r J_r \parallel \mathbb{V}^{(\text{e-e})} \parallel \gamma_s P_s J_s \rangle = \langle \gamma_r P_r J_r \parallel \mathbb{V}^{(\text{Coulomb})} \parallel \gamma_s P_s J_s \rangle + \langle \gamma_r P_r J_r \parallel \mathbb{V}^{(\text{Breit})} \parallel \gamma_s P_s J_s \rangle.$$

For scalar operators, the full and reduced matrix elements coincide with each other and need not to be distinguished, since the Clebsch-Gordan coefficient in the Wigner-Eckert theorem then simply evaluates to  $\langle J_r M_r, 00 \mid J_s M_s \rangle = \delta_{J_r J_s} \delta_{M_r M_s}$  for  $K = Q = 0$ .

- Since the Coulomb and Breit interaction operators are both scalar operators and since they contribute *additively* to the total electron-electron interaction, the same (pure) angular coefficients  $v(L_t; a_t b_t c_t d_t; K = 0)$  occur in the decomposition of the amplitudes above, although different angular and parity selection rules apply for the various interaction strengths themselves, cf. section 3.1. In the computation of these amplitudes, the Breit interaction can therefore be added quite easily to the (usual) instantaneous Coulomb repulsion, if this appears appropriate for some particular process:

$$X^{(L)}(abcd) = X^{(\text{L, Coulomb})}(abcd) + X^{(\text{L, Breit})}(abcd).$$

- The electron-electron interaction amplitudes above are indeed utilized (and calculated) in many components of the JAC tools.

### Electron-photon interaction:

- The (relativistic) interaction of an electron with the radiation field is central for describing all photo-excitation, ionization, emission and capture processes.
- The electron-photon interaction is described by the one-particle operator:  $\mathcal{R}_\lambda(\mathbf{k}) = \sum_i \boldsymbol{\alpha}_i \cdot \mathcal{A}_{\lambda,i}(\mathbf{k})$ ; cf. chapter 5 below.

### Electron-nucleus (hyperfine) interactions:

- For a nuclear spin  $I > 0$ , the hyperfine interaction describes the interplay of each atomic electron with the electric and magnetic (multipole) fields of the nucleus, apart from the dominant (electric-monopole) field of the nucleus due to its nuclear charge  $Ze$ .
- The two dominant contributions to the hyperfine interaction arise from the nuclear magnetic-dipole field  $\mathbf{A} = \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3}$  and the electric-quadrupole field  $\Phi(r) = \sum_{ij} \frac{r_i r_j}{2r^5} Q_{ij}$ , while all higher magnetic and electric multipole fields, that may in principle occur for nuclei with spin  $I > 1$ , are typically negligible.

## 3.8. Atomic density operators and matrices

### 3.8.a. Single-electron reduced density matrix

#### First-order reduced density matrix:

- **First-order reduced density matrix:** This single-electron density matrix is known also as **generalized density function** and is given in terms of the  $N$ -electron wave function  $\Psi(\mathbf{q}_1, \dots, \mathbf{q}_N)$  by

$$\rho^{(1)}(\mathbf{q}_1, \mathbf{q}'_1) = N \int d\mathbf{q}_2 \dots d\mathbf{q}_N \Psi(\mathbf{q}_1, \dots, \mathbf{q}_N) \Psi^*(\mathbf{q}'_1, \dots, \mathbf{q}'_N)$$

From this first-order reduced density matrix, the (spin-less) electron density is simply obtained by the summation over all spin projections for  $\mathbf{q}_1 = \mathbf{q}'_1$ , and is usually normalized to number of electron of the system

$$\rho(\mathbf{r}_1) = \sum_{\sigma_1} \rho^{(1)}(\mathbf{q}_1, \mathbf{q}'_1), \quad \int d\mathbf{r} \rho(\mathbf{r}) = \int dr d\vartheta d\varphi r^2 \sin \vartheta \rho(\mathbf{r}) = N.$$

### 3.8.b. Atomic density matrix formalism

#### Motivation

- **Density matrix formalism:** In this formalism, the state of a physical system is characterized by means of statistical operators  $\rho$  which describe a single system or an ensemble of equally prepared **collision systems in either a pure quantum state or in a mixture of different states with any given degree of coherence**.
- The great benefit of using the (atomic) density matrix theory is that it enables one to “accompany” such an ensemble through one or several steps of excitation, decay and/or collision process, **and without loss of quantum-mechanical information**.
- **Transition operators  $R$  of the density-matrix elements** If one starts from a well-specified initial state of the system, as described by the operator  $\rho_i$ , all information about the atomic interactions, that govern the process, simply resides in the (so-called) *transition operators*  $R$ , and the final state operator just follows from the well-known relation:  $\rho_f = R \rho_i R^+$ .

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

- **Building blocks:** The electron-photon, electron-electron interaction and electron-nucleus interaction amplitudes from above are the building blocks to form the (scattering or) transition matrix for all atomic processes of interest and, hence, the density matrices of the system at the various steps of some particular excitation or decay process.
- For scattering states with a single electron in the continuum, these interaction amplitudes can be readily calculated by means of the JAC tools.
- Apart from the efficient computation of these building blocks, one also requires a simple book-keeping of these amplitudes in order to set-up the (atomic) density matrices at the various steps. To facilitate this handling and the book-keeping of these amplitudes, they are typically provided in JAC by some (amplitude) array, and together with all quantum numbers that are needed for their unique classification.
- The prior computation of the many-electron amplitudes enables one to start directly from the amplitudes (for one or several elementary processes) and to combine them into an appropriate form, in order to support the prediction of different atomic properties and parameters.
- **Set-up of the density matrix:** In practice, the computation of all interaction amplitudes is performed within three steps: (i) the generation of all necessary bound-state wave functions, (ii) the evaluation of the transition amplitudes between bound states and scattering states in the continuum, and (iii) the set-up and handling of the density matrices, i.e. by applying the formulas from chapter 8.

#### Density operator of an atom in level $(\alpha\mathbb{J})$ :

- **Mixed states of a level  $(\alpha\mathbb{J})$  :** For an atom in a well-defined and isolated level  $(\alpha\mathbb{J})$ , a general mixed state with regard to its magnetic subspace (i.e. its projections  $M$ ) can always be written as

$$\hat{\rho} = \sum_{MM'} c_{MM'} |\alpha \mathbb{J} M\rangle \langle \alpha \mathbb{J} M'|.$$

- **Statistical tensor:** Often, it is most convenient to represent the intermediate state of the ions in terms of its so-called statistical tensors

$$\rho_{kq}(\alpha\mathbb{J}) = \sum_{MM'} (-1)^{J-M'} \langle JM, J(-M') | kq \rangle \langle \alpha JM | \rho | \alpha \mathbb{J} M' \rangle.$$

and which are non-zero only for  $0 \leq k \leq 2J$  and  $-k \leq q \leq k$ . These statistical tensors transform like the spherical harmonics.

- Although both, the (reduced, mixed) density matrix and the statistical tensors of some level  $(\alpha\mathbb{J})$  are mathematically equivalent, the latter form can be transformed more easily and analogue to the spherical harmonics of rank  $k$  under a rotation of the coordinates.



- **(Initial) polarization state of an atom:** The polarization state of the initial atom can be characterized by the statistical tensors  $\rho_{kq}^{\mathbf{n}_t}(\alpha_i \mathbb{J}_i)$ , if defined with regard to the axis of the (target) polarization  $\mathbf{n}_t = (\vartheta_t, \varphi_t)$ . While the odd-rank tensors  $k = 1, 3, \dots$  are known to characterize the orientation of the target atom, the even-rank tensors  $k = 2, 4, \dots$  describe its alignment. The maximal rank of these tensors is limited by the condition  $k \leq 2J$ .

## 3.9. Parity- and time-violating atomic interactions

### 3.9.a. Interactions beyond the standard model

#### Standard electro-weak model:

- The success of the standard electro-weak model of elementary particles is indeed extraordinary. It has been tested by many physical processes that cover more than ten orders of magnitude in momentum transfer. The standard model also correctly predicted the existence of new particles, such as the neutral  $Z$  boson.
- The standard model is sometimes understood also as a low-energy manifestation of a more complete theory that, perhaps, unifies the four forces. Many well-motivated extensions to the standard model have been proposed, such as supersymmetric, technicolour and left-right symmetric models, and they often predict physical phenomena quite different from those of the standard model.
- **CP symmetry:** This symmetry refers to the combined symmetry of charge conjugation  $C$  and parity  $P$ .
- **Violation of CP symmetry:** The violation of CP symmetry was first discovered in 1964 in decays of the neutral  $K$  mesons, and this violation is taken into account by the standard electro-weak model by just a **single complex phase in the quark-mixing matrix (the so-called Kobayashi-Maskawa mechanism)**.
- Various extensions of the standard model, such as supersymmetry, predict considerably larger EDM of the particles. **Any observation of these EDM would therefore lead unambiguously to a hint of new physics.**
- In addition, the standard model of particle physics is sometimes said to violate time-reversal ( $T$ ) invariance, but again only through just a single phase in the Cabibbo-Kobayashi-Maskawa matrix, that mixes the quark flavors.
- For a rather long time,  $K$  mesons remained the only system in which CP-violation were observed explicitly. In 2001, however, the BaBar and Belle collaborations detected CP violation also for neutral  $B$  mesons, although this is still consistent with the predictions of the standard model.

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

- **CPT symmetry:** The (mathematical) structure of most gauge theories suggest that the combined symmetry of charge conjugation  $C$ , parity change  $P$  and time-reversal violation  $T$  has to be conserved.
- **If CPT is conserved, as suggested by gauge theories, then CP-violation must be strictly accompanied by T (time-reversal) violation.** Until the present, however, there has been no (undisputed) direct observation of T violation and its detection is of fundamental interest by itself. A direct detection of T-violation may shed further light also on the origin of CP-violation.
- **Permanent electric dipole moment (EDM)** The measurement of a per of neutrons, atoms, or molecule would show explicit evidence of T-violation.
- **New physics:** theories in physics beyond the standard model predict new sources of T-violation and these sources may lead to EDM that are many orders of magnitude larger than those from the standard model. This may allow EDM measurements by means of current experiments. Already the parameter space of quite popular extensions of the standard model, such as such as supersymmetry, multi-Higgs models, and left-right symmetric models, are strongly restricted by current measurements.
- **Schiff theorem:** If an external electric field acts upon a neutral atom, that consists out of non-relativistic point-like charged particles with some EDM and that only interact via electrostatic forces with each other, the field is screened exactly at each particle. This screening arises due to the polarization of the atomic electrons by the external field. Therefore, an external electric field cannot induce an atomic EDM. As shown by Schiff, however, this **shielding is incomplete if magnetic or finite-size effects are taken into account**, and this may give rise in principle to an atomic EDM.

### High-precision measurements on fundamental symmetries of atoms:

- **Atomic high-precision experiments:** High-precision measurements on the (violation of fundamental) symmetries in atoms are suitable to test the standard model of elementary particles and to search for new physics beyond it. Such precision experiments in atomic physics complement measurements in high-energy physics.
- Indeed, atomic experiments have played an important role in the verification of the standard model for more than 30 years ago already. While the first evidence for neutral-weak currents, i.e. the existence of the neutral Z boson, was discovered in neutrino scattering, a parity violation was first established in atomic experiments, and before it was later observed also in high-energy electron scattering.
- Today, **atomic physics plays a major role in the search for new physics beyond the standard model.**
- **PNC measurements for cesium:** For example, the cesium measurement on parity non-conservation in atomic physics have been found in excellent agreement with the standard model.

- **Atomic PNC measurements:** Instead of more and more accurate PNC measurements and computations, it appears useful today to perform such measurements for different isotopes of the same atom, since the ratio of the PNC signals for two different isotopes is rather insensitive to the details of the electron structure. For such measurements, the largest uncertainty to the PNC amplitudes arise from the unknown neutron distribution of the isotopes (Roberts *et al.*, 2014).

### 3.9.b. Parity-violating (P-odd, T-even) interactions

#### Motivation:

- **Parity non-conservation (PNC) effects:** These effects arise in atoms largely due to the exchange of  $Z^0$ -bosons between the atomic electrons and the nucleus.
- The exchange of  $Z^0$  bosons is formally described by the Weinberg-Salam theory and leads to (observable) phenomena, such as circular dichroism and optical rotation, and which have been investigated in order to detect P-violation in cesium, thallium, bismut and plumbum.
- There is also another contribution to atomic parity violation due to the exchange of  $Z^0$  bosons between each pair of electrons; however, this effect is negligibly small for heavy atoms and well suppressed by a factor  $10^{-3} \dots 10^{-4}$ . This contribution is usually neglected in most PNC studies.
- PNC effects in atoms can be caused also by nuclear moments, i.e. by parity-violating electromagnetic form factors that occur in addition to the usual nuclear magnetic-dipole and electric-quadrupole moments (form factors).
- **Rare-earth atoms:** Several PNC experiments in rare-earth atoms have been suggested for close-lying levels of opposite parity in order to enhance the PNC effects. Moreover, rare-earth often have various stable isotopes and, hence, the dependence on atomic theory can be removed by taking ratios of the measured PNC contributions for different isotopes.
- **Enhancement of PNC signals:** Several physical factors can contribute to an enhancement (or suppression) of the measured parity-violating signal for selected atomic transitions: (i) The PNC amplitude is expected to scale slightly faster than  $Z^3$  with the nuclear charge of the ions and make heavy elements even more favorable; and (ii) the existence of close-lying levels of different parity. For the alkaline-earth elements, there are often levels with a splitting  $\sim 10 \text{ cm}^{-1}$  which need to be compared to the well-studied  $6s - 7s$  PNC transition in Cs with a splitting  $\sim 104 \text{ cm}^{-1}$  (Roberts *et al.*, 2014).

### Nuclear-spin independent P-odd electron-nucleus interactions:

- **Nuclear-spin independent Hamiltonian:** For non-relativistic nucleons, the nuclear-spin independent Hamiltonian for the P-odd electron-nucleus interaction is given by the effective single-electron operator

$$\mathbb{H}^{(\text{weak-charge})} = -\frac{G}{\sqrt{2}} \gamma_5 [Z C_{1p} \rho_p(r) + N C_{1n} \rho_n(r)] ,$$

where  $Z$  and  $N$  are the number of protons and neutrons, and where the proton and neutron densities are normalized to unity,  $\int dr \rho_p(r) = 1 = \int dr \rho_n(r)$ .

- If the proton and neutron densities coincide,  $\rho_p = \rho_n \equiv \rho$ , the nuclear-spin independent Hamiltonian simplifies and can be described in terms of a nuclear weak-charge  $Q_W$ ,

$$\mathbb{H}^{(\text{weak-charge})} = -\frac{G}{2\sqrt{2}} \gamma_5 Q_W \rho .$$

- **Nuclear weak charge  $Q_W$ :** This charge is very close to the neutron number and is in lowest order in the electro-weak interaction given by

$$Q_W = -N + Z (1 - 4 \sin^2 \theta_W) \approx -N .$$

This value for  $Q_W$  is modified however by radiative corrections.

- The nuclear-spin independent electron-neutron interaction is a scalar that mixes levels (states) with the same total electron angular momentum but different parity.
- For heavy atoms, the nuclear-spin independent interaction due to the nuclear weak-charge gives the dominant contribution to parity violation, when compared to other mechanisms.

### Nuclear-spin dependent P-odd electron-nucleus interactions:

- **P-odd interactions that depend on the nuclear spin  $I$ :** There are different interactions that depend on the nuclear spin  $I$  due to: i) the neutral weak current; ii) hyperfine-induced neutral currents; or iii) the nuclear anapole moment.
- **Spin-dependent electron-nucleus interactions:** The dominating contribution in heavy atoms comes from the nuclear anapole moment ( $\kappa_a$ ), while smaller contributions still arise from the  $Z_0$  exchange due to spin-dependent electron-nucleus weak interactions ( $\kappa_z$ ) as well as the interaction of the weak charge ( $\kappa_Q$ ) with the magnetic hyperfine interaction (Roberts *et al.*, 2014).
- **Interaction with the nuclear anapole:** The anapole moment gives typically the dominant nuclear-spin dependent P-odd electron-nucleus interaction. The nuclear anapole moment arises from P-odd interactions inside the nucleus. These interactions manifest themselves in atoms through a slightly modified electro-magnetic interaction of the nucleus with atomic electrons.
- The anapole moment  $\kappa_a$  increases with the atomic mass number,  $\kappa_a \propto A^{2/3}$  and, thus, dominates in heavy atoms, when compared to other nuclear-spin dependent mechanisms listed above.
- **Hamiltonian for the electron-anapole (-moment) interaction:** For an external nucleon with orbital angular momentum  $\ell$ , the Hamiltonian is given by (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{anapole})} = \frac{G}{\sqrt{2}} \kappa_a \frac{K}{I(I+1)} \boldsymbol{\alpha} \cdot \mathbf{I} \rho(r), \quad K = (I + 1/2) (-1)^{I+1/2-\ell}.$$

### Anapole moment:

- **Anapole moment:** The anapole moment arises from P-odd, T-even nuclear moments (i.e. parity-violating nuclear forces) and usually requires less accurate atomic structure calculations. This may simplify the search for favorable conditions and atomic systems.
- The notion of the anapole moment was introduced by Zel'dovich just after the discovery of parity violation.
- However, an **nuclear anapole moment was unambiguously detected only 30 years later**. In 1997, a group at Boulder measured a nuclear anapole moment in  $^{133}\text{Cs}$  to an accuracy of 14 % in an atomic experiment. This is considered as the first observation of an electromagnetic moment that violates fundamental discrete symmetries (Ginges and Flambaum, 2003).

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

- A P-odd, T-even anapole moment of the nucleus arises due to the presence of a parity violating weak interaction between nucleons.
- The anapole moment is directed along the nuclear spin  $\mathbf{I}$ :  $\langle \mathbf{a} \rangle = -\pi \langle r^2 \mathbf{j} \rangle = a \mathbf{I}/I$ . Since the current vector  $\mathbf{j}$  changes its sign under reflection of coordinates, but not the spin  $\mathbf{I}$ , **an anapole moment need to violate parity but not time-reversal symmetry.**

#### 3.9.c. Time-reversal violating (P-odd, T-odd) interactions

##### Motivation:

- **Time-reversal symmetry:** Many physical systems and processes are asymmetric under time-reversal. In classical mechanics, for example, a velocity reverses its direction under time reversal,  $v \rightarrow -v$ , while an acceleration does not. This time-reversal asymmetry is often associated with some energy dissipation and, hence, with the second law of thermodynamics. Without dissipation, the laws of mechanics are usually considered to be invariant with regard to time-reversal.
- In nuclei, P-odd and T-odd nuclear moments can arise due to an intrinsic EDM of the nucleons, or due to P-odd and T-odd nuclear forces. The P-odd and T-odd nuclear forces induce larger nuclear moments than a single nucleon EDM.
- Various P-odd and T-odd interactions can be considered, especially for heavy atoms and ions. These interaction include the **tensor-pseudotensor electron-nucleon (e-N) interaction, the scalar-pseudoscalar (e-N) interaction, the nuclear Schiff moment and the interaction of the electron EDM with the internal nuclear magnetic field of the atom.**
- An atomic EDM can be induced if the nucleus possesses P-odd and T-odd nuclear moments.

##### P-odd & T-odd Hamiltonians due to electron-nucleus interactions:

- The expressions for  $\mathbb{H}^{(\text{scalar-pseudoscalar})}$  and  $\mathbb{H}^{(\text{weak charge})}$  as well as  $\mathbb{H}^{(\text{I-independent})}$  are quite similar.
- These electron-nucleus interactions mixes atomic states of opposite parity and induces a static electric-dipole moments in atoms.

##### P-odd & T-odd nuclear moments:

- The operators  $\mathbb{H}^{(\text{scalar-pseudoscalar})}$  and  $\mathbb{H}^{(\text{tensor})}$  have both electronic and nuclear components. While these Hamiltonians are overall scalar, the electronic and nuclear operators can be of any (equal) rank. To obtain any non-zero matrix element, therefore, the triangle rule for coupling of angular momenta imposes restrictions on the angular momenta of the electron and nuclear states.

- **Nuclear moments that violate parity and time-reversal invariance:** electric dipole, magnetic quadrupole, electric octupole. For an nuclear electric-dipole moment, the Hamiltonian must be of the form  $\mathbb{H}^{(\text{Schiff moment})}$  in order to mix electron states of opposite parity.
- **Nuclear electric-dipole (Schiff) moments:** If  $\mathbf{S}$  is nuclear Schiff moment, the associated P-odd and T-odd Hamiltonian is given by

$$\mathbb{H}^{(\text{Schiff-moment})} = -e \phi^{(\text{Schiff-moment})} = -4\pi e \mathbf{S} \cdot \nabla \delta(r).$$

Here  $\phi^{(\text{Schiff-moment})}$  is the electrostatic potential of the nucleus that corresponds to a P-odd and T-odd charge distribution.

- **Nuclear magnetic-quadrupole moments (MQM):** A general expression for the nuclear MQM can be constructed in terms of the total angular momentum of the system  $I$ ,

$$M_{ij} = -e \frac{3}{2} \frac{M}{I(2I-1)} \left[ I_i I_j + I_j I_i - \frac{2}{3} I(I+1) \delta_{ij} \right].$$

The quantity  $M$  is conventionally referred to as the nuclear MQM and is defined as the maximum projection of  $M_{ij}$  upon the nuclear axis,  $M = M_{zz}$ . The magnetic quadrupole moment violates parity and time-reversal invariance.

### 3.9.d. Time-reversal violating atomic electric-dipole moments

#### Motivation:

- A non-zero electric-dipole moment (EDM) of atoms require P-odd and T-odd interactions, either among the nucleons or the electrons and the nucleus.
- Therefore, the **null measurements of EDM in atoms place severe restrictions upon new sources of CP-violation** that often arise in models beyond the standard model, such as supersymmetry.
- The nuclear EDM exceeds the EDM of single nucleons by one to two orders of magnitude. P-odd and T-odd nuclear forces generate all P-odd and T-odd nuclear moments, such as the Schiff and MQM moments. These nuclear moments can be 10-to-100 times larger than those generated by the presence of a nucleon EDM.
- In the standard model, an atomic EDM is suppressed by many orders when compared to predictions from (so-called) *new* theories. Therefore, the detection of an EDM would be **unambiguous evidence of new physics**, even if it contributes only weakly to a very small signal in atomic parity violation.

### 3. Many-electron atomic interactions, state functions, density operators and statistical tensors

- An atomic EDM can arise from various P-odd and T-odd mechanisms (Ginges and Flambaum, 2004): i) an intrinsic EDM of an electron; (ii) a P-odd and T-odd electron-nucleon interaction; (iii) an intrinsic EDM of an external nucleon; (iv) a P-odd and T-odd nucleon-nucleon interaction.
- Until the present, no permanent EDMs in neutrons, atoms or molecules have been detected.
- The best limits on the electron electric dipole moment is presently derived from measurements of atomic EDM.

#### Physics of the atomic EDM:

- An atomic EDM is associated with an atomic level  $(\alpha\mathbb{J})$  and arises due to the admixture of levels (states)  $(\nu\mathbb{J}_\nu)$  with opposite-parity wave functions. This atomic EDM has the form

$$d^{(\text{atomic EDM})} = 2 \sum_{\nu} \frac{\langle \alpha\mathbb{J} | \mathbb{D} | \nu\mathbb{J}_\nu \rangle \langle \nu\mathbb{J}_\nu | \mathbb{H}^{(\text{PT})} | \alpha\mathbb{J} \rangle}{E_\alpha - E_\nu} = d^{(\text{atomic EDM})} \frac{\mathbf{F}}{F},$$

where  $\mathbb{D}$  is the electric dipole operator,  $\mathbb{H}^{(\text{PT})}$  the P-odd and T-odd operator that mixes  $|\alpha\mathbb{J}\rangle$  with the set of wave functions  $|\alpha_\nu\mathbb{J}_\nu\rangle$ , and  $F$  is the total angular momentum of the atom corresponding to the state  $|\alpha\mathbb{J}\rangle$ .

- A typical EDM experiment is performed in parallel electric and magnetic fields and can be described by the Hamiltonian

$$\mathbb{H}^{(\text{em field})} = -\mu \cdot \mathbf{B} - \mathbf{d} \cdot \mathbf{E}.$$

- A linear Stark shift is measured by observing the change in frequency when the electric field is reversed, since it is sensitive to the P-odd and T-odd term  $\mathbf{E} \cdot \mathbf{B}$ .
- Interaction Hamiltonian of the electron EDM with an internal atomic electric field  $\mathbf{E}^{\text{int}}$ : The Hamiltonian for interaction of the electron EDM with internal atomic electric field  $\mathbf{E}^{\text{int}}$  can be written as (Dzuba and Flambaum, 2009)

$$\mathbb{H}^{\text{eEDM-electric}} = -d_e \sum_{i=1}^N (\gamma_o - 1)_i \boldsymbol{\Sigma}_i \cdot \mathbf{E}^{\text{int}}, \quad \boldsymbol{\Sigma}_i = \begin{pmatrix} \boldsymbol{\sigma}_i & 0 \\ 0 & \boldsymbol{\sigma}_i \end{pmatrix}.$$

- Atomic EDM: An atomic EDM can be caused by the interaction of the electron EDM (if it exists) with either the internal electric field of the atom or the scalar-pseudoscalar electron-nucleon (T-odd, P-odd) interaction; an EDM of atoms in their ground state is then given by

$$\mathbf{d}_{\text{atom}} = 2 \sum_{\nu} \frac{\langle 0 | \mathbb{D} | \nu \rangle \langle \nu | \mathbb{H}^{\text{eEDM-..}} | 0 \rangle}{E_o - E_\nu}$$



where  $|0\rangle$  is the atomic ground state,  $\mathbb{D} = -e \sum_i \mathbf{r}_i$  is the electric-dipole operator and  $\mathbb{H}^{\text{eEDM}}$  the (P-odd, T-odd) interaction operator. Here, the summation need formally to be performed over the complete many-electron spectrum of the intermediate levels  $\nu$  with total energies  $E_\nu$ .

- Measurements of EDMs in paramagnetic atoms, i.e. for a total electron angular momentum  $J \neq 0$ , are most sensitive to leptonic sources of P- and T-violation, and especially the electron EDM.
- In contrast, measurements of EDM in diamagnetic systems with zero total electron angular momentum are most sensitive to P-odd and T-odd mechanisms in the hadronic sector.

## 3.10. Elements from atomic spectroscopy

### 3.10.a. Line shifts and profiles

#### Line profiles in atomic spectroscopy:

- **Experimental photon energy distribution:** In order to fit the observed spectra to Fano's formula, the experimental photon energy distribution (window function) need usually to be taken into account. This experimental window function can often be represented by Gaussian with a full-width-at-half maximum (FWHM) according to the experimental energy spread. Therefore, the Fano profile has to be convoluted with a Gaussian. Analogue convolutions are known from the Voigt line profiles in the emission spectroscopy of hot gases which also includes the convolution of a Lorentzian with a Gaussian line curve.
- **Convolution of a Lorentzian and a Gaussian line profile:** The Voigt profile arises from the convolution of a Lorentzian and a Gaussian line profile with the Lorentzian and Gaussian FWHM  $\Delta_L$  and  $\Delta_G$

$$L(E) = \frac{2A}{\pi} \frac{\Delta_L}{4(E - E_r)^2 + \Delta_L^2}, \quad G(E) = \frac{2}{\Delta_G} \sqrt{\frac{\ln 2}{\pi}} \exp \left[ -\frac{4(\ln 2) E^2}{\Delta_G^2} \right], \quad \int dE L(E) = A, \quad \int dE G(E) = 1$$

$$V(E) = \int_{-\infty}^{\infty} dE' L(E') G(E' - E) = A \frac{4\sqrt{\ln 2}}{\pi^{3/2} \Delta_G} \int_{-\infty}^{\infty} dE' \frac{\Delta_L}{4(E' - E_r)^2 + \Delta_L^2} \exp \left[ -\frac{4(\ln 2) (E - E')^2}{\Delta_G^2} \right].$$

- **Convolution of a Lorentzian and a Gaussian line profile:** The convolution of a Lorentzian profile with a Gaussian function generally results in a **Faddeeva function that can be utilized for a fast and accurate evaluation of the convolution, e.g., in peak fitting routines** (Schippers 2018). With the following definitions, the Voigt profile can be expressed in terms of the Fadeeva function as

$$t = \frac{2\sqrt{\ln 2}(E' - E)}{\Delta_G}, \quad x = \frac{2\sqrt{\ln 2}(E_r - E)}{\Delta_G}, \quad y = \frac{\Delta_L \sqrt{\ln 2}}{\Delta_G}, \quad z = x + iy$$

$$V(E) = A \frac{2\sqrt{\ln 2}}{\Delta_G \sqrt{\pi}} \frac{1}{\pi} \int_{-\infty}^{\infty} dt \frac{y e^{-t^2}}{(t - x)^2 + y^2} dt = A \frac{2\sqrt{\ln 2}}{\Delta_G \sqrt{\pi}} \Re[w(z)]$$

➤ **Faddeeva function  $w(z)$ :** The Faddeeva function is a scaled complex error function which, for  $\Im z = y > 0$ , is defined as (Schippers 2018)

$$w(z) = e^{-z^2} \operatorname{erfc}(-iz) = \frac{i}{\pi} \int_{-\infty}^{\infty} dt \frac{e^{-t^2}}{z - t}, \quad \Re[w(z)] = \frac{1}{\pi} \int_{-\infty}^{\infty} dt \frac{ye^{-t^2}}{(t-x)^2 + y^2}, \quad \Im[w(z)] = \frac{-1}{\pi} \int_{-\infty}^{\infty} dt \frac{(t-x)e^{-t^2}}{(t-x)^2 + y^2}.$$

$\Re[w(x+iy)]$  and  $\Im[w(x+iy)]$  can be displayed as functions of the scaled energy  $x$  for different ratios  $y$  of Lorentzian and Gaussian widths.

➤ **Convolution of a Fano and a Gaussian line profile:** One can re-define the Fano line profile slightly differently from above with a positive amplitude  $a > 0$  and with the same definition of  $t$ ,  $x$  and  $y$  as above. This definition of the Fano profile is consistent with the theoretical treatment of the atomic photoabsorption cross section. For the convolution of a Fano and a Gaussian line profile, this gives rise to (Schippers 2018):

$$F(E) = \frac{2a}{q^2 \Delta_L \pi} \left[ \frac{(q + \epsilon)^2}{1 + \epsilon^2} - 1 \right], \quad \lim_{q \rightarrow \infty} F(E) \rightarrow L(E).$$

$$C(E) = \int_{-\infty}^{\infty} dE' F(E') G(E' - E) = \frac{2a}{q^2 \Delta_L \pi} \left[ \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt \frac{[qy + (t-x)]^2 e^{-t^2}}{(t-x)^2 + y^2} dt - 1 \right], = \frac{a}{q^2} \frac{2\sqrt{\ln 2}}{\Delta_G \sqrt{\pi}} \left\{ (q^2 - 1) \Re(w) - 2q \Im(w) \right\}.$$

## Doppler-shifted transition frequencies:

➤ **Doppler shift of atomic transition frequency  $\nu_o$ :** If the atom moves with velocity  $\mathbf{v}$  under the angle  $\vartheta = \angle(\mathbf{v}, \text{atom-observer, line of sight})$  with regard to the observer (or, *vice versa*, the observer w.r.t the atom), the atomic line appears for the observed *Doppler-shifted* at frequency

$$\nu = \frac{\nu_o}{\gamma(1 - \beta \cos \vartheta)} = \nu_o \sqrt{1 - \beta^2} (1 - \beta \cos \vartheta)^{-1}, \quad \beta = \frac{v}{c}, \quad \gamma = (1 - \beta^2)^{-1/2}.$$

➤ **Uncertainty estimation of a *Doppler-shifted* frequency:** To estimate how the uncertainties in  $\beta$  and  $\vartheta$ , the following partial derivatives

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are needed:

$$\Delta \nu = \left| \frac{\partial \nu}{\partial \beta} \right| \Delta \beta + \left| \frac{\partial \nu}{\partial \vartheta} \right| \Delta \vartheta, \quad \frac{\partial \nu}{\partial \beta} = \nu_o \frac{\gamma (1 - \beta)}{(1 - \beta \cos \vartheta)^2}, \quad \frac{\partial \nu}{\partial \vartheta} = -\nu_o \frac{\beta \sin \vartheta}{\gamma (1 - \beta \cos \vartheta)^2}$$

$$\left| \frac{\partial \nu}{\partial \beta} \right| \frac{\Delta \beta}{\nu} = \frac{\gamma \beta (1 - \beta)}{(1 - \beta \cos \vartheta)} \frac{\Delta \beta}{\beta}$$

The second line just displays the frequency ratio  $\Delta \nu / \nu$  due to an uncertain (normalized) velocity  $\Delta \beta / \beta$  of the atoms.

- **Mean Doppler frequency of an atomic transition:** If photons are observed from atoms with relative velocity  $v$  and both, in forward ( $\vartheta = 0 \pm \delta_o$ ) and backward directions ( $\vartheta = \pi \pm \delta_\pi$ ) with overall small misalignments, the mean Doppler-shifted frequency can be defined in terms of the *averaged* frequency in both directions

$$\langle \nu \rangle = \frac{\nu_o}{2\gamma} \left[ \frac{1}{(1 - \beta \cos \delta_o)} + \frac{1}{(1 - \beta \cos(\pi + \delta_\pi))} \right] = \left[ \frac{1}{(1 - \beta \cos \delta_o)} + \frac{1}{(1 + \beta \cos \delta_\pi)} \right] \approx \frac{\nu_o \gamma}{2} \quad \text{for } \delta_o = \delta_\pi = 0.$$

#### 3.10.b. Atomic target distributions

##### Target distributions:

- **Gaussian target distribution:** A localized but macroscopic target can be described by a Gaussian probability distribution that is centred with width  $\sigma$  around the impact parameter  $\mathbf{b}_0$  with regard to the beam axis. Then the probability distribution is given by

$$f(\mathbf{b}; \mathbf{b}_0) = \frac{1}{2\pi\sigma^2} e^{-\frac{(\mathbf{b}-\mathbf{b}_0)^2}{2\sigma^2}} = \frac{1}{2\pi\sigma^2} e^{-\frac{b^2 + b_0^2 - 2\mathbf{b} \cdot \mathbf{b}_0 \cos \phi_b}{2\sigma^2}}.$$

### 3.10.c. Manipulation of light beams

#### Optical elements:

- **Half-wave plate *versus* mirror:** A half-wave plate reverses the spin angular momentum, i.e. the circular polarization of an incident light beam. A half-wave plate can therefore be seen as the **angular variant of a mirror** which reverses the linear momentum of the light (reflection). A similar analogy in the response to an incident light beam exists also for the Doppler shift: If the mirror moves with velocity  $\mathbf{v}$ , an incident photon experiences a linear momentum transfer  $\mathbf{q}$  and a **linear (Doppler) shift**  $\Delta E = \mathbf{q} \cdot \mathbf{v}$ , while photons transmitted through a rotating half-wave plate with angular velocity  $\mathbf{\Omega}$  experience an angular momentum transfer  $\mathbf{Q}$  and an **angular Doppler shift**  $\Delta E = \mathbf{Q} \cdot \mathbf{\Omega}$ . Both, the linear and angular Doppler shift can be related to a broken symmetry (invariance) in the light-matter interaction due to the motion of the medium.
- **Jones' matrix formalism:** In classical optics, the propagation of beams through optical elements, such as polarizers, wave plates, etc. are often described by Jones' matrix formalism and by making use of a basis of well-defined spin angular momentum (e.g., linear or circular polarization).

### 3.10.d. Miscellaneous

#### Experimental features & conditions:

- **Resonant behaviour:** A resonance generally refers to a drastic change in the intensity of some signal, while the energy (or some other parameter) changes only little. In quantum physics, resonances in the intensity pattern are often accompanied by some – more or less strong – interference of different quantum amplitudes.
- **Energy calibration of photon-ion merged-beams measurements:** Since the ions move opposite to the photon beam, the (photon) energy needs to be Doppler corrected within the framework of the ion. If  $E^{(\text{lab})}$  is the photon energy in the laboratory and  $\theta \simeq 180^\circ$  the angle between the beams, the Doppler-shifted energy is:

$$E^{(\text{merged-beam})} = \frac{E^{(\text{lab})}}{\gamma(1 + \cos \theta)}, \quad \gamma = \frac{1}{\sqrt{1 - \beta^2}}, \quad v = \beta c.$$

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- **Energy calibration of photon-ion merged-beams measurements:** The ion velocity  $v$  can be derived from the acceleration voltage  $U^{(\text{acceleration})}$  via the kinetic energy  $E^{(\text{kin})}$  of the ions as well as their mass  $M^{(\text{ion})}$  and their Lorentz factor  $\gamma$  as (Müller *et al.*, 2018)

$$E^{(\text{kin})} = qe U^{(\text{acceleration})} = (\gamma - 1) M^{(\text{ion})} \quad \longrightarrow \quad \beta = \sqrt{1 - \frac{1}{(\gamma - 1)^2}}, \quad x = \frac{qe U^{(\text{acceleration})}}{M^{(\text{ion})} c^2}$$

$$E^{(\text{merged-beam})} = \frac{E^{(\text{lab})}}{(1 + x) + \sqrt{2x + x^2} \cos \theta} \quad \longrightarrow \quad E^{(\text{lab})} \left[ (1 + x) + \sqrt{x} \sqrt{2 + x} \right] \quad \text{for } \theta \approx 180^\circ.$$

- **Madelung ordering versus Coulomb ordering of shells:** While the Coulomb order of (sub-) shells follow from the hydrogenic solutions  $n\ell$ ,  $\ell = 0, \dots, n-1$ ,  $n = 1, 2, \dots$ , the **Madelung order describes the shell order as it is filled by the elements from the periodic table**

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, \dots$$

- **Cauchy moments:** For an atomic level  $(\alpha\mathbb{J})$  with energy  $E_o$  and oscillator strength  $f_{\nu o}$  to neighbored levels  $(\alpha_\nu\mathbb{J}_\nu)$  with excitation energies  $\Delta E_{\nu o}$ , the Cauchy moment is defined by (Mitroy *et al.*, 2010)

$$S(-q) = \sum_{\nu} \frac{f_{\nu o}}{(\Delta E_{\nu o})^q}.$$

The Cauchy moments appear in atomic physics as various places:  $S(0) = N$ , i.e. the number of electrons (**Thomas-Reiche-Kuhn sum rule**), while  $S(-3)$  is related to the non-adiabatic polarizabilities.

- **Voigt function:** The Voigt function is defined by

$$K(a, x) = \frac{k(\nu)}{k_o} = \frac{a}{\pi} \int_{-\infty}^{+\infty} dt \frac{e^{-t^2}}{a^2 + (x - t)^2}.$$

- Several numerical methods for the computation of the Voigt integral are known from the literature as, for instance, the algorithm by Humlicek.

### Rate coefficients $\alpha(T)$ :

- **Rate coefficients  $\alpha(T)$  :** The rate coefficient of a capture or transfer process [in  $\text{cm}^3/\text{s}$ ] is generally temperature-dependent and obtained by averaging the energy-dependent cross section  $\sigma_{fi}(E)$  over a Maxwellian velocity distribution (Babb *et al.*, 2017)

$$\alpha(T) = \left(\frac{8}{m\pi}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty dE E \sigma_{fi}(E) \exp\left(-\frac{E}{k_B T}\right), \quad k_B = 1.380 \times 10^{-23} \text{ J K}^{-1}.$$

Here,  $m$  refers to the (reduced) electron mass-

- **Quasi-rate  $R(E)$  :** An effective energy-dependent rate of a capture or transfer process from state  $i \rightarrow f$  can be obtained from the relationship (Babb *et al.*, 2017)

$$R_{fi}(E) = v \sigma_{fi}(E) = \sqrt{2E/m} \sigma_{fi}(E) \quad [\text{in cm}^3 \text{ s}^{-1}]$$

and can be used for estimating the rate coefficients  $\alpha(T)$  of the given process if the energy  $E$  of the incident particles is converted into a temperature  $T$ .





## 4. Atomic representations

### Methods, characterization & applications. An overview:

- **Post-HF methods:** Moller-Plesset (Rayleigh-Schrödinger) perturbation theory, configuration interaction (CI) expansions, coupled cluster (CC) theory, convergent close-coupling.
- Various *ab-initio* many-electron methods have been developed during the last decades to accurately describe the level structure and properties of atoms and ions with a relatively simple shell structure, such as the configurations interaction (CI), many-body perturbation theory (MBPT), coupled-cluster (CC) theory, correlation potential (CP) or multiconfigurational Dirac-Fock (MCDF) methods. *These ab-initio methods are frequently applied for atoms and ions with just a (very) few valence electrons above a closed-shell core but cannot be applied so easily to systems with more than, say, four valence electrons.*
- **Weak or dynamic correlations:** These correlation can be captured in a systematic fashion by various post-HF methods. More often than not, these weak correlations are built upon a single Slater determinant, although a multi-reference formulation also exist for most of these methods. In single-reference methods, however, very large expansions are often needed in order to retrieve the *strong (static) correlation*.
- **Size-consistency of (molecular) wave functions:** For two noninteracting subsystems, the total wavefunction should be separable and the total energy additive. While the coupled-cluster method is always size-consistent because of its exponential wavefunction ansatz, a typical configuration-interaction wave function with  $k$  virtual excitations is usually not size-consistent for  $N > k$  electrons in the system.
- An independent optimization of the wave functions for level groups of different total symmetry  $J$  still ensures that *parts of the electron relaxation of the electron density is taken into account*. Of course, an independent variation finally also results in a set of orbitals which, for a given level group, are not orthogonal to the orbitals of any other group.
- In the study of transition probabilities and other atomic processes, this *relaxation of the electron density* causes technical problems but, otherwise, often yields results that are in better agreement with experiments.
- **Atomic resonances:** Since inner-shell hole states lay — by its very nature — high up embedded within the continuum of the next higher charge state, these atomic states have to be treated as *resonances*. From scattering theory, several (formal) approaches, such as the K-matrix

#### 4. Atomic representations

, exist in order to treat the interaction among different resonances or decay channels properly. Up to the present, it remains **open whether and to which extent such sophisticated scattering approaches can be properly implemented into many-electron structure codes and how well they are suitable also for open-shell systems.**

- **Description of scattering states:** The size of the CSF expansions often increases very rapidly if the atomic bound-state density is *coupled* to the electron continuum, since the presence of one (or more) electrons in the continuum automatically leads to extra open shells. Such an *additional* increase of the CSF expansion and, hence, of the computations practically occurs in the study of all ionization, autoionization and scattering processes.
- Less attention was paid overall the years to the **calculation of atomic properties other than line strength, hyperfine structures or isotopes shifts.** With the **JAC tools**, we here wish to provide a simple access to the computation of (relativistic) atomic transition, ionization and capture properties, including the description of scattering states with one or more electrons in the continuum, and along with many other features of these tools.
- **CSF basis:** In practice, the **definition of a physically appropriate basis turns out to be less simple.** In particular, the difficulties in calculating *open-shell* atoms and ions have long been underrated. The first (successful) structure calculations of a few simple atoms and ions in the sixties and seventies quickly led to the **popular fallacy, that it would take only a bit more effort and computational power in order to theoretically predict the structure and properties of atoms in rather arbitrary configurations.**
- We know much better now: **Many atomic properties have been found to depend rather sensitive on the *correlated* motion of the electrons and, thus, on the shell structures of the atoms and ions.** Although much larger computations are feasible today, most open-shell atoms are yet not well understood. In fact, the *real* challenge when dealing with open-shell structures concerns the very rapidly growing wave function expansions, if one or several open shells are already involved within the reference configuration(s).
- **Many-particle states close to the particle emission threshold:** These states often display unusual properties, such as **halo and Borromean structures, clusterization** phenomena, or cusps in various observables. This behaviour arises due to the strong coupling of (quasi-) bound states to the continuum.
- **Complex eigenvalue Schrödinger equation (CESE) method:** The SE with a complex or non-hermitian potential has been studied at various places, especially in order to describe resonance states.

#### Elements from atomic representation theory:

- **Atomic state function (ASF):** Similar to the well-known – non-relativistic and symmetry-adapted – Hartree-Fock (HF) method, in which the state of an atom or ion is approximated by a single (symmetry-adapted) Slater determinant, an **atomic state function** is written in

the CI or multi-configuration Dirac-Hartree-Fock (MCDHF) method as **linear combination of configuration state functions (CSF) with well adapted symmetry**

$$|\alpha \mathbb{J}M\rangle \equiv \psi_\alpha(\mathbb{J}M) = \sum_{r=1}^{n_c} c_r(\alpha) |\gamma_r P J M\rangle .$$

In this ansatz,  $n_c$  is the number of CSF,  $\mathbb{J} \equiv J^P$  the total angular momentum and parity of the state, and  $\alpha$  refers to all (further) quantum numbers that are needed to specify the state uniquely. Moreover,  $\{c_r(\alpha)\}$  denotes the representation of the atomic state in the given basis.

- **Secular equation:** For a given CSF basis, the representation of an atomic state above (i.e. the mixing coefficients  $\mathbf{c}(\alpha) \equiv (c_1(\alpha), c_2(\alpha), \dots, c_{n_c}(\alpha))$ ) is obtained by solving the **secular equation**

$$\det(\mathbf{H} - E_\alpha^{(n_c)} \mathbf{I}) = 0, \quad \mathbf{H} = (H_{rs}) = (\langle \gamma_r P J M | \mathbb{H} | \gamma_s \bar{P} \bar{J} \bar{M} \rangle \delta_{P\bar{P}} \delta_{J\bar{J}} \delta_{M\bar{M}})$$

and where  $E_\alpha^{(n_c)}(PJ)$  denotes the eigenvalue.

- **Hamiltonian matrix:** This matrix is **block-diagonal in the total parity and angular momentum of the atom**, and this is independent of the particular choice of the electron-electron interaction in the Hamiltonian.
- **Hamiltonian matrix:** Since the **Hamiltonian matrix is real and symmetric**, all atomic states are orthogonal for  $E_\alpha \neq E_\beta$  or can be chosen in this way for  $E_\alpha = E_\beta$ . In practice, an efficient decomposition of the many-electron matrix elements  $H_{rs}$  in the Hamiltonian matrix above is central to every implementation of the CI or related method.
- **Hamiltonian matrix:** Owing to the symmetry of the Hamiltonian, the computational effort of the MCDHF method can be reduced by a rather large factor ( $> 10$ ), if the various (total) angular momenta and parities  $\mathbb{J} = J^P$  of the atomic states of interest are considered independently.
- **Hamiltonian matrix:** Formally, the number of basis states and, hence, the size of the Hamiltonian matrix grows exponentially with the number of electrons as well as the size of the active space; cf. section 4.1.c.
- **Choice of atomic Hamiltonian:** The decision about the atomic Hamiltonian operator, that is utilized in a particular CI or MCDHF computation, is often made on the basis of (1) the nuclear charge, (2) the charge state of the atom or ion, (3) its particular **shell structure** as well as (4) the atomic property under consideration. **Further relativistic and radiative corrections** to the (total energies of the) atomic levels can be added in various (effective) approximations.

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- **Spin-angular integrals:** For symmetry-adapted CSF, the integration over the spin-angular variables of all  $N$  electrons can be performed algebraically and enables one to write the Hamiltonian matrix elements always in the form (Grant, 1989)

$$H_{rs} = \sum_t u_{rs}(a_t b_t) \langle a_t \| \mathbb{h}_D \| b_t \rangle + \sum_t v_{rs}^{(L_t)}(a_t b_t c_t d_t) X^{(L_t)}(a_t b_t c_t d_t).$$

In this expansion,  $u_{rs}(ab)$  and  $v_{rs}^{(L_t)}(abcd)$  are one- and two-particle (scalar) angular coefficients, while the  $X^{(L)}(abcd)$  describe the effective interaction strengths of (formally) the four electrons  $a, b, c, d$  that are involved in the interaction. As usual, we here abbreviate the one-particle quantum numbers  $a = (n_a, \kappa_a)$ ,  $b = (n_b, \kappa_b)$ , ... to have a compact notation for the subshells of equivalent electrons.

- **Reduced one-electron matrix elements of the Dirac Hamiltonian:** As usual, the reduced matrix elements of the (one-electron) Dirac Hamiltonian,

$$\langle a \| \mathbb{h}_D \| b \rangle = \delta_{\kappa_a \kappa_b} \int_0^\infty dr \left[ c Q_a \left( \frac{d}{dr} + \frac{\kappa_a}{r} \right) P_b + c P_a \left( -\frac{d}{dr} + \frac{\kappa_a}{r} \right) Q_b - 2c^2 Q_a Q_b + V_{\text{nuc}}(r) (P_a P_b + Q_a Q_b) \right],$$

describe the kinetic and potential energy of an electron in subshell  $a$  and can be expressed in terms of the large and small (radial) components,  $P_a(r)$  and  $Q_a(r)$ , of the corresponding one-electron orbital functions.

- These reduced matrix elements can be considered as the one-particle *analogua* to the effective interaction strength  $X^{(L)}(abcd)$  as discussed above in section 3.1 for the electron-electron interaction.
- **Restricted active spaces:** In most standard all-electron implementations of the CI method and beyond, the electrons are often divided into (closed) core-shell and valence electrons, and with virtual excitations only included for the valence electrons within a restricted active orbital space.

## 4.1. In JAC implemented atomic representations

### 4.1.a. Mean-field basis (Atomic)

#### Use:

- Using JAC: Generate an `Atomic.Representation(..., MeanFieldBasis(meanFieldSettings))` for a given set of reference configurations and given settings; cf. `? MeanFieldSettings` or `MeanFieldSettings()`.
- Using JAC, see also the functions: `Basics.generate()`.

### 4.1.b. Configuration interaction (CI) expansions (Atomic)

#### Use:

- Using JAC: Generate an `Atomic.Representation(..., CiExpansion(orbitals, excitations, ciSettings))` for a given set of reference configurations as well as given orbitals, excitation and settings; cf. `? CiSettings` or `CiSettings()`. The dictionary of (fixed) orbitals can be generated, for instance, by a `MeanFieldBasis` expansion from Section 4.1.a.
- Using JAC: The virtual excitations to be included with regard to the reference configurations can be defined by `RasStep(seFrom=..., seTo=..., deFrom=..., deTo=, ..., frozen=...)`, where all optional parameters refer to shell lists in order to specify single excitations (se) from  $\rightarrow$  to, double excitations (de) from  $\rightarrow$  to as well as the list of frozen shells.
- Using JAC, see also the functions: `Basics.generate()`.

### 4.1.c. Restricted active space (RAS) expansions (Atomic)

#### Use & notations:

- **Restricted active space (RAS) method:** This method includes the *correlated motion of the bound electrons* in a (much) more systematic fashion; it is based either on mean-field DHF or MCDHF solutions of the one-electron orbitals *and a restricted active space that is formed by a subset of occupied and virtual orbitals*. The idea of the RAS method is to account for an *excitation of the active electrons* from the outer shells (into a number of predefined *unoccupied orbitals*), while some ‘electronic core’ remains often fixed in the set-up of the RAS self-consistent field (RAS-SCF) computations.
- Using JAC: Generate an `Atomic.Representation(.., RasExpansion(LevelSymmetry(..), NoElectrons, steps, rasSettings))` for a given set of reference configurations as well as a specified level symmetry, number of electrons, the requested (list of excitation) steps and settings; cf. `? RasSettings` or `RasSettings()`.
- Using JAC: The individual steps of the RAS computations are defined by `RasStep(seFrom=.., seTo=.., deFrom=.., deTo=, .., frozen=..)`, where all optional parameters refer to shell lists in order to specify single excitations (se) from  $\rightarrow$  to, double excitations (de) from  $\rightarrow$  to as well as the list of frozen shells.
- Using JAC, see also the functions: `Basics.generate()`.
- **Classes of virtual excitations:** It is often useful to *divide the virtual excitations of the active electrons into different classes, namely single (S), double (D), triple (T), ... excitations*, in dependence of how many electrons are *to be replaced* with regard to the set of reference configurations. While single and double excitations are typically treated quite equally, because of Brillouin’s theorem for the Dirac-Hartree-Fock approximation, the triple and higher excitations are typically less important and, if considered at all, are incorporated only for/within the valence shells.
- **Implementation of the (RAS-SCF) method:** The RAS and SCF parts are often implemented by means of a *two-step cycle to (1) re-optimize the self-consistent field and (2) to enlarge the (layers of) shells in the representation of the atomic state vectors*.
- **Computation of level energies:** Different computational schemes have been applied to choose a restrictive active space for atomic level computations. If just the separation of the low-lying level energies are of interest, a closed core is often treated as *inactive*, and electron-electron correlations are considered only among the outer valence electrons. These valence-valence correlation scheme assumes a strict cancellation of all core-correlation contributions to the different levels. While this scheme often appears justified for core-core correlations, it is often less suitable for core-valence (CV) contributions, i.e. the polarization of the ionic core due to the valence electrons.

- **Core polarization:** To incorporate CV correlations, CSF with orbital replacements  $a \rightarrow r$  or even  $ab \rightarrow cr$  need to be taken into account, and where  $a, b, c$  refer to core orbitals and  $r$  to either valence or excited orbitals. Several systematically-enlarged case studies have been carried out, which basically include all core-valence excitations up to a maximally-occupied correlation layer. Although the separation energies are often improved by including these core-valence correlations, the separation of core and valence orbitals is much less obvious. For atom or ion, this separation need to be explore in further detail, in particular, if accurate excitation energies are needed.

#### 4.1.d. Approximate many-electron Green function for atomic levels (GreenFunction)

##### Formal representation & notations:

- **Formal quantum notation:**  $[\{E_{\nu_1}, |\psi_{\nu_1}(\beta_1 \mathbb{J}_1)\rangle\}, \{E_{\nu_2}, |\psi_{\nu_2}(\beta_2 \mathbb{J}_2)\rangle\}, \dots] \longrightarrow \mathbb{G}(E) = \sum_{\nu_1 \nu_2 \dots} \frac{|\psi_{\nu_i}(\beta_i \mathbb{J}_i)\rangle \langle \psi_{\nu_i}(\beta_i \mathbb{J}_i)|}{E - E_{\nu_i}} .$
- **Spectral (many-electron) Green function representation for the levels of one or several (given) configurations:** Such a representation refers to just one or several lists of many-electron levels  $\{E_{\nu_i}, |\psi_{\nu_i}(\beta_i \mathbb{J}_i)\rangle, \nu_i = 1, \dots, \nu_i^{(\max)}\}$ ,  $\mathbb{J}_i \in \mathbb{J}^{(\max)}$  from a list of total symmetries  $\mathbb{J}^{(\max)} = [\mathbb{J}_1, Jsym_2, \dots]$  and with up to  $n = n^{(\max)}$  electrons within the continuum, i.e. with  $n = 0, \dots, n^{(\max)}$  free (unbound) electrons.
- **Classification of Green functions:** Each Green function is classified by the (maximum) number of free electrons and a pre-specified (*de*-) *excitation scheme* that is to be applied in order to generate from a list of given configurations all those (nonrelativistic) configurations that are to be considered in the many-electron (CSF) basis of the Green function representation.
- **Classification of the many-electron Green functions:** In JAC, the major classification of Green function representations is based on the number of free electrons in the continuum. The many-electron basis must hereby include both, bound-type CSF as well as CSF with up to the maximum number of free electrons, and this CSF basis should be constructed in a systematic manner. **At present, we restrict ourselves to Green function representations with at least  $N - 1$  bound electrons and, hence, just up to a single electron in the continuum.**
- **Green function channel:** A channel refers to the set of atomic levels  $\{E_{\nu_i}, |\psi_{\nu_i}(\beta_i \mathbb{J}_i)\rangle\}$ , all with same total symmetry  $\mathbb{J}_i$ . Each Green function representation typically contains several (Green function) channels.
- **Atomic levels in a Green function representation:** The levels in such a many-electron representation formally belong to both, the bound-state spectrum of the atom ( $E_{\nu_i} < 0$ ) as well as to the continuum spectrum (scattering states) with 1, 2, ... electrons in the continuum. All these levels are constructed from a single set of one-electron orbitals, and which has to be properly chosen to represent reasonably well the bound-state levels of the given configurations.

#### 4. Atomic representations

- ‘Infinites’ in Green function representations: Already a single-electron Green function generally implies three *infinites* due to the electron’s spatial degrees of freedom, and which are often treated numerically by restricting the principal quantum number  $n^{(\max)}$  and the angular momentum quantum numbers  $j^{(\max)}$ ,  $m_j^{(\max)}$ . An  $N$ -fold multiple of such infinites arise for  $N$ -electron Green functions and make their approximation a real challenge. In JAC, approximation many-electron Green functions are restricted by:
- orbitals with a principal quantum number  $n^{(\max)}$  which applies for to all  $\kappa$  symmetry blocks;
  - a specified list of orbital angular momenta  $[\ell_1, \ell_2, \dots]$  for the virtual excitations and the generation of all non-relativistic configurations;
  - the coupling of the  $N$  orbitals to total symmetries  $\mathbb{J}_1, \mathbb{J}_2, \dots$ .
- Each of these total symmetries represent a many-electron continuum, and in which the Hamiltonian is still diagonal.

#### Use:

- Approximate many-electron Green functions play an essential role in studying all second- and higher-order perturbation processes as well as for various dynamic processes in atomic systems. For many-electron atoms and ions, however, the construction of proper Green function approximations is still rare in the literature because of their complexity and the required computational resources. More often than not, Green functions have mainly been used in the past in order to describe either single-electron or quasi-single-electron atoms.
- Using JAC: Generate an `Atomic.Representation(..., GreenExpansion(approach::Atomic.AbstractGreenApproach, scheme::Basics.AbstractExcitationScheme, levelSymmetries, NoElectrons, greenSettings))` for a given set of reference configurations as well as a specified (Green function) approach, excitation scheme, (list of) level symmetries, number of electrons and settings; cf. ? `GreenSettings` or `GreenSettings()`.
- Using JAC: The `approach::Atomic.AbstractGreenApproach` determines how and to which extent correlations among the bound and continuum electrons are taken into account into the Green function representation.
- Using JAC: The `scheme::Basics.AbstractExcitationScheme` determines how and to which extent excitations from the reference configurations into the specified *active* set of orbitals are included into the representation.
- In JAC, further details about the requested Green function can be specified by the maximum principle quantum number  $n^{(\max)}$  and a list of orbital angular momenta  $[\ell_1, \ell_2, \dots]$  that are allowed within the given (de-) excitation scheme in order to generate the many-electron (CSF) basis. These parameters have to be specified in `GreenSettings(...)`.
- In JAC, the output of a Green (function) expansion is a list of `GreenChannel`’s, i.e. a list of multiplets that are suitable for numerical computations and/or summation over many-electron levels..



- Using JAC, see also the functions: `Basics.generate()`.
- Using JAC: Perform an `Atomic.Computation(..., properties=[Green, ...], configs=[...], greenSettings=GreenFunction.Settings(...), ...)` or call directly functions from the module `GreenFunction`.
- **Green function approaches:** Several approaches are distinguished in JAC in order to determine how the set of many-electron levels  $\{E_{\nu_i}, |\psi_{\nu_i}(\beta_i \mathbb{J}_i)\rangle\}$  are to be generated and how much of the electron-electron interaction is to be taken into account in order to represent *both*, the bound and continuum spectra of the atom or ion:
  - (a) **Diagonal CSF basis without configuration interaction (SingleCSFwithoutCI):** This is a fast though very rough approximation, in which each CSF with total symmetry  $\mathbb{J}_i(\beta_i \mathbb{J}_i)$  also just represents a single level ( $\psi_{\nu_i}$ ) of the spectrum. This approximation fully omits all configuration interactions within the CSF basis (of a fixed  $\mathbb{J}_i$  symmetry).
  - (b) **Configuration interaction only between bound-state orbitals (CoreSpaceCI):** This approach diagonalizes (in turn) the Hamiltonian matrices of symmetry  $(\beta_i \mathbb{J}_i)$  by including the electron-electron interaction only between bound-state orbitals, while their interaction with and among the free electrons are neglected.
  - (c) **Damped configuration-interaction approach (DampedCI):** This approach again diagonalizes the Hamiltonian matrices of symmetry  $(\beta_i \mathbb{J}_i)$  by including the electron-electron interaction for all pairs of electrons but *damped* by some exponential factor  $e^{-\tau r}$ . The use of such a *damping function* in the Slater integrals (and, possibly the Breit integrals – although this has not been realized so far) ensures that the bound-bound, bound-free and free-free interactions are treated equally without that a *continuation* of the continuum orbitals for  $r \rightarrow \infty$  need to be considered in the numerical evaluation of the radial integrals.
- **(De-) Excitation schemes of electrons for the representation of approximate Green functions:** Since many-electron Green functions are very complex entities with many ‘infinities’ involved already within their formal definition, further control about the generation of such Green function approximations is obtained by specifying a proper (de-) excitation scheme of the electrons with regard to the given configurations:
  - (i) **(De-) excitation of a single electron from a given set of (nonrelativistic) configurations (DeExciteSingleElectron):** Cf. section 3.3
  - (\*) Further (de-) excitation schemes will be implemented as the needs arises in selected applications.

### Green functions for scattering processes:

- **Green functions for the study of scattering processes:** Formally, most scattering processes can be analyzed by solving the Schrödinger equation for some given many-electron Hamiltonian  $\mathbb{H}$ , the collision energy  $E$  and by including the proper scattering boundary conditions

$$\mathbb{H} |\Psi^+\rangle = E |\Psi^+\rangle.$$

#### 4. Atomic representations

- **Lippman-Schwinger representation:** A formal solution to the Schrödinger equation above is given by the Lippman-Schwinger equation which provides an integral form of the scattering wave function  $|\Psi^+\rangle$  in terms of the initial state  $|\Psi_o\rangle$  and the many-electron Green function  $\mathbb{G}^+(E)$  (cf. Tong *et al.*, 2009)

$$|\Psi^+\rangle = |\Psi_o\rangle + \frac{1}{E - \mathbb{H} + i\eta} \mathbb{V} |\Psi_o\rangle + \dots = |\Psi_o\rangle + \mathbb{G}^+(E) \mathbb{V} |\Psi_o\rangle + \dots$$

Here,  $\eta > 0$  is a small positive infinitesimal which ensures that the boundary conditions of an outgoing wave are properly taken into account, and where a (radiative) loss rate can be incorporated into the representation of  $|\Psi^+\rangle$  by means of a complex energy  $E$ .

- **Green function with optical potential:** The Green function of the scattering system with total scattering energy  $E$  can be formally written as

$$\mathbb{G}^+(E) = \sum_{\nu} \frac{|\psi_{\nu}\rangle \langle \psi_{\nu}|}{E - E_{\nu} + i\eta},$$

and where the summation runs over all (generalized) eigenfunctions of the Hamiltonian  $\mathbb{H}$ . This Green function can be utilized also for many scattering and dynamical processes if just a proper (sub-) set of many-electron levels  $\{E_{\nu}, |\psi_{\nu}\rangle\}$  is taken into account.

- **Optical potential:** If a proper optical potential is added to the (inner-) atomic potential, the outgoing wave is formally absorbed due to the occurrence of complex single-electron energies. Tong *et al.* (2009) suggest an energy-dependent optical potential of the form

$$V^{(\text{optical})}(r; \varepsilon) = \begin{cases} 0 & \text{for } r < r_c \\ V_o \left( \frac{r - r_c}{r_{\max} - r_c} \right) & \text{for } r \geq r_c \end{cases}, \quad \frac{\varepsilon^{1/2}}{r - r_c} < V_o < \varepsilon^{1/2} (r_{\max} - r_c),$$

and where the optical potential becomes *nonzero* at  $r_c$ . However, **little experience exists so far how the parameters  $r_c, r_{\max}, \varepsilon$  need to be chosen in order to obtain a realistic representation of the Green function, and how useful such an approximation is in different physical contexts.**

- **Diagonalization of the Hamiltonian matrix with an optical potential:** For an optical potential, the **Hamiltonian matrix is no longer hermitian but symmetric complex**, and it generally includes both diagonal and off-diagonal matrix elements due to the electron-electron interaction. From the diagonalization of the Hamiltonian matrix in a CSF basis with well-defined total symmetry  $\mathbb{J}_i$ , one then obtains the eigenenergies  $\{E_{\nu}\}$  and (atomic) eigenvectors  $\{E_{\nu_i}, |\psi_{\nu_i}\rangle\}$ , but which need to be calculated just once.

## 4.2. In JAC partly-implemented atomic representations

### 4.2.a. Multi-configuration Dirac-Hartree-Fock (MCDHF) expansions (Atomic)

#### Use & notations:

- **Multi-configuration Dirac-Hartree-Fock (MCDHF) method:** This method has been found a versatile tool for calculating the level structure and approximate wave functions for atoms and ions of all elements across the periodic table. In contrast to the CI method above, **both the radial (one-electron) functions as well as the expansion coefficients  $\{c_r(\alpha), r = 1, \dots, n_e\}$  are optimized simultaneously** on the basis of the Dirac-Coulomb Hamiltonian.
- **Using JAC:** Generate an `Atomic.Representation(..., McdhfExpansion(ciSettings))` for a given set of reference configurations and given settings; cf. `? McdhfSettings` or `McdhfSettings()`.
- **Using JAC, see also the functions:** `Basics.generate()`.
- **Steps for practical MCDHF computations:** In the MCDHF method and in JAC as well, the atomic bound states are typically generated by a series of steps:
  - Definition of the nuclear parameters as well as the angular structure (and extent) of the CSF basis  $\{|\gamma P J M\rangle\}$  in the MCDHF ansatz;
  - Algebraic evaluation and **computation of the spin-angular integrals (the so-called angular coefficients)**, based on standard techniques from Racah's algebra;
  - Generation or collection of proper radial start orbitals and self-consistent field (SCF) calculations, based on the Dirac-Coulomb Hamiltonian;
  - **Configuration interaction (CI) calculations** in order to incorporate further relativistic contributions into the Hamiltonian matrix and/or to enlarge the CSF basis beyond the given SCF model.

Often, **these four steps are repeated at several stages by systematically enlarging the one-electron (active) orbital space.**

- **Radiative corrections:** There are two dominant corrections for all medium and heavy elements which arise from QED; cf. section 3.5. When compared to missing correlation contributions, these **QED corrections are relevant only if the inner-shell electrons of these elements are involved in some (atomic) property or process**, and they are often negligible otherwise, at least as the present level of computational accuracy.

#### 4. Atomic representations

- **Other MCDHF codes:** During the last decades, a number of codes have become available, which implement the MCDHF method for free atoms and ions and which provide the approximate energies and wave functions for atomic bound states. For example, GRASP2K and later versions of the former Oxford package (Jönsson *et al.* 2013, 2018) now facilitate large-scale computations and supports wave function expansion of up to or beyond a million CSF as required for many open-shell atoms.
- **MCDHF method:** In this variational method, both the radial (single-electron) **orbital functions and the mixing coefficients are optimized on a (predefined) energy expression**. Often, this energy expression is given by a weighted sum of expectation values of some atomic Hamiltonian with regard to a geometrically-selected set of basis states for the atom or ion of interest. The systematic enlargement of this many-electron basis requires however to use non-spectroscopic (virtual) orbital functions, which just represent 'corrections' to the atomic state functions and which cannot be interpreted physically and independent of the chosen many-electron basis. In atomic and molecular physics, these corrections mainly arise from the **cusp condition** due to the singularities in the (pairwise) electron-electron interaction.
- **MCDHF method:** The introduction and use of systematically-enlarged wave function expansions have significantly improved the performance of the MCDHF method. More often than not, these expansions are based on (all) single and double (SD) excitations from a multi-reference (MR) set of generating configurations or expansions into a restrictive set of active orbitals; cf. section refsect:representation-RAS.

#### 4.2.b. Combined configuration interaction & perturbation theory (CI-PT) expansions (...)

##### Formal representation:

- **Combined CI-PT method:** While the **diagonalization of the many-electron Hamiltonian matrix** is perhaps the simplest way to take electronic correlations into account, only very few core excitations can typically be included by the CI method. In practice, further correlations between the valence and core electrons can be calculated and incorporated into the CI matrix by means of many-body perturbation theory (MBPT). Of course, no correlations between the core and valence electrons are included if excitations from the core are prohibited.
- **CI-PT method:** In this method, most of the weakly-correlated many-electron basis states (usually with rather high excitation energy) are not directly included into the diagonalization of the CI matrix but are treated instead perturbatively (Dzuba *et al.*, 2017). This approach significantly reduces the size of the CI matrix and, hence, removes one of the major limitations of this method for any larger number of valence electrons.

- **Partitioning of CI spaces:** In the CI-PT method, all CSF  $\{|\gamma_r \mathbb{J} M\rangle, r = 1, \dots, N_c\}$  as many-electron basis are assumed to be ordered in energy and divided into the (CI) model space  $P$  with  $r = 1, \dots, N_p$  CSF and a complementary space  $Q$  with  $N_q = N_c - N_p$  CSF, and for  $r = N_p + 1, \dots, N_c$ . The CI matrix ( $H_{rs} \equiv \langle \gamma_r \mathbb{J} M_r | H | \gamma_s \mathbb{J} M_s \rangle$ ,  $r, s = 1, \dots, N_p$ ) is diagonalized only within the  $P$  space, while all off-diagonal matrix elements from the  $Q$  space are neglected.
- **Effective CI matrix:** For the coupling between the  $P$  and  $Q$  spaces, all off-diagonal matrix elements ( $H_{rs}$ ,  $r = 1, \dots, N_p$ ,  $s = N_p + 1, \dots, N_c$ ) as well as all diagonal matrix elements ( $H_{ss}$ ,  $s = N_p + 1, \dots, N_c$ ) are taken into account explicitly in terms of an **effective CI matrix with modified matrix elements**:

$$H_{rs} \longrightarrow H_{rs} + \sum_k \frac{\langle r | H | k \rangle \langle k | H | s \rangle}{(E - E_k)}, \quad N_p < k \leq N_p + N_Q.$$

In these matrix elements,  $E$  formally refers to the (exact) energy from the many-electron SE. Owing to the overall symmetry of the Hamiltonian, this effective CI matrix can be computed and solved independently for each level symmetry  $\mathbb{J}$  of interest.

- **Iteration of the effective CI matrix:** Since the exact energy  $E$  is not known, it need to be initially replaced by some proper approximation  $E \rightarrow E^{(0)}$  and, hence, the **set-up and diagonalization of the effective CI matrix need to be solved iteratively**, using the CI energy  $E^{(t)}$ ,  $t = 0, \dots$  from the previous iteration. If more than one level of symmetry  $\mathbb{J}$  is required, this iteration of the effective CI matrix need to be done separately because of the different energies  $E^{(t)}(\alpha \mathbb{J}) \rightarrow E(\alpha \mathbb{J})$ , making the approach much less efficient. Moreover, the **use of different energies  $E(\alpha \mathbb{J})$  in the effective CI matrix results in ASF that are not quite orthogonal to each other**.

## Use & notations:

- **Using JAC:** Perform an `Atomic.Computation(..., properties=[Green, ...], configs=[...], greenSettings=GreenFunction.Settings(...), ...)` or call directly functions from the module `GreenFunction`.
- **In JAC, we provide ...**
- The CI-PT method can be easily applied if: (i) only a few low-lying levels are required with a large projection within the chosen  $P$  space already, (ii) all many-electron CSF are ordered in terms of their energy and (iii) if there is a reasonable *energy gap* between the CSF included directly into the CI matrix and those treated perturbatively. In practice, these conditions mean that the perturbative summation over the high-energy CSF must overall result in a rather small correction; the method fails if these conditions are not fulfilled.
- **Parallelization:** Since the summation over the high-energy CSF is very time-consuming but need to be performed independently for each matrix element, the CI-PT method is very suitable for parallel computations.

## Applications:

- Such a combined CI and perturbation theory (CI-PT) treatment has been applied especially for (super-) heavy elements and multiply-charged ions with open  $p$ -,  $d$ - and  $f$ -shells. Because of the particular shell structure, many of these multiply- and highly-charged ions have optical transitions near to their ground level and might be sensitive to **physics beyond the standard model**. This refers to possible variations of the fine-structure constant or violations of the (local) Lorentz invariance and Einstein equivalence principle as well as to potential interactions with dark matter.
- Two multiply-charged ions have been considered in the search for time variations of the fine-structure constant; these are  $\text{Ir}^{17+}$  ions with a  $4f^{13} 5s$  and  $\text{Ho}^{14+}$  ions with a  $4f^6 5s$  ground configuration.
- Dzuba *et al.* (2017) apply the  $V^{N-M}$  approximation in order to generate the initial Dirac-Hartree-Fock basis for the CI-PT procedure. In this approximation, only the core-shell electrons are included into the Dirac-Hartree-Fock, while all valence-shell are treated a *virtual* at this step of the computation. However, the set-up of the CI matrices then follows the standard procedure by using the orbitals from the Dirac-Hartree-Fock orbitals from the single-electron basis.
- Owing to the effective completeness of B-splines, Dzuba and Johnson (1998) showed for the low-lying levels of barium that a combined CI-MBPT method may significantly improve the convergence and numerical accuracy of many-electron computations.

### 4.2.c. Fast configuration interaction & perturbation theory (FCI-PT) expansions (...)

## Formal representation:

- **Fast CI:** Dzuba *et al.* (2019) suggest a further modification to the CI-PT method from above which is termed fast configuration interaction (fast CI). In this modification, the denominator in the perturbative sum of the CI-PT method is approximated by  $|E - E_k| \approx |E - E_c|$ , where  $E_c$  denotes some mean configuration energy of the basis state  $|k\rangle$ . This approximation enables one to re-write the summation as

$$\sum_k \frac{\langle r | H | k \rangle \langle k | H | s \rangle}{(E - E_k)} \approx \sum_{\text{configurations}} \frac{1}{E - E_c} \sum_{k_c} \langle r | H | k_c \rangle \langle k_c | H | s \rangle, \quad N_p < k \leq N_p + N_Q.$$

- While, at the first glance, this seem to make not much difference to the CI-PT method, it can considerably accelerate the computation of the second summation  $\sum_{k_c} \langle r | H | k_c \rangle \langle k_c | H | s \rangle$ . Such a simplification is possible for the evaluation of the many-electron matrix elements, since all the matrix elements can be traced back to a rather small number of radial integrals *times* some angular coefficients which only depend on the configuration but not on the detailed coupling of the basis states. Moreover, the mean configuration energy can also be expressed in terms of simple radial matrix elements or computed numerically just from the trace of the corresponding submatrix.
- A similar reduction in computation time might be obtained however by a careful arrangement of the many-electron basis states  $|k\rangle$  and by the re-use of angular coefficients and radial integrals.

### Use & notations:

- Using JAC: Perform an `Atomic.Computation(.., properties=[Green, ..], configs=[..], greenSettings=GreenFunction.Settings(..), ..)` or call directly functions from the module `GreenFunction`.
- In JAC, we provide ... .
- Because of the rapid increase in the computational costs, a reasonable active space can be applied in (standard) CI expansions only for a moderate number of (active) valance electrons, often not more that for 3-4 valence electrons above of closed shells otherwise.

### 4.3. Further atomic representations, not yet considered in JAC

#### 4.3.a. Many-body perturbation theory

##### Formal representation:

- **Decomposition of the Hamiltonian operator:** The standard perturbation theory starts from a suitable decomposition of the total Hamiltonian  $\mathbb{H}$ , and where solutions to  $\mathbb{H}_o$  are supposed to be known for a complete set of many-particle states.

$$\mathbb{H} = H_o + V, \quad \mathbb{H}_o \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)}, \quad V_{mn} = \langle \phi_m^{(0)} | V | \phi_n^{(0)} \rangle.$$

- **Expansion for energies and wave functions:**

$$\begin{aligned} E_n &= E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots; & \phi_n &= \phi_n^{(0)} + \phi_n^{(1)} + \dots \\ E_n^{(1)} &= V_{nn}, & \phi_n^{(1)} &= \sum_{m \neq n} \frac{|\phi_m^{(0)}\rangle V_{mn}}{E_n^{(0)} - E_m^{(0)}} \\ E_n^{(2)} &= \sum_{m \neq n} \frac{V_{nm} V_{mn}}{E_n^{(0)} - E_m^{(0)}}, & \phi_n^{(2)} &= \sum_{m, p \neq n} \frac{|\phi_m^{(0)}\rangle V_{mp} V_{pn}}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_p^{(0)})} - E_n^{(1)} \sum_m \frac{|\phi_m^{(0)}\rangle V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2}. \end{aligned}$$

In general, however, it is by far not easy to apply the formalism above to many-electron system due to the degeneracy of the zero-order solutions and a rather sophisticated book-keeping.

- **Basic steps of many-body perturbation theory (MBPT):** If we assume the decomposition from above and can express the **unperturbed Hamiltonian  $\mathbb{H}$  as a symmetric one-particle operator**, the solutions to  $\mathbb{H}$  are given by (orthogonal) Slater determinants  $\{\Phi_a\}$

$$\mathbb{H} = H_o + V, \quad \mathbb{H}_o = \sum_i h_o(\mathbf{r}_i), \quad \mathbb{H}_o \Phi_a = E_a^{(o)} \Phi_a, \quad \langle \Phi_a | \Phi_b \rangle = \delta_{ab}.$$

- **Slater determinants  $\Phi_a$**  can be readily built from the one-electron functions  $\phi_k$ :  $h_o \phi_k = \varepsilon \phi_k$ .
- **Goal of MBPT:** Solutions of the Schrödinger equation  $H \Psi_a = E_a \Psi_a$  for a finite number  $a = 1, \dots, d$  of atomic states.



- **Model space:**  $\mathcal{M} = \text{span}\{\Phi_a, a = 1, \dots, d\}$ ; all other solutions  $\Phi_r$  of  $\mathbb{H}_o$  with  $\Phi_r \notin \mathcal{M}$  lay in the (complementary) space that is orthogonal to  $\mathcal{M}$ .
- **1-dimensional model space:** For a 1-dimensional model space with the two projectors  $P = |\Phi_a\rangle\langle\Phi_a|$  and  $Q = 1 - |\Phi_a\rangle\langle\Phi_a| = \sum_{r \neq a} |\Phi_r\rangle\langle\Phi_r|$ , the energy corrections and wave function can be written as

$$|\Psi_a\rangle = |\Phi_a\rangle + |\Psi_a^{(1)}\rangle + |\Psi_a^{(2)}\rangle + \dots, \quad E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

- **Projection operator:** Obviously, the projection operator commutes with  $\mathbb{H}_o$ ; if  $\Psi_a$  is known,  $\Phi_a$  just refers to the projection of the exact solution upon the model space. More general, the projection operator fulfil the standard relations:

$$P = \sum_{a \in \mathcal{M}} |\Phi_a\rangle\langle\Phi_a|, \quad Q = 1 - P = \sum_{r \notin \mathcal{M}} |\Phi_r\rangle\langle\Phi_r|, \quad \Phi_a = P \Psi_a$$

$$P = P^+ = P^2, \quad PQ = QP = 0, \quad [P, \mathbb{H}_o] = [Q, \mathbb{H}_o] = 0$$

- **Wave operator (Möller, 1945):** One can formally define the (opposite) operator  $\Omega$  that maps the state in the model space upon the exact state, although  $\Omega$  and  $P$  are not *inverse* operators.

$$\Psi_a = \Omega \Phi_a$$

- **Generalized Bloch equation:** Using the definitions above and the (so-called) intermediate normalization, the Schrödinger equation can be

#### 4. Atomic representations

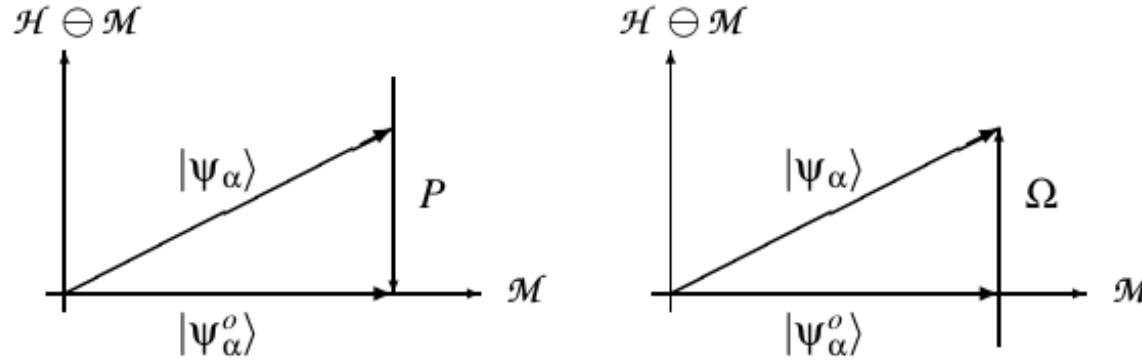


Figure 4.1.: Simplified representation of the operators  $P$  and  $\Omega$  in IN. The projector  $P$  transforms a  $d$ -dimensional space  $\{\Phi_a, a = 1, \dots, d\}$  of the Hilbert space into the model space  $\mathcal{M}$  of the same dimension. The wave operator  $\Omega$  reverses this transformation. Note, however, that  $P$  and  $\Omega$  are **not inverse operators**.

re-formulated as operator equation (Lindgren and Morrison, 1978):

$$\langle \Psi_a | \Phi_a \rangle = \langle \Phi_a | \Phi_a \rangle = 1 \iff P = P \Omega P$$

$$\cdot \Omega P | \quad \quad \quad \Omega P \mathbb{H}_o \Psi^a + \Omega P V \Psi_a = E_a \Omega P \Psi_a$$

$$- \mathbb{H}_o \Omega P \Psi_a + V \Omega P \Psi_a = E_a \Omega P \Psi_a$$

$$(\Omega \mathbb{H}_o - \mathbb{H}_o \Omega) P \Psi_a + (\Omega P V \Omega P - V \Omega P) \Psi_a = 0 \quad \quad \quad \forall a = 1, \dots, d$$

$$[\Omega, \mathbb{H}_o] P = (V \Omega - \Omega P V \Omega) P$$

For the states of interest  $\{\Psi_a, a = 1, \dots, d\}$ , this equation is completely equivalent to Schrödinger's equation. **Instead an equation for the wave function, we now have an (operator) equation for the wave operator  $\Omega$ .**

➤ **Expansion of the wave operator:**  $\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots$  gives rise to

$$[\Omega^{(1)}, H_o] P = Q V P$$

$$[\Omega^{(2)}, H_o] P = Q V \Omega^{(1)} P - \Omega^{(1)} V P$$

$$\vdots$$

$$[\Omega^{(n)}, H_o] P = Q V \Omega^{(n-1)} P - \sum_m^{n-1} \Omega^{(n-m)} V \Omega^{(m-1)} P$$

➤ **Second quantization:** The operators  $H_o, V, \Omega, \dots$  can be written also quite easily in second quantization and can be utilized for the (complex) coefficients  $x_j^{i(1)}$  and  $x_{kl}^{ij(1)}$

$$\Omega^{(1)} = \sum_{ij} a_i^+ a_j x_j^{i(1)} + \sum_{ijkl} a_i^+ a_j^+ a_k a_l x_{kl}^{ij(1)}$$

### 4.3.b. Complex-scaling method

#### Formal representation:

➤ **Complex scaling:** This scaling method is based on the global rotation of all radial coordinates  $\vartheta, r \rightarrow r e^{i\vartheta}$ . This rotation generally transforms hermitian into non-hermitian Hamiltonians whose (bound) eigenstates then describe both, bound and resonant states of the quantum system. **The resonant states have complex energies whose imaginary part describe the width (lifetime) of the resonances** (with regard to autoionization).

#### Use & notations:

➤ **Boundary conditions become irrelevant:** Since a complex-scaled function vanishes for  $r \rightarrow \infty$ , a representation of the resonances can be obtained by diagonalizing the rotated Hamiltonian within a square-integrable basis, and without taking special care of the boundary conditions.

#### 4. Atomic representations

- **Rotation of the Hamiltonian:** A rotation of the radial coordinates by an angle  $\vartheta$  is possible only, if the **potential is (so-called) dilatation-analytic**. While this is the case for any reasonable atomic Hamiltonian, this property is not necessarily fulfilled for pseudo- or polarization potentials, which can either be nonanalytical or even diverge within the complex plane for small values of  $\vartheta$  (Fossez *et al.*, 2015).
- **Exterior complex scaling:** The (so-called) infinite-range exterior complex scaling method provides an efficient tool for modelling an absorbing boundary in (time-dependent) many-electron calculations, such as many-electron atoms in an intense laser pulse. The exterior complex scaling is based on the transformation:  $r \rightarrow z(r) = R + r e^{i\vartheta}$ .

#### 4.3.c. Many-electron scattering functions

##### Formal representation:

- **Scattering functions within the vicinity of an isolated resonance:** For a given (positive) energy  $E$  of the stationary Schrödinger equation with Hamiltonian  $\mathbb{H} = \mathbb{H}_o + \mathbb{V}$ , the exact scattering solution in the vicinity of an isolated resonance can be written as superposition of a localized component  $|\psi_o\rangle$  and unbound components  $|\phi(\mathbf{r}; E)\rangle$  as (Nicolaidis and Themelis, 1992)

$$\begin{aligned}
 (\mathbb{H} - E) |\psi(\mathbf{r}; E)\rangle &= 0, & \mathbb{H} |\psi_o\rangle &= E_o |\psi_o\rangle \\
 |\psi(\mathbf{r}; E)\rangle &= a(E) |\psi_o\rangle + \int dE' b(E'; E) \phi(\mathbf{r}; E') \\
 &= a(E) \left( |\psi_o\rangle + \mathcal{P} \int dE' \frac{|\phi(\mathbf{r}; E)\rangle \langle \phi(\mathbf{r}; E) | \mathbb{H} | \psi_o\rangle}{E - E'} + c(E) |\phi(\mathbf{r}; E)\rangle \langle \phi(\mathbf{r}; E) | \mathbb{H} | \psi_o\rangle \right) \\
 E &= E_o + \mathcal{P} \int dE' \frac{|\langle \phi(\mathbf{r}; E) | \mathbb{H} | \psi_o\rangle|^2}{E - E'} + c(E) |\langle \phi(\mathbf{r}; E) | \mathbb{H} | \psi_o\rangle|^2
 \end{aligned}$$

Here,  $E$  is a real number on the positive energy axis and not an eigenvalue.

#### 4.3.d. Berggren expansion method

##### Formal representation:

- **Berggren expansion method (BEM):** In this single-particle method, (complex-energy) resonance states are described by a particular completeness relation for bound, decaying and scattering states, first introduced by Berggren in 1968. Because of the quasi-localized nature of the single-particle states, the BEM method does not require a precise treatment of the boundary conditions at infinity.
- **Completeness relation of Berggren ensembles:** A (single-particle) Berggren ensemble satisfies for each partial wave  $\kappa$  the relation

$$\sum_{n \in b,d} |u_{n\kappa}\rangle \langle u_{n\kappa}| + \int_{\mathcal{L}_{\kappa}^+} |u_{\varepsilon\kappa}\rangle \langle u_{\varepsilon\kappa}| = 1.$$

Here,  $|u_{n\kappa}\rangle$  are the radial wave functions of the bound (b) and decaying (d) states, while  $|u_{\varepsilon\kappa}\rangle$  represent scattering states, and  $\mathcal{L}_{\kappa}^+$  denotes the contour that encompasses the decaying states in the fourth quadrant of the complex  $\varepsilon$ -plane.

- **Coupled-channel formalism:** A Berggren ensemble represents a single-particle spectrum in the vicinity of some resonance and can be combined quite easily with the coupled-channel method in order to describe (resonant) behaviour in nuclei, atoms and molecules.

##### Use & notations:

- **Berggren ensemble:** This ensemble refers to the single-particle spectrum of a Hamiltonian with complex eigenvalues; it generally contains bound (b), decaying (d), and scattering (s) single-particle states along the contour  $\mathcal{L}_{\kappa}^+$  for each partial wave  $\kappa$ .
- **Slater determinants built from a Berggren ensemble:** The Berggren single-particle states can be also utilized to construct a many-particle basis, in which the (many-particle) Hamiltonian is diagonalized. This scheme has so far been applied especially in nuclear-structure theory in order to describe the behaviour of valence nucleons outside of a closed core. Since the contour of the Berggren ensemble is discretized, the same applies also to the many-body basis that is spanned from this ensemble.
- **Gamow shell model (GSM):** This model is an extension of the traditional nuclear shell model with complex-energy single-particle states. In this model, a single-particle Berggren basis is generated in a finite-depth potential, independent for each partial wave  $\kappa$ , and then comprises Gamow (or resonant) discrete states as well as the nonresonant scattering continuum.

#### 4. Atomic representations

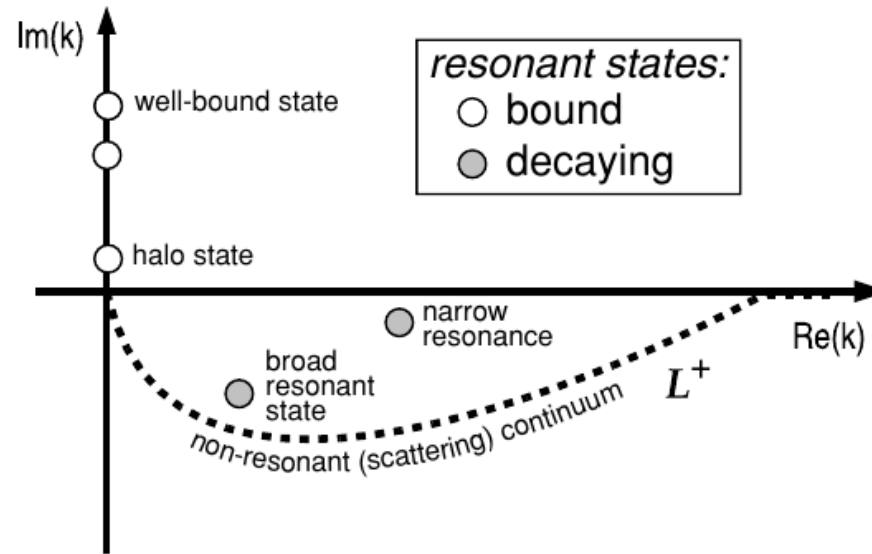


Figure 4.2.: Illustration of the Berggren ensemble in the complex  $k$ -plane. While the bound states are all located on the positive imaginary axis, the weakly bound halo states lay close to the origin and the positive-energy resonant states in the fourth quadrant. All states with a small imaginary part can be interpreted as resonances. The complex- $k$  shells on the contour  $\mathcal{L}^+$  represent the nonresonant scattering continuum. From Rotureau *et al.* (2009).

- **Complex-energy Gamow shell model (GSM):** The structure and representation of weakly bound and unbound nuclear states close to particle drip lines has attracted much recent interest in nuclear physics. A proper treatment of these states goes beyond the traditional shell model, which makes only use of localized states, but requires to allow particle emission. The GSM enables one to describe resonant and nonresonant many-body states on equal footing (Jaganathan *et al.*, 2017).

#### Applications:

- Fosse *et al.* (2015) applied the Berggren expansion method to parts of the unbound spectrum of dipolar molecules and achieved both, a much higher accuracy for the representation of the weakly-bound as well as the unbound resonance states.
- **Structure of light nuclei:** Light nuclei have been traditionally applied to test microscopic nuclear structure models. The work by Lane (1955)

and Kurath (1956) on  $p$ -shell nuclei have become a cornerstone of nuclear structure theory and provided great guidance to analyzing the wealth of spectroscopic data on energy levels, electromagnetic transitions, nuclear moments, and various particle decays during the past decades (Jaganathan *et al.* 2017).

#### 4.3.e. Convergent close-coupling (CCC) method

##### Formal representation:

- **Coupled-channel equations:** For scattering problems, the convergent close-coupling method refers to a reformulation of the SE in terms of an **infinite set of coupled-channel equations**. This reformulation assumes a complete set of target states.
- The Convergent Close-Coupling (CCC) method has been worked out originally in order to compute accurate cross sections for the scattering of light projectiles on (quasi-) one- and two-electron targets. In the original representation of this method, the scattering wavefunctions are often given in momentum space and are based on the Lippmann-Schwinger equation.
- **Advantages of the CCC method:** This method enables one to treat the many-particle continuum systematically by means of square-integrable functions. In particular, the CCC starts from an expansion of the target into a complete set of orthogonal  $L^2$  functions to span the Hilbert space.

##### Use & notations:

- **Difficulties with the CCC method** The continuum channels at *intermediate* energies are particularly important and need to be well represented in their coupling to other channels.
- **Convergence:** Convergence in the scattering amplitudes can (and need to be) shown as the size of the square-integrable functions increases.

#### 4.3.f. Density-matrix renormalization group (DMRG) method

##### Formal representation:

#### 4. Atomic representations

- **Ab-initio DMRG method:** This method can be described either in terms of the renormalization group and renormalized operators, and as it was formulated originally, *or* by means of **matrix product states and matrix product operators (MPS & MPO)**, a more recent language. These two languages use different vocabularies and appear to be quite different in their formulation (Chan *et al.*, 2016).
- **Use of MPS & MPO language:** The power of this language consists in new perspectives and algorithms, rather than in just re-writing the original renormalization group operator (RGO) language. For example, the algebra of the MPS & MPO language provides various new operations beyond the scalar computation of expectation values, and which can be utilized for instance to describe time evolutions.
- **Matrix product state (MPS):** For a given quantum many-particle system, the MPS generally refer to some **low-rank decomposition of the full interaction matrix**. In atomic physics and quantum chemistry, this matrix is **known also as the (full) configuration-interaction matrix or tensor**.
- **In atomic physics** and elsewhere, the **DMRG method provides a nonperturbative scheme that is useful to replace the (full) configuration interaction method in restricted active spaces**.
- The DMRG method has attracted increasing interest in quantum chemistry during the past two decades.

#### Use & notations:

- **Matrix product ansatz:** The power of the DMRG method mainly arise from the **matrix product ansatz** which enables one to express the low entanglement nature of one- or few-dimensional low-energy quantum eigenstates, including the ground-state (Chan *et al.*, 2016).
- **Dimension of MPS:** The (virtual) dimension of the MPS designates the rank of the decomposition and, hence, the dimension of many-body Hilbert subspace that is taken into account. In the DMRG method, this dimension can be increased systematically until numerical convergence is reached (Wouters and van Neck, 2014).
- **Left- and right-bases:** To support a simple translation from the renormalization-group operators to the MPS & MPO language (and back, if requested), emphasis must be placed to the relation between the left- and right-bases *and* the tensors in the MPS & MPO language. Moreover, these relations need to be worked out for (i) the renormalized wavefunctions, (ii) the representation of the Hamiltonian, (iii) the minimization of energies as well as (iv) for the evaluation of expectation values within these two schemes.
- **Difficulties in 2D and 3D:** The DMRG has difficulties with achieving good accuracy for two- and three-dimensional systems since the need of computational resources increase more or less exponentially with system size. From a detailed comparison of 1D and 2D lattices, it was recognized that this behaviour is **closely related to scaling of entanglement in many-body states** as described, for instance, by the area laws (Schollwöck 2011).



## Matrix product states:

- **Matrix product states (MPS):** These product states refer to a particular wavefunction representation that help define the variational space of the DMRG. For an orthonormal Fock-space basis  $\{|n_1 n_2 \cdots n_K\rangle\}$  of  $K$  orbitals (including spin labels), an atomic wave function is written in **occupation representation** as

$$|\psi\rangle = \sum_{n_1 n_2 \cdots n_K} \psi^{n_1 n_2 \cdots n_K} |n_1 n_2 \cdots n_K\rangle.$$

For a fixed particle number  $N$ , moreover, we have the condition

$$\psi^{n_1 n_2 \cdots n_K} = \begin{cases} \psi^{n_1 n_2 \cdots n_K} & \sum_{k=1}^K n_k = N \\ 0 & \text{else.} \end{cases}$$

- **MPS amplitudes:** For any state of the atom or ion, the wavefunction amplitude can be written

$$\psi^{n_1 n_2 \cdots n_K} = \sum_{\{\alpha_k\}} A_{\alpha_1}^{n_1}[1] A_{\alpha_1 \alpha_2}^{n_2}[2] \cdots A_{\alpha_{K-1}}^{n_K}[K]$$

as a product of  $M \times M$  matrices  $A^{n_k}[k]$ , of equal dimension, apart from the  $1 \times M$  leftmost and  $M \times 1$  rightmost matrices. This particular construction of the MPS ensures that the matrix product always results in the *scalar* amplitude  $\psi^{n_1 n_2 \cdots n_K}$ . In a non-relativistic formulation, moreover, the dimension of these matrices is  $2 \times M \times M$  if the spin-index of the (spin-) orbitals is taken into account.

- **MPS bond dimension  $M$ :** The number of renormalized states gives rise to the dimension  $M$  of the matrices and makes the representation of the state with increasing  $M$  more flexible. **For bound-state systems, it can be assumed that the matrices  $A^{n_k}[k]$  are all real.**
- **Graphical representation of MPS:** A general wavefunction amplitude can always be represented graphically as a tensor with  $K$  legs, while the MPS as a whole is just represented by a connected set of 2-index and 3-index tensors, each associated with a certain site. In addition, graphical rules can be derived to contract the tensors in various ways.
- **DMRG sweep algorithm:** The MPS & MPO language also suggests a **new formulation of the *ab-initio* DMRG sweep algorithm** itself (Chan *et al.*, 2016).

### Applications:

- The entanglement perspective of the DMRG method made it possible to extent its application towards new fields, such as matrix product operator representations, the time-evolution of atoms and molecules, infinite systems, systems at finite temperatures as well as towards higher-dimensions. In addition, the language of matrix product and tensor network states is nowadays quite widely applied to reason about the structure of many-particle quantum states (Chan *et al.*, 2016).
- Earlier *ab-initio* DMRG applications in quantum chemistry have mainly focused upon level and excitation energies as well as reduced density matrices, which can be computed stepwise by running through all orbitals.
- **1D spin chains:** The DMRG method has been found a versatile tool especially for simulating the static and dynamical behaviour of strongly correlated 1D quantum lattice systems (Schollwöck 2011). The use of MPS, in particular, has lead to a much deeper understanding of the DMRG method itself including both, its great potential and limitations.
- For such 1D spin chains, the accuracy of DMRG simulations has been found limited only by machine precision, rather independent of the particular choice of Hamiltonian.
- **Application of 1D spin chains:** 1D and 2D strongly-correlated systems have applications in condensed matter physics, such as for studying spin chains and ladders, high-temperature superconductance of frustrated magnets in low spatial dimensions and at several places elsewhere. These **spin chains have found interest also in exploring ultra-cold gases in optical lattices.**
- **Applications in nuclear physics:** The DMRG method (may) enable configuration interaction studies of weakly bound and unbound strongly-interacting complex systems, which cannot be treated by any direct diagonalization because of the prohibitively large Fock space (Rotureau *et al.* 2009). Any theoretical description of such states requires a rigorous treatment of the many-body correlations in the presence of decay channels and a scattering continuum.
- **Applications to nonequilibrium systems:** While most of the previous DMRG studies were focused on equilibrium properties in strongly-correlated closed quantum systems with a hermitian density matrix, nonequilibrium systems with non-hermitian and non-symmetric density matrices can also be treated, though with rather mixed success.

## 4.4. Other representations, related to JAC

### 4.4.a. Natural-orbital functional theory (NOFT)

#### Natural-orbital functionals:

- **Scope of the theory:** The natural-orbital functional theory (NOFT) has been developed as alternative to both, the density functional theory (DF) and to a large variety of wavefunction-based methods. In NOFT, the electronic structure of atoms or molecules is described by **natural orbitals (NO)** and their **occupation numbers (ON)**. The use of approximate NO functionals has been found both, more accurate than DFT computations and to scale (much) better in their computational costs than correlated wavefunction representations.

### 4.4.b. Density functional theory (DFT)

#### Formal representation:

- **Hohenberg-Kohn theorem:** Hohenberg and Kohn showed that all ground-state properties of atoms, molecules, etc. are uniquely determined by the electron density alone. In particular, **there exist a unique universal functional of the electron density that can be utilized in order to obtain the ground state energy and density.**
- **Kohn-Sham theorem:** The universal functional of the electron density can be re-written as a sum of kinetic energies of noninteracting (so-called Kohn-Sham) particles *and* some **exchange-correlation functional**. This representation enables one to represent the electron density by means of a single (Kohn-Sham) Slater determinant, even if the exact form of the exchange-correlation functional remains unknown.
- **Hohenberg-Kohn theorem:** This theorem tells that the energy of any (finite quantum) system can be written as a functional of the **electron density**, the well-known basis of Density Function Theory (DFT). Various approximate density functionals have been developed and explored with regard to different physical and chemical properties. For instance, concepts from DFT have been applied in order to obtain **chemical reactivity indices** and to characterize the chemical reactions of molecular systems in terms of perturbations (distortions) of the electron density.
- **Approximate exchange-correlation functionals:** Many approximate semi-empirical exchange-correlation functionals have been proposed in the literature with different strengths and complexity.

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- **Strength and weaknesses of DFT:** Since the exact exchange-correlation functional remains unknown, not all correlation can usually be retrieved by the DFT method. Indeed, **DFT has been found good in capturing dynamic correlations**, i.e. if the main physics can be described by means of the single Slater determinant, **but it often fails for strong correlations** for which multireference methods are then required.

#### Applications:

- Today, the simple Kohn-Sham representation of DFT is the basis for its great success for different – and partly very complex – systems, such as clusters, biomolecules and nanostructures.

#### 4.4.c. Relativistic coupled-cluster (RCC) theory

#### Formal representation:

- **All-order techniques:** One of the most popular all-order technique is the **CC approach in which correlation contributions are classified due to the number of excited particles rather than by the order of the perturbation**.
- **All-order techniques:** From many-body and coupled-cluster (CC) computations, one knows that only certain classes of correlation diagrams need to be incorporated to all orders in order to obtain very accurate results.

#### Applications:

- In practice, most CC computations include just single and pair correlations to all orders but neglect triple and higher correlations, though selected triple and quadrupole excitations might be included (Dzuba and Johnson, 1998).

#### 4.4.d. Miscellaneous methods for the representation of many-electron systems

##### Eigenvector continuation techniques:

- **Eigenvector continuation:** Demol *et al.* (2020) mention the method of eigenvector continuation as an efficient and reliable tool for the **resummation of wave function expansions**; although this text is quite difficult to follow, the method is said to be robust and based on simple mathematical principles. If, in particular, a quantum system is described by the Hamiltonian  $H \equiv H(1)$ , that smoothly depend on a single parameter  $H(c)$ , the **power of the eigenvector continuation method** refers to (Demol *et al.*, 2020):
  1. There exist formally a parameter regime  $0 \leq c \leq c_e \leq 1$  for which the many-body problem is easier to solve than for the target value  $c = 1$ .
  2. The stability of the eigenvectors of  $H(c)$  with regard to variations of  $c$  remains for the many-body state of interest ( $c = 1$ ) within a low-dimensional manifold of the full  $A$ -body Hilbert space when  $c$  is changed from  $[0, c_e] \rightarrow 1$ .

##### Direct quantum dynamics:

- **Direct quantum dynamics:** Direct dynamical methods refer to a **branch of molecular-dynamical simulations** that combines and applies methods from quantum chemistry in order to calculate potential energy surfaces and their derivatives for a particular nuclear geometry. Although these energy surfaces are usually computed *on-the-fly*, some intermediate results are stored in databases to help re-cycle the expensive quantum chemical computations. First applications of direct quantum dynamics were performed already in the 1970s using the local gradient in order to generate approximate Born-Oppenheimer trajectories during chemical reactions. The propagation of the wave functions was later improved by using a local Hessian matrix, and which typically allows for larger step sizes in the propagation. **Direct quantum dynamic methods are today often integrated into quantum chemistry programs and are as easy to apply as static methods for any system that remains feasible.**
- **Direct quantum dynamics:** Nowadays, **(direct) quantum dynamics is a key technique for molecular dynamics simulations** in order to understand different physico-chemical processes at (ultra-) short time scales. These techniques are for instance applied to interpret experiments in femto-chemistry. In contrast to other classical and semi-classical simulations, quantum-dynamics methods suppose the prior knowledge of the (whole) potential energy function in order to solve the time-dependent Schrödinger equation for the nuclear motion (Lasorne *et al.*, 2007). Since accurate potential energy surfaces (PES) cannot be calculated globally for more than, say, five or six degrees of freedom, they are then often combined with classical mechanics and the use of the Car-Parinello method.

#### 4.4.e. Transformation of atomic into qubit Hamiltonians

##### Formal representation:

➤

##### Quantum hardware and algorithms for atomic physics:

- **Atomic computations & quantum computing:** Quantum computing may affect atomic computations due to: (1) Running atomic computations on quantum hardware and (2) Transformation of atomic Hamiltonians into qubit Hamiltonians and quantum circuits [cf. McClean *et al.* (2019) and the code OPENFERMIUM].
- **Qubit transformation of atomic Hamiltonians:** Once the problem has been recast in the second quantized, it needs to be mapped upon qubits. While electrons are indistinguishable fermions, qubit representations have to be distinguishable in order to support useful computations.
- **Qubit transformation:** Several transformations, such as the Jordan-Wigner (JW), Bravyi-Kitaev (BK), and Bravyi-Kitaev super fast (BKSF) transformations, are known today to support the mapping of indistinguishable fermions to distinguishable qubits. These transformations also take the antisymmetry (particle statistics) of the electronic wave functions into account. In particular, the **Jordan-Wigner transformation directly returns an equivalent ‘qubit operator’ for the atomic Hamiltonian.**
- **Quantum computational supremacy:** Fault-tolerant quantum computing can speed-up significantly the solutions of various NP-hard problems, such as the factorization of prime numbers, search algorithms, linear-algebra and various others. While, until to the present, most realizations of multi-qubit realizations are fragile and suffer from noise and sub-universal behaviour, newly emerging quantum processors are expected to be developed and to be powerful enough in order to outperform classical computers for selected tasks, known also as **quantum computational supremacy** (Killoran *et al.*, 2019).
- **Atomic Hamiltonian in second quantization:**

$$\mathbb{H} = \sum_{ij} h_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} h_{ijkl} a_i^\dagger a_j^\dagger a_k a_l.$$

The one- and two-particle amplitudes  $h_{ij}$ ,  $h_{ijkl}$  are usually computed classically and are provided as input to the quantum simulations.

- **Jordan-Wigner transformation:** This transformation helps re-write the electronic Hamiltonian as a sum over products of Pauli spin operators, i.e. as a series of qubit gates. To do so, the individual terms of the Hamiltonian are converted into unitary gates. In the Jordan-Wigner

transformation, a single fermionic creation or annihilation operator is represented by  $\mathcal{O}(n)$  qubit operations. Even if the individual terms of the electronic Hamiltonian **do not** commute with each other (as usual), a Trotter decomposition and sequential execution of the corresponding gate operations will eventually support an approximate unitary propagator.

- **Jordan-Wigner transformation:** To encode the occupation-number (Fock-space) basis, one can simply replace the antisymmetric many-electron basis by the corresponding multi-qubit state

$$|f_1, f_2, \dots, f_n\rangle \quad \Longrightarrow \quad |q_1\rangle \otimes |q_2\rangle \otimes \dots \otimes |q_n\rangle, \quad f_i = q_i \in \{0, 1\}.$$

In this transformation, one qubit is used to encode one occupation number. To represent the corresponding (qubit) creation and annihilation operators in the qubit basis, we can use the Pauli matrices as

$$\begin{aligned} q^+ |0\rangle &= |1\rangle, & q^+ |1\rangle &= 0, & q^- |1\rangle &= |0\rangle, & q^- |0\rangle &= 0, \\ q^+ |1\rangle \langle 0| &= \frac{1}{2} (\sigma_x - i \sigma_y), & q^- |0\rangle \langle 0| &= \frac{1}{2} (\sigma_x + i \sigma_y). \end{aligned}$$

Here, the mutual anti-commutation of the three Pauli matrices ensures that  $q^\pm$  anti-commutes also with  $\sigma_z$ . This eventually enables one to represent the (electronic) creation and annihilation operators  $a^\pm$  by the corresponding qubit operators  $q^\pm$ .

- **Bravyi-Kitaev transformation:** This transformation provides a more efficient mapping of electronic Hamiltonians upon qubit Hamiltonians than the Jordan-Wigner transformation. It represents single fermionic creation or annihilation operator by  $\mathcal{O}(\log n)$  qubit operations.
- **Quantum computing** is known as a rapidly growing discipline that aims for the discovery of exponentially faster quantum algorithms than the best-known classical algorithms. However, one first need to know and control the required resources in order to realize such algorithms.
- **Resources of quantum computing:** In pure-state quantum computations, entanglement is often considered as a necessary resource in order to achieve an exponential speed-up in the computations. Although this seems not to be true for mixed-state quantum computations, until the present, it is largely unclear which entities help quantify the resource in such a computational model. Moreover, there is no simple relationship known between different resources for mixed-state quantum computations.
- **Application of quantum simulations:** Modern simulations make use of **approximate quantum optimization algorithms, quantum annealing or the sampling from computationally expensive probability distributions**. Similar techniques may be applied also to tackle problems in quantum chemistry, machine learning or even at stock markets.

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- **Quantum simulations:** At present, rather large-scale quantum simulations are the most promising application of quantum computers within the foreseeable future, and with direct applications in quantum chemistry and condensed matter. In contrast to the standard **qubit representation** of most quantum protocols, the simulation of fermionic many-particle systems is a great challenge, since all fermionic operator must be transformed into a representation of distinguishable qubits. In atomic or molecular physics, a useful quantum simulation protocol (algorithm) should be able to reliably predict energy spectra, reaction rates, correlation functions or other (atomic and molecular) properties. Such quantum simulation protocols will become superior to classical computers, if larger systems can be calculated than currently accessible by (classical) calculations.

#### Continuous variable (CV) model of quantum computing:

- **Continuous variable (CV) model of quantum computing:** In the CV model, the basic (information-processing) unit is an **infinite-dimensional bosonic mode** as it can be realized and manipulated with light. While such a CV model of quantum computing retains the major features from the standard qubit model, it promises simpler implementations for various bosonic systems, such as photons, electromagnetic fields, trapped atoms, harmonic oscillators or Bose-Einstein condensates. More general, a CV model of quantum computing may facilitate quantum computations and simulations for all those systems where continuous quantum operators are naturally occur, such as position and momentum.
- **Systems based on continuous variables (CV):** Many quantum systems have (also) spatial degree of freedoms and, hence, are intrinsically continuous. With these systems, an infinite-dimensional Hilbert space is associated, and any representation in such a space is very different from a discrete qubit representation. Indeed, the CV model of quantum computing got its name from the continuous spectra of the quantum operators associated with spatial degrees of freedoms and which offers a paradigm for quantum computations.
- **Qubits *versus* continuous variables (CV):** It can be shown that every qubit-based computation can be realized also by means of CV representations. This makes the **CV model of quantum computing a powerful extension of the familiar qubit model**.
- **Systems based on continuous variables (CV):** Perhaps, the most simple CV system is the 1D bosonic harmonic oscillator which can be defined either by its (canonical) mode operators  $a$  and  $a^+$  with  $[a, a^+] = \mathbb{1}$  or, equivalently, by its the – position and momentum – (quadrature) operators

$$\hat{x} = \sqrt{\frac{\hbar}{2}} (a + a^+), \quad \hat{p} = -i\sqrt{\frac{\hbar}{2}} (a - a^+), \quad [\hat{x}, \hat{p}] = i\hbar \mathbb{1}.$$

In a optical fibre or waveguide, for instance, a fixed harmonic oscillator mode can be considered (drawn) as a single 'wire' in a quantum circuit, and these modes are the fundamental units of CV quantum computers.



### Software tools for qubit transformations:

- **OPENFERMION:** This is an open-source software library in Python for simulation of fermionic and bosonic models. It aims to provide a (preliminary) **interface for translating the atomic or quantum chemistry specification of problems into a (qubit) representation**, suitable for quantum hardware. The goal is to specify a quantum circuit for solving or studying electronic structure problems, and without that the user need to have *domain expertise* in quantum information theory.
- **OPENFERMION:** This toolbox provides some preliminary functionality for developing (new) quantum algorithms for solving electronic-structure problems. Until the present, however, efficient algorithms for atomic physics and quantum chemistry are still a challenge and their implementation on quantum hardware remains a rather formidable task. This toolbox also aims to facilitate the communication between quantum-chemistry and quantum-information community.
- **STRAWBERRY FIELDS:** This Python package refers to an open-source software architecture for photonic quantum computing. It is based on the new quantum programming language **Blackbird** and is especially designed for dealing with CV models of quantum computing. This package makes us of **different circuit decompositions from quantum photonics, such as the Williamson, Bloch-Messiah or Clements decompositions** (Killoran *et al.*, 2019). STRAWBERRY FIELDS can be utilized either as Python package or as a browser-based interface for the set-up of quantum circuits.
- **Decompositions of STRAWBERRY FIELDS:** Several decompositions are realized, including: (a) the **Williamson decomposition** to decompose arbitrary Gaussian states into some symplectic transformation that can be applied on thermals states, (b) the **Bloch-Messiah decomposition** for modelling interferometers and single-mode squeezing as well as (c) the **Clements decomposition** for representing multi-mode linear interferometers in terms of arrays of beamsplitters and rotations of fixed depth.

### 4.4.f. qumodes

#### Formal representation:

- **Representation of qumodes:** In a CV model and with the vacuum state  $|0\rangle$ , each qumode can be written in terms of the quadrature

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states

$$|\psi\rangle = \int dx \, \psi(x) |x\rangle, \quad \hat{x} |x\rangle = x |x\rangle, \quad x \in \mathbb{R}$$

$$|\psi\rangle = \exp(-i \mathbb{H} t) |0\rangle,$$

and where  $\mathbb{H}$  is a bosonic Hamiltonian, i.e. a function of the mode operators  $a, a^+$  and of the time  $t$ ; the quadrature states are a sub-class of the so-called Gaussian states of qumodes.

- **Gaussian states:** For these states, the Hamiltonian  $\mathbb{H}$  is at most quadratic in  $a, a^+$ . Gaussian single-qumode states can be parametrized by two complex variables, a **displacement parameter**  $\alpha \in \mathbb{C}$  and a **squeezing parameter**  $z \in \mathbb{C}$ .

# 5. Atomic interactions with the radiation field

## 5.1. Wave equations & optical fields

### 5.1.a. Homogeneous wave equation

#### General solutions:

- **Monochromatic plane-wave light:** Monochromatic plane-wave light is uniquely determined by either the electric ( $\mathbf{E}$ ) or magnetic ( $\mathbf{B}$ ) field. Without restriction, we here consider a plane-wave along  $\mathbf{k} \parallel \mathbf{e}_z$ .
- **Waves that propagate along the wave vector  $\pm \mathbf{k}$ :** We consider the homogenous wave equation (for  $\psi = \{\mathbf{E}, \mathbf{B}, \Phi, \mathbf{A}, \dots\}$ ) with the known solution (proof by substitution and by means of the chain rule), whose wave fronts propagate along  $\pm \mathbf{k}$

$$\square \psi(\mathbf{r}, t) = 0 \qquad \psi(\mathbf{r}, t) = \psi_+(\mathbf{k} \cdot \mathbf{r} + \omega t) + \psi_- \underbrace{(\mathbf{k} \cdot \mathbf{r} - \omega t)}_{\text{phase}}$$

for arbitrary functions  $\psi_{\pm}(\mathbf{k} \cdot \mathbf{r} \pm \omega t)$ , and if they fulfill the dispersion relation  $\omega = (\pm) c k$ .

- **(Complex) monochromatic plane waves:** If we restrict ourselves to periodic (harmonic) solutions, two obvious solutions are

$$\psi(\mathbf{r}, t) = A_- e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \qquad \text{or} \qquad \psi(\mathbf{r}, t) = A_+ e^{i(\mathbf{k} \cdot \mathbf{r} + \omega t)}$$

$$\psi = \text{const.} \quad \text{for} \quad t = t_o \qquad \Longleftrightarrow \qquad \mathbf{k} \cdot \mathbf{r} = \text{const.}$$

Here, the vector  $\mathbf{k}$  is called the wave or propagation vector and  $\omega$  the frequency of the plane waves.

### 5.1.b. Plane-wave radiation

#### Plane-wave solutions:

➤ **Plane waves:** Plane waves always propagate into the direction of the wave vector and can be written as

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_o e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad \mathbf{B}(\mathbf{r}, t) = \mathbf{B}_o e^{i(\tilde{\mathbf{k}} \cdot \mathbf{r} - \tilde{\omega} t)}$$

However, since the em field must satisfy not only the homogenous wave equation  $\square \psi = 0$  but also Maxwell's equations for the coupling of the  $\mathbf{E}$ - und  $\mathbf{B}$  fields

$$\text{rot } \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \iff i(\mathbf{k} \times \mathbf{E}_o) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = i\tilde{\omega} \mathbf{B}_o e^{i(\tilde{\mathbf{k}} \cdot \mathbf{r} - \tilde{\omega} t)}, \quad \omega = \tilde{\omega}; \quad \mathbf{k} = \tilde{\mathbf{k}}; \quad \mathbf{k} \times \mathbf{E}_o = \omega \mathbf{B}_o.$$

Of course, this Maxwell equation need to be fulfilled for all times and places.

➤ If we use of the three other Maxwell equations, we furthermore obtain:

$$\text{div } \mathbf{E} = 0 \implies \mathbf{k} \cdot \mathbf{E}_o = 0$$

$$\text{div } \mathbf{B} = 0 \implies \mathbf{k} \cdot \mathbf{B}_o = 0$$

$$\text{rot } \mathbf{B} = \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} \implies \mathbf{k} \times \mathbf{B}_o = -\frac{\omega}{c^2} \mathbf{E}_o \implies (\mathbf{k} \times \mathbf{B}_o)^2 = k^2 B_o^2 = \frac{\omega^2}{c^4} E_o^2 \implies E_o^2 = c^2 B_o^2.$$

Therefore, the **three vectors  $\mathbf{E}_o$ ,  $\mathbf{B}_o$ ,  $\mathbf{k}$**  form (up to any even permutation) an **orthogonal and right-handed system**, i.e. the vectors  $\mathbf{E}$  and  $\mathbf{B}$  are perpendicular on  $\mathbf{k}$  for plane waves.

➤ **Vector potential:**

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_\pm e^{i(\mathbf{k} \cdot \mathbf{r} \pm \omega t)} = \sum_{\lambda} A_{o,\lambda} \mathbf{e}_\lambda e^{i(\mathbf{k} \cdot \mathbf{r} \pm \omega t)}$$

➤ **Equation of a plane:** For plane waves, all spatial points  $\mathbf{r}$  with  $\mathbf{k} \cdot \mathbf{r} = \text{const.}$  have the same value at any time  $t = t_o$ .

➤ **Wave crest:** The wave crest of a plane wave is  $A_\pm e^{i(\mathbf{k} \cdot \mathbf{r} \pm \omega t)}$  and propagates into the direction  $\pm \mathbf{k}$ .

- **Monochromatic light field:** Most simply, a classical monochromatic light field with frequency  $\omega > 0$ , (complex) envelope or field amplitude  $\mathcal{E}(t)$  and polarization  $\mathbf{u}$  (complex unit vector) is given by

$$\mathcal{E}(t) = \frac{1}{2} \mathcal{E}(t) \mathbf{u} e^{-i\omega t} + \text{c.c.}$$

- **(Time-averaged) Poynting vector & intensity:** For a plane electro-magnetic wave, the (time-averaged) Poynting vector is given by

$$\mathbf{S} = \frac{c}{8\pi} \mathcal{E}_o^2 \mathbf{e}_k, \quad I = |\mathbf{S}| = \frac{c}{8\pi} \mathcal{E}_o^2 \quad \dots \quad \text{intensity}$$

$$\mathbf{u}^* \cdot \mathbf{u} = 1,$$

$$\mathbf{u}^* \times \mathbf{u} = i P_3 \mathbf{e}_k,$$

and where the **degree of circular polarization**  $P_3$  coincides with the third Stokes parameter (right-circularly polarized  $P_3 = 1$ , left-circularly polarized  $P_3 = -1$  and linearly-polarized  $P_3 = 0$ ). Obviously, a *real* polarization vector  $\mathbf{u}$  refers to  $P_3 = 0$  and to a linear polarization for a (pure) plane-wave from above. Moreover, the degree of circular polarization can be described also in terms of the **eccentricity  $\epsilon$  of the polarization ellipse** by  $|P_3| = 2\sqrt{1 - \epsilon^2} / (2 - \epsilon^2)$ .

- **Electric-field of a superposition of two plane waves:** With the (real) wave vectors  $\mathbf{k}_1, \mathbf{k}_2$  and the (complex) polarization vectors  $\mathbf{u}_1, \mathbf{u}_2$ , the electric field of a plane electromagnetic wave is given by:

$$\mathcal{E}(\mathbf{r}, t) = \frac{1}{2} [\mathcal{E}_1 \mathbf{u}_1 e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \omega_1 t)} + \mathcal{E}_2 \mathbf{u}_2 e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \omega_2 t)}] + \text{c.c.}$$

- **Electric-field of a *standing* plane waves:** For  $\mathbf{k}_1 = -\mathbf{k}_2 = \mathbf{k}$ ,  $\omega_1 = \omega_2 = \omega$ ,  $\mathbf{u}_1 = \mathbf{u}_2 = \mathbf{u}$ ,  $\mathcal{E}_1 = \mathcal{E}_2 = \frac{\mathcal{E}}{2}$  in the superposition of two plane waves above, the electric field becomes

$$\begin{aligned} \mathcal{E}(\mathbf{r}, t) &= \frac{1}{2} \left[ \frac{\mathcal{E}}{2} \mathbf{u} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \frac{\mathcal{E}}{2} \mathbf{u} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right] + \text{c.c.} = \frac{1}{2} \mathcal{E} \mathbf{u} e^{-i\omega t} \left[ \frac{e^{i\mathbf{k} \cdot \mathbf{r}} - e^{-i\mathbf{k} \cdot \mathbf{r}}}{2} \right] + \text{c.c.} \\ &= \cos(\mathbf{k} \cdot \mathbf{r}) \left[ \frac{1}{2} \mathcal{E} \mathbf{u} e^{-i\omega t} + \text{c.c.} \right] = \cos(\mathbf{k} \cdot \mathbf{r}) \bar{\mathcal{E}}(t) \end{aligned}$$

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Here, the factor  $\cos(\mathbf{k} \cdot \mathbf{r})$  shows the *standing wave*, while  $\bar{\mathcal{E}}(t)$  refers to some time-harmonic electric field, i.e. an uniformly oscillating field. This standing wave can be interpreted also as 1D optical lattice (Beloy 2009).

### Conserved properties of plane waves with $\mathbf{k} \parallel \mathbf{e}_z$ :

➤ (Linear) momentum:

$$p_k = -i \partial_k, \quad p_{x,y} \mathbf{A}(\mathbf{r}, t) = 0, \quad p_z \mathbf{A}(\mathbf{r}, t) = k_z.$$

➤ Orbital angular momentum:

$$\ell_z = -i (x \partial_y - y \partial_x) = -i \frac{\partial}{\partial \varphi}, \quad \ell_z \mathbf{A} = 0.$$

➤ Spin (of photons):

$$s_z = -i \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad s_z \mathbf{A} = \lambda \mathbf{A}.$$

➤ Total angular momentum:

$$j_z = \ell_z + s_z, \quad j_z \mathbf{A} = \lambda \mathbf{A}.$$

➤ For plane waves, the (four) good quantum numbers refer to  $\mathbf{p} = (p_x, p_y, p_z)$  and  $\lambda_c$ .

### 5.1.c. Polarization of plane waves in classical electrodynamics

#### Polarization of plane-waves beams:

- Apart from the (well-defined) frequency of plane-wave photons, each photon has generally a spin angular momentum  $\hbar$  that can be (partly) aligned in parallel or antiparallel to the direction of propagation. A full alignment of all photon spins gives then rise to a circularly-polarized light beam.
- A beam with a circularly-polarized planar wavefront has an azimuthal component of the Poynting vector that is proportional to the radial intensity gradient, even if it has no orbital angular momentum. This gives rise to a finite value, if integrated over the total cross-section of the beam.
- **Polarization of the electric field:** Polarization is an additional property of (em) waves that describes the orientation of their oscillations; by convention, the polarization  $-1 \leq p \leq 1$  refers to the electric field. The polarization of light is associated with the spin-angular momentum (density) of the em wave.
- The polarisation is said to be linear if  $p = 0$ , and is left- or right-circular for  $p = -1$  and  $p = +1$ , respectively. For all other values of  $-1 < p < 1$ , the wave is said to be elliptically polarized. Sometimes, one also refers to the chirality or handedness of the waves in order to denote the left- or right-circular polarization of the light beam.
- **Vector potential of a circularly-polarized plane wave:**

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{e}_\lambda e^{i(kz - \omega t)}; \quad \mathbf{e}_\lambda = (\mathbf{e}_x + i\lambda \mathbf{e}_y) \quad \begin{cases} \lambda = +1 & \text{left circular} \\ \lambda = -1 & \text{right circular} \end{cases}$$

- **Spin angular momentum (SAM):** The circular polarization of light is usually associated with a well-defined SAM.
- **Complex spherical unit vectors  $\mathbf{e}_\pm$ :**

$$\mathbf{e}_\pm = \frac{1}{\sqrt{2}} (\mathbf{e}_x \pm i\mathbf{e}_y) \quad \Longleftrightarrow \quad \begin{aligned} \mathbf{e}_x &= \frac{1}{\sqrt{2}} (\mathbf{e}_+ + \mathbf{e}_-) \\ \mathbf{e}_y &= \frac{-i}{\sqrt{2}} (\mathbf{e}_+ - \mathbf{e}_-) \end{aligned}$$

- **Complex electric field  $\mathbf{E}^{(c)} = (E_x^{(c)}, E_y^{(c)}, 0)$ :** Although a complex notation of em fields is often very convinient, the transverse, real

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electric field is given by

$$\left. \begin{aligned} E_x^{(c)} &= |E_x^{(c)}| e^{i\gamma} \\ E_y^{(c)} &= |E_y^{(c)}| e^{i(\gamma+\delta)} \end{aligned} \right\} \quad \mathbf{E}^{(c)} = \Re \left[ (E_x^{(c)} \mathbf{e}_x + E_y^{(c)} \mathbf{e}_y) e^{i(kz - \omega t)} \right] = E_x \mathbf{e}_x + E_y \mathbf{e}_y$$

$$E_x = |E_x^{(c)}| \cos(kz - \omega t + \gamma), \quad E_y = |E_y^{(c)}| \cos(kz - \omega t + \gamma + \underbrace{\delta}_{!!}) \dots \text{real.}$$

- **Relative phase  $\delta$  to distinguish different polarization:** This relative phase  $\delta$  refers to the complex field amplitudes  $E_x^{(c)}$  and  $E_y^{(c)}$
- **Linear polarization along the angle  $\alpha$ :** For  $\delta = n\pi$  ( $n \in \mathbb{N}$ )

$$\mathbf{E}^{(c)} = (|E_x^{(c)}| \mathbf{e}_x \pm |E_y^{(c)}| \mathbf{e}_y) \cos(kz - \omega t + \gamma) = |\mathbf{E}^{(c)}| \mathbf{e}_\alpha \cos(kz - \omega t + \gamma)$$

$$|\mathbf{E}^{(c)}| = \sqrt{|E_x^{(c)}|^2 + |E_y^{(c)}|^2}, \quad \tan \alpha = \pm \frac{|E_y^{(c)}|}{|E_x^{(c)}|} \quad \dots \left\{ \begin{array}{ll} (+) & n = \text{gerade} \\ (-) & n = \text{ungerade} \end{array} \right.$$

$$\mathbf{e}_\alpha = \cos \alpha \mathbf{e}_x + \sin \alpha \mathbf{e}_y$$

The angle  $\alpha$  denotes the (polarization-) direction of  $\mathbf{E}$  with regard to the  $x$ -axis.

- **General monochromatic plane wave:** Any plane wave can always be written as superposition of two components

### 5.1.d. Atom-light interaction in the electric-dipole approximation

#### Atom-light interaction operator:

- **Electric-dipole approximation to the atom-light interaction:** In the electric-dipole approximation, the interaction operator between an atom and the light field can be expressed in terms of the electric-dipole operator  $\mathbb{D}$  of the atom and the electric field  $\mathcal{E}(t)$  by

$$\mathbb{H}^{(E1)} = -\mathcal{E} \cdot \mathbb{D} = -\frac{1}{2} \mathcal{E}(t) \mathbf{u} \cdot \mathbb{D} e^{-i\omega t} - \frac{1}{2} \mathcal{E}^*(t) \mathbf{u}^* \cdot \mathbb{D} e^{i\omega t}.$$



## 5.2. Representation and parametrization of photons in atomic theory

### 5.2.a. Stokes parametrization and density matrix of a photon

#### Stokes parameters:

- **Stokes parameters:** These parameters provide a simple and alternative characterization for the polarization of plane waves and are given in terms of three real parameters that describe the polarization state of (transversal) electromagnetic radiation.
- **Stokes parameters  $P_1, P_2, P_3$ :** The first two Stokes parameters quantify the *relative* asymmetries between intensities  $I_\chi$  of light that is linearly polarized under different angles  $\chi$  with regard to the reaction plane:  $P_1 = (I_o - I_{90})/(I_o + I_{90})$  and  $P_2 = (I_{45} - I_{135})/(I_{45} + I_{135})$ . The parameter  $P_3$  reflects the degree of circular polarization of the emitted photons.
- The Stokes parameters were defined by George Gabriel Stokes in 1852 as a mathematically convenient alternative to the more common description of incoherent or partly polarized radiation in terms of its total intensity  $I$ , the degree of polarization  $P$ , and the orientation of the (so-called) polarization ellipse.
- **Degree of polarization:** The polarization state of the photon is said to be *pure* if they obey the Stokes parameters obey the restriction  $\sum_{i=1}^3 P_i^2 = 1$ .
- **Degree of linear polarization:** The parameter  $P_\ell = \sqrt{P_1^2 + P_2^2}$  is called the **degree of linear polarization**.
- **Stokes parameters  $P_3 = P_c$ :** Photons with  $\lambda = +1$  are called **right-circularly polarized photons**, and photons with  $\lambda = -1$  are called **left-circularly polarized photons**.
- Note that the notation in optics is often opposite to that used in quantum electrodynamics for historical reasons.

#### Alternative representation of polarized photons:

- Instead of the Stokes parameters  $P_1$  and  $P_2$ , it is often convenient for the analysis of different experimental situations to use the degree of linear polarization  $P_\ell$  and the direction of the principal axis of the polarization ellipse  $\varphi_0$ .

Table 5.1.: Stokes parametrization of photons for selected polarization of photons with  $\mathbf{k} \parallel \mathbf{e}_z$ .

Selected photon polarization	$P_1$	$P_2$	$P_3$
unpolarized	0	0	0
polarized along $x$ -axis	1	0	0
polarized along $y$ -axis	-1	0	0
right-circularly polarized	0	0	1
left-circularly polarized	0	0	-1

- **Polarization ellipse:** If, in the chosen coordinate frame, the  $x$ -axis is directed along the principal axis of a polarized photon beam ( $\varphi_0 = 0^\circ$ ), the Stokes parameter  $P_1$  takes the largest value  $|P_1| = P_\ell$ , while the Stokes parameter  $P_2$  vanishes. This easily shows that the Stokes parameters  $P_1$  and  $P_2$  depend on the choice of the  $x$ -axis even if the  $z$ -axis is fixed along the beam, while the degree of linear polarization  $P_\ell$  remains invariant.
- **Polarization ellipse:** It is often convenient to introduce the angle  $\varphi_0$  by the relations

$$\cos 2\varphi_0 = \frac{P_1}{P_\ell}, \quad \sin 2\varphi_0 = \frac{P_2}{P_\ell}$$

- **Probability for measuring a linearly polarized photon along  $\varphi$  in the  $xy$ -plane:** For a density matrix with given  $P_\ell, \varphi_0$  Balashov *et al.* (2001) shows the probability distribution

$$W(\varphi) = \frac{1}{2}(1 + P_\ell \cos 2(\varphi - \varphi_0))$$

for measuring linearly-polarized photon along  $\varphi$  in the  $xy$ -plane.

- **Angle of the polarization vector:** The angle  $\varphi_0$  indicates the *principal axis of the polarization ellipse of the photon beam*. It describes the direction of the axis (with regard to the  $x$ -axis) which the intensity of the transmitted photon beam is the largest, while it is lowest intensity perpendicular to this direction.

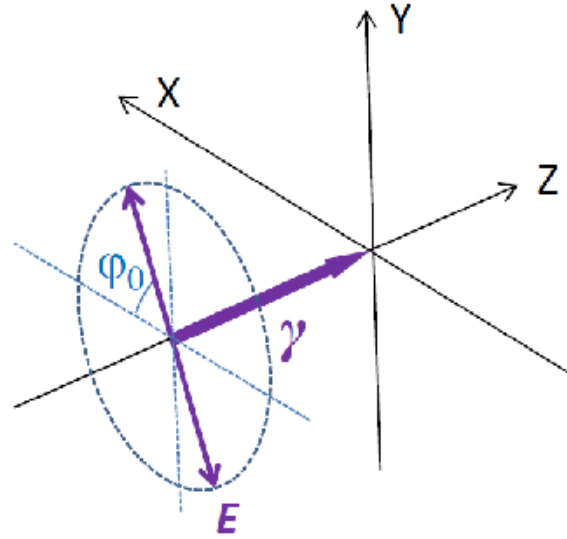


Figure 5.1.: Laboratory coordinate system.

### Photon density matrix:

- **Photon density matrix in helicity representation:** Most naturally, the spin state of an incident photon is expressed within its **helicity representation**

$$\rho_\gamma = \sum_{\lambda\lambda'} c_{\lambda\lambda'} |\mathbf{k}\lambda\rangle \langle \mathbf{k}\lambda'|,$$

where the helicity  $\lambda$  is the spin projection of the photon upon the direction of its propagation, i.e. along the momentum or wave vector  $\mathbf{k}$ .

- Since for a photon (with intrinsic spin  $s \equiv 1$ ) the helicity just takes the values  $\lambda = \pm 1$ , only three real parameters are required to describe the spin state of the photons. These parameters in the photon density matrix are closely connected to the Stokes parameters of light (Rose,

1961)

$$(c_{\lambda\lambda'}) = \langle \mathbf{k} \lambda | \rho_\gamma | \mathbf{k} \lambda' \rangle = \frac{1}{2} \begin{pmatrix} 1 + P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1 - P_3 \end{pmatrix}.$$

Note that this definition differs from those in Balashov *et al.* (2005) by a factor  $-1$  for the  $P_1$  and  $P_2$  parameters because of the different convention of the spherical unit vectors  $\mathbf{e}_\pm$ .

## 5.2.b. Pure polarization states of photons

### Linearly-polarized plane-wave photons with $\mathbf{k} \parallel \mathbf{e}_z$ :

- In this section, we consider **pure polarization states of an incoming photon**, i.e. light with a photon density matrix  $P_1^2 + P_2^2 + P_3^2 = 1$ , and which is thus equivalent to a density-matrix with  $\rho^2 = \rho$ .
- With this restriction in mind, **any polarized state of a transverse photon** can be described by the linear combination

$$|\mathbf{e}\rangle = g_+ \mathbf{e}_+ + g_- \mathbf{e}_-,$$

where  $\mathbf{e}_\lambda$  ( $\lambda = \pm$ ) are the **unit polarization vectors within the circular basis**, and with  $|g_+|^2 + |g_-|^2 = 1$ .

- The state of a linearly-polarized photon along some given direction  $\varphi_0$  in the  $x - y$  plane can be written in the form

$$|\mathbf{e}_{\varphi_0}\rangle = -\frac{1}{\sqrt{2}} (e^{-i\varphi_0} \mathbf{e}_+ - e^{i\varphi_0} \mathbf{e}_-).$$

- **Pure linearly-polarized light with  $P_\ell = 1$ :**  $|g_+| = |g_-|$ .

### Elliptically-polarized plane-wave photons with $\mathbf{k} \parallel \mathbf{e}_z$ :

- **Photon density matrix in terms of the  $g_\pm$  coefficients:** With these notations, an **arbitrarily polarized pure state of a (transversal) photon** can be expressed in terms of the  $g_\pm$  coefficients by either a  $2 \times 2$  matrix or by means of the corresponding Stokes parameters:

$$\langle \mathbf{k} \lambda | \rho | \mathbf{k} \lambda' \rangle = \begin{pmatrix} |g_+|^2 & g_+ g_-^* \\ g_+^* g_- & |g_-|^2 \end{pmatrix}, \quad P_1 = -2 \Re(g_+ g_-^*), \quad P_2 = 2 \Im(g_+ g_-^*), \quad P_3 = |g_+|^2 - |g_-|^2.$$

➤ **Polarization ellipse:** The linear polarization can be characterized also by  $P_\ell$  and  $\varphi_0$  with

$$P_\ell = 2|g_+ g_-^*| = 2|g_+||g_-| \cos 2\varphi_0 = -\frac{\Re(g_+ g_-^*)}{|g_+ g_-^*|}, \quad \sin 2\varphi_0 = -\frac{\Im(g_+ g_-^*)}{|g_+ g_-^*|}.$$

These simple relations can be used to also find the  $g_\pm$ -coefficients for given parameters  $P_\ell$  and  $\varphi_0$ .

➤ **Fully-polarized light with  $P_\ell \neq 1$ :**

$$\text{for } |g_+| > |g_-|: \quad |g_+| = \frac{1}{2} \left( \sqrt{1+P_\ell} + \sqrt{1-P_\ell} \right), \quad |g_-| = \frac{1}{2} \left( \sqrt{1+P_\ell} - \sqrt{1-P_\ell} \right)$$

$$\text{for } |g_+| < |g_-|: \quad |g_+| = \frac{1}{2} \left( \sqrt{1+P_\ell} - \sqrt{1-P_\ell} \right), \quad |g_-| = \frac{1}{2} \left( \sqrt{1+P_\ell} + \sqrt{1-P_\ell} \right)$$

➤ The relative phase of the coefficients:  $g_+ = |g_+| e^{i\xi_+}$ ;  $g_- = |g_-| e^{i\xi_-}$  can be found from the equation:  $\xi_- - \xi_+ = 2\varphi_0 + \pi$ .

➤ **Polarization vectors  $\epsilon_1, \epsilon_2$  of elliptical-polarized plane-wave radiation:** An alternative representation of the polarization vector is given by:

$$\epsilon_j = \left( \mathbf{e}_x \cos\left(\frac{\xi_j}{2}\right) + i \mathbf{e}_y \sin\left(\frac{\xi_j}{2}\right) \exp\left(\frac{i\eta_j}{2}\right) \right), \quad \epsilon_j^* = \left( \mathbf{e}_x \cos\left(\frac{\xi_j}{2}\right) - i \mathbf{e}_y \sin\left(\frac{\xi_j}{2}\right) \exp\left(\frac{-i\eta_j}{2}\right) \right), \quad j = 1, 2.$$

➤ **Two elliptically-polarized beams with the same angular momentum but opposite helicity:** The easiest way to describe such a superposition is  $\xi_1 = \xi_2 = \pi/2$ ,  $\eta_1 = \eta_2 = 0$ , and this leads to

$$\epsilon_1 = \epsilon_2 \equiv \epsilon, \quad \epsilon_1^* = \epsilon_2^* \equiv \epsilon^*, \quad \epsilon \cdot \epsilon^* = 1, \quad \epsilon \cdot \epsilon = \epsilon^* \cdot \epsilon^* = 0.$$

➤ **Two elliptically-polarized beams with the same helicity and opposite angular momentum:** These beams are described by  $\xi_1 = -\xi_2 = \pi/2$ ,  $\eta_1 = \eta_2 = 0$ , and the two polarization vectors then fulfill

$$\epsilon_1 = \epsilon_2^* \equiv \epsilon, \quad \epsilon_1^* = \epsilon_2 \equiv \epsilon^*, \quad \epsilon \cdot \epsilon^* = 1, \quad \epsilon \cdot \epsilon = \epsilon^* \cdot \epsilon^* = 0.$$

### Beams of fully-polarized light with $\mathbf{k} \parallel \mathbf{e}_z$ :

- **Sequences of completely polarized light pulses:** In experiments, one often considers a sequence of (fully polarized) photon pulses, which propagate however into different directions.
- **Hierarchy of angles in defining the em pulses:** For such a sequence of pulses, all angles are defined with respect to a fixed laboratory frame  $\Sigma = (x, y, z)$ , and where we assume all coordinate systems to be properly ‘right-handed’.
- In the (primed) coordinates  $\Sigma'$  as associated with some given pulse, the polarization coefficients are assumed to be:

$$g_+ = 1, \quad g_- = 0 \quad (\text{for ‘helicity : } +1' )$$

$$g_+ = 0, \quad g_- = 1 \quad (\text{for ‘helicity : } -1' )$$

$$g_+ = -\frac{1}{\sqrt{2}} e^{-i\phi_0}, \quad g_- = \frac{1}{\sqrt{2}} e^{i\phi_0} \quad (\text{for ‘linear’ and given } \phi_0).$$

- **First pulse:** The wave vector of the first pulse always defines the  $z$ -axis and its linear polarization ( $\phi_0$ ) the  $x$ -axis of the fixed frame  $\Sigma$ , i.e. the first pulse defines the  $x - z$  scattering plane. For a circularly polarized pulse, the  $x$ -axis is defined indirectly due to the definition of subsequent pulses (see below); it need not to be defined explicitly if there is only a single, circularly-polarized pulse.
- **Parameters of the first pulse:**

$$\phi_1 = 0; \quad \theta_1 = 0; \quad (\phi_1 = 0 \quad \text{for circularly polarized light})$$

### 5.2.c. Spherical tensors of polarization vectors

#### Spherical tensors:

- **Spherical tensor  $[\mathbf{u}^* \otimes \mathbf{u}]_q^{(K)}$ :** The compound spherical tensor of the (complex) polarization vectors can be written in terms of its spherical tensor components of  $\mathbf{u}$

$$[\mathbf{u}^* \otimes \mathbf{u}]_q^{(K)} = \sum_{r,s=0,\pm 1} (-1)^{q+s} \sqrt{2K+1} \begin{pmatrix} 1 & K & 1 \\ r & -q & s \end{pmatrix} u_r u_{-s}^*$$

and, hence, is related also to the cartesian (vector) components  $\mathbf{u} = (u_x, u_y, u_z)$  of the polarization vector.

- **Tensor products of the polarization vector:** The tensorial products of the polarization vector can be evaluated in terms of the unit vectors of the coordinates and the electro-magnetic field as

$$[\mathbf{u}^* \otimes \mathbf{u}]_0^{(0)} = -\frac{1}{3} (\mathbf{u}^* \cdot \mathbf{u}) = -\frac{1}{3}$$

$$[\mathbf{u}^* \otimes \mathbf{u}]_0^{(1)} = -\frac{i}{\sqrt{2}} (\mathbf{u}^* \times \mathbf{u}) \cdot \mathbf{e}_z = \frac{P_3}{\sqrt{2}} (\mathbf{e}_\mathbf{k} \cdot \mathbf{e}_z) = \frac{P_3}{\sqrt{2}} \cos \vartheta_k$$

$$[\mathbf{u}^* \otimes \mathbf{u}]_0^{(2)} = \frac{1}{\sqrt{6}} [3 (\mathbf{u}^* \cdot \mathbf{e}_z) (\mathbf{u} \cdot \mathbf{e}_z) - (\mathbf{u}^* \cdot \mathbf{u})] = \frac{1}{\sqrt{6}} [3 |\mathbf{u} \cdot \mathbf{e}_z|^2 - 1] = \frac{1}{\sqrt{6}} [3 \cos^2 \vartheta_u - 1] .$$

Here,  $\vartheta_k$  is the angle of the  $\mathbf{k}$ -vector with regard to the  $z$ -axis,  $\vartheta_u$  the angle of the polarization direction with regard to the  $z$ -axis. Often, however, other parameters are chosen characterize the polarizabilities and (ac) Stark shifts.

## 5.3. Multipole decomposition of the radiation field

### 5.3.a. Elements from the theory of multipole transitions

#### Electron-photon interaction:

- **Electron-photon interaction operator:** To account for different gauges in the interaction with monochromatic, plane-wave light, this (interaction) operator can be written in terms of the wave vector  $\mathbf{k}$  and the (complex) polarization vector  $\mathbf{u}$  as

$$R(\mathbf{k}, \mathbf{u}) = \boldsymbol{\alpha} \cdot (\mathbf{u} + G \mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} - G e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{pLM} i^{L-|p|} \left[ \mathbf{u} \cdot \mathbf{Y}_{LM}^{(p)}(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}) \right] a_{LM}^{(p)}(r)$$

Here, the gauge parameter can be set to  $G = 0$  for the Coulomb (velocity) gauge and to  $G = \sqrt{(L+1)/L}$  for the Babushkin (length) gauge. Moreover,  $\mathbf{Y}_{LM}^{(p)}(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}})$  are the vector spherical harmonics and  $a_{LM}^{(p)}(r)$  are the electric ( $p = 1$ ), magnetic ( $p = 0$ ) and longitudinal ( $p = -1$ ) multipole components of the radiation field (or briefly, multipole fields).

- **Orthogonality of the vector spherical harmonics:**

$$\int d\Omega_k \left[ \mathbf{u}^* \cdot \mathbf{Y}_{LM}^{(p)}(\vartheta_k, \varphi_k) \right] \left[ \mathbf{u} \cdot \mathbf{Y}_{L'M'}^{(p')*}(\vartheta_k, \varphi_k) \right] = \delta_{pp'} \delta_{LL'} \delta_{MM'},$$

#### Transition amplitudes:

- Johnson (2008) provide a systematic decomposition of the transition amplitudes into multipole components.
- **Transition amplitudes due to a transverse-gauge vector potential  $\mathbf{A}^{(\text{transverse})}(\mathbf{r}, \omega)$ :** For a single-electron atom, the transition amplitude from state  $a = |n_a \kappa_a m_a\rangle \rightarrow b = |n_b \kappa_b m_b\rangle$  due to the interaction with a plane-wave radiation field with the transverse-gauge vector potential  $\mathbf{A}^{(\text{transverse})}(\mathbf{r}, \omega) = \boldsymbol{\epsilon} e^{i\mathbf{k} \cdot \mathbf{r}}$ , with  $\boldsymbol{\epsilon} \cdot \mathbf{e}_z = 0$  is

$$T_{ba} = \int d^3\mathbf{r} \psi_b^* \boldsymbol{\alpha} \cdot \mathbf{A}^{(\text{transverse})}(\mathbf{r}, \omega) \psi_a.$$



### Multipole potentials:

- **Plane-wave multipole potentials  $\mathbf{a}_{LM}^{(p)}(\mathbf{r})$ :** In the **multipole expansion** of the plane-wave vector potential, the multipole potentials satisfy both, the Helmholtz equation and **transversality condition**

$$\nabla^2 \mathbf{a}_{LM}^{(p)} + k^2 \mathbf{a}_{LM}^{(p)} = 0, \quad \nabla \cdot \mathbf{a}_{LM}^{(p)} = 0 \quad p = 0, 1.$$

- The multipole potentials  $\mathbf{a}_{LM}^{(p)}$  with  $p = 0$  are the magnetic multipole potentials and with  $p = 1$  the electric multipole potentials.
- **Electron-multipole interaction operator:** The interaction operator  $\boldsymbol{\alpha} \cdot \mathbf{a}_{LM}^{(p)}$  is an irreducible tensor operator of rank  $L$  and parity  $(-1)^{L+1-p}$ .
- The **multipole expansion of the (transverse-gauge) plane-wave vector potential** still contains all information about the polarization and propagation direction of the photons.
- **Representation of the multipole potentials:** Using the well-known identities of the spherical Bessel functions, the multipole potentials  $\mathbf{a}_{LM}^{(p)}$  can be expressed as (Johnson, 2007)

$$\mathbf{a}_{LM}^{(0)}(\mathbf{r}) = j_L(kr) \mathbf{Y}_{LM}^{(0)}(\mathbf{r}), \quad \mathbf{a}_{LM}^{(1)}(\mathbf{r}) = \left[ j_L'(kr) + \frac{j_L(kr)}{kr} \right] \mathbf{Y}_{LM}^{(1)}(\mathbf{r}) + \sqrt{L(L+1)} \frac{j_L(kr)}{kr} \mathbf{Y}_{LM}^{(-1)}(\mathbf{r}).$$

### 5.3.b. Single-electron (reduced) multipole-transition matrix elements

#### Johnson's single-electron reduced multipole-transition matrix elements:

- **Transverse (velocity) gauge:** Johnson (2007, section 6.3) derives the **reduced multipole-transition matrix elements** for  $\mathbb{M} = (L, p)$  and

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$q = \omega/c$  as:

$$\begin{aligned}\langle a \parallel \mathbb{T}^{(\mathbb{M}, \text{magnetic})}(\omega) \parallel b \rangle &= \langle -\kappa_a \parallel \mathbb{C}^{(L)} \parallel \kappa_b \rangle \int_0^\infty dr \frac{\kappa_a + \kappa_b}{L+1} j_L(qr) [P_a Q_b + Q_a P_b] \\ \langle a \parallel \mathbb{T}^{(\mathbb{M}, \text{electric})}(\omega) \parallel b \rangle &= \langle \kappa_a \parallel \mathbb{C}^{(L)} \parallel \kappa_b \rangle \int_0^\infty dr \left\{ -\frac{\kappa_a - \kappa_b}{L+1} \left[ j'_L(qr) + \frac{j_L(qr)}{qr} \right] [P_a Q_b + Q_a P_b] + L \frac{j_L(qr)}{qr} [P_a Q_b - Q_a P_b] \right\}.\end{aligned}$$

➤ **Length gauge:** While the reduced multipole-transition matrix elements are the same in length gauge, Johnson (2007, section 6.3) derives the reduced multipole-transition matrix elements in length gauge as:

$$\begin{aligned}\langle a \parallel \mathbb{T}^{(\mathbb{M}, \text{electric})}(\omega) \parallel b \rangle \\ = \langle \kappa_a \parallel \mathbb{C}^{(L)} \parallel \kappa_b \rangle \int_0^\infty dr \left\{ j_L(qr) [P_a P_b + Q_a Q_b] + j_{L+1}(qr) \left[ \frac{\kappa_a - \kappa_b}{L+1} [P_a Q_b + Q_a P_b] + [P_a Q_b - Q_a P_b] \right] \right\}.\end{aligned}$$

### Johnson's frequency-dependent multipole-moment operators:

➤ **Multipole-moment matrix elements:** Following Johnson (2007), the **reduced multipole-moment matrix elements** can be calculate for the reduced multipole-transition matrix elements

$$\langle a \parallel \mathbb{Q}^{(\mathbb{M})}(\omega) \parallel b \rangle = \frac{(2L+1)!!}{q^L} \langle a \parallel \mathbb{T}^{(\mathbb{M})}(\omega) \parallel b \rangle.$$

### 5.3.c. Many-electron (reduced) multipole emission and absorption amplitudes

#### JAC's (standard) multipole amplitudes for photon absorption and emission:

- **Multipole (absorption) amplitude**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}, \lambda) \rightarrow |\alpha_f \mathbb{J}_f\rangle$ : For the absorption of a photon with energy  $\omega$ , well-defined multipolarity (angular momentum)  $L$  and helicity  $\lambda = \pm 1$ , we always use the notation

$$\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{absorption})}(\omega) || \alpha_i \mathbb{J}_i \rangle.$$

- **Photon emission:** from an atom or ion  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega(\mathbb{M})$ .
- Care has to be taken about the many-electron multipole amplitudes which appear in many expressions. While we need formally to distinguish between the absorption  $a_L^\lambda$  and emission operators  $a_L^{\lambda+}$  operators, **all (one- and many-electron) multipole-transition matrix elements are always evaluated in absorption.**
- For any photon emission process, this would then require to 'interchange' the sequence *final-state* — *operator* — *initial-state* explicitly. This is a (very) high price however in such a large software project, since such an interchange affects the intuitive description of many processes in terms of initial-intermediate-final levels as well as still possibly other subsequent (final) states/levels.

## 5.4. Electromagnetic light pulses

### 5.4.a. High-intensity pulses

#### Matter in intense fields:

- The exposure of atoms and matter to high-intensity laser fields is known to give rise to **high-harmonic generation, above-threshold ionization and well as laser-induced dissociation and plasma formation**, and which are all fundamentally different from processes in the weak-field regime.
- These phenomena are often outside of what is described by (standard) atomic-structure methods since the external field, that acts upon the electrons in typical strong-field experiments, is then comparable to the Coulomb potential of the nucleus.
- **Pump-probe experiments:** In these experiments, two short pulses are typically required. While the pump pulse starts the reaction, the probe pulse investigates the state of the system after a defined time delay. These measurements is repeated several times with increasing time delays in order to finally obtain a **molecular movie**.
- If the level structure of the atoms is not affected by the (moderately intense) laser pulses, the time-dependent density matrix may allow to model the (time-dependent) level occupation and coherences of an atoms and, eventually, all the photoexcitation and ionization processes.
- **Two-color absorption in strong laser fields:** The simultaneous absorption of a single high-frequency photon in a strong optical laser field generally leads to equally spaced sideband peaks in the photoelectron spectra due to the (additional) absorption or emission of several laser photons. This (XUV + IR) two-color absorption has been first observed in high-order harmonic generation by overlapping high harmonics with the fundamental laser frequency. With a femtosecond XUV pulse from a FEL, the two-color absorption in strong laser fields can be explored without the contributions from neighboured harmonics (Gramajo *et al.*, 2017).
- **Two-color absorption in strong laser fields:** Two different interaction regimes can be distinguished for the interaction of atoms with a combined and overlapping XUV and IR pulses owing to their relative pulse duration: (i) If the XUV pulse duration  $\tau^{(\text{XUV})} \gtrsim \tau^{(\text{IR})}$  is longer than the IR pulse, the intensity of the sideband peaks in the photoelectron spectrum directly reflect the intensity of the IR laser; (ii) for  $\tau^{(\text{XUV})} \ll \tau^{(\text{IR})}$ , in contrast, the photoelectron spectrum acts as as *streak camera* and reflects the shape and duration of an IR laser pulse. Moreover, variations of the polarization state of the XUV and/or IR laser fields gives generally rise to **dichroic effects in the photoelectron spectrum** (Gramajo *et al.*, 2017).

- **Normalized vector potential  $a_o$ :** For a time-harmonic light field with the electric-field amplitude  $\mathcal{E}_o$  and frequency  $\omega$ , the (frequency-) normalized amplitude of the vector potential can be expressed by the amplitude

$$a_o = \frac{e \mathcal{E}_o}{m \omega c} = 0.85 \times \lambda [\mu\text{m}] \times \sqrt{I [\times 10^{18} \text{ W cm}^{-2}]}; \quad I \propto a_o^2 \propto \mathcal{E}_o^2$$

For  $a_o \approx 1$ , the field is strong enough to accelerate electrons to relativistic velocity and then requires to account for both, the electric and magnetic fields.

### 5.4.b. Pulse shapes and optical cycles

#### Pulse shaping in physics and science:

- **Pulse shaping is frequently used in physics, science and technology.** Pulse shaping generally refers to the the process of changing the waveform of a (transmitted) pulse, for instance, in order to make a transmitted signal better suited for a particular communication channel. In telecommunication, for example, pulse shaping is essential in order to ensure that the signal fit to a given frequency band.
- In femtosecond physics and chemistry, pulse shaping describes a technology for generating nearly arbitrary pulses with user defined, ultrafast optical waveforms, and by controlling its phase, amplitude, and polarization. Here, the most widely applied technique is **Fourier transform pulse shaping**.

#### Frequently applied pulse shapes for time-dependent atomic computations:

- In pump- and/or pump-probe experiments, all (symmetric) light pulses are typically defined in terms of a **central frequency  $\omega$  and a (delay) time  $T_d$**  for the arrival of the pulse center with regard to same reference time  $t_0 = 0$ . Moreover, the shape function is always normalized to  $\max[f_s(t)] = \max[f(t)/f_o] = 1$  and, hence, the **intensity of the em field must be captured properly by the constant  $f_o$** .
- In JAC, the following (symmetric) shapes of the em pulses have been pre-defined: "sin^2", "sin^2: plateau", "sin^2: cycles" and "gaussian" facilitate the description of experimentally specified pulses. Further pulses shapes might be added if the need arises from the side of experiment.
- It is important to ensure that the pulse-shape function  $f_s(t)$  (envelope) just contains an **integer number of optical cycles**. Therefore, one often starts with an  $\sin^2$  envelope. For example, an envelope function  $\sin^2 10T$  pulse refers to a pulse with 10 optical cycles.

## 5. Atomic interactions with the radiation field

- **Laser pulse:** In time-resolved computations, the laser-atom interaction can be described either by a **smooth or a square pulse with envelope** (Gharibnejab *et al.*, (2020))

$$\mathcal{E}(t) = \begin{cases} \mathcal{E}_o \sin^2\left(\frac{\pi t}{T}\right) \mathbf{e}_z & 0 \leq t < T \\ 0 & \text{otherwise} \end{cases}, \quad \mathcal{E}(t) = \begin{cases} \mathcal{E}_o \mathbf{e}_z & 0 \leq t < T \\ 0 & \text{otherwise} \end{cases}$$

- **Vector potential of laser pulses in velocity gauges:** For a smooth or square pulse and  $\phi^{(\text{CEP})} = 0$ , the vector potential in the interval  $0 \leq t < T$  is (Gharibnejab *et al.*, 2020)

$$A(t) = c\mathcal{E}_o \left( \frac{\sin^2(a^+ t/2)}{2a^+} - \frac{\sin^2(a^- t/2)}{2a^-} - \frac{\sin^2(\omega t/2)}{\omega} \right), \quad a^+ = \frac{2\pi}{T} + \omega, \quad a^- = \frac{2\pi}{T} - \omega \quad \text{smooth pulse}$$

$$A(t) = -c \int_0^t d\tau \mathcal{E}(\tau) = -2c \mathcal{E}_o \frac{\sin^2(\omega t/2)}{\omega} \quad \text{square pulse}$$

- In time-dependent studies, various findings about the relative timing and the convergence of numerical results with regard to the step size are independent of the particular type of the laser pulse, i.e. are similar for smooth and square pulse.
- **Length versus velocity gauge:** In length gauge, the interaction with the external electro-magnetic field is local and gives rise to a straightforward time evolution due to the given Hamiltonian. In the velocity gauge, in contrast, the Hamiltonian is hermitian and the interaction is *non-local*. In realistic problems, therefore, the choice of the gauge can make significant differences in dependence of the given wavelength. This dependence is also a direct consequence which (high) angular momenta are relevant for the coupling of the radiation field to the electrons.

### 5.4.c. Maximum pulse intensity

#### Vector potential:

- **Amplitude of the vector potential:** This amplitude need to be derived from the (maximum) intensity of a laser pulses that is typically given in  $\text{W}/\text{cm}^2$ . In general, this relation between intensity and amplitude is non-trivial since the relationship between intensity and the electric field depends also slightly on the polarization of the pulse. A simple relation only occurs for a linearly-polarized laser beam.

- **Average intensity of a pulse:** If only the average intensity is given, the conversion factor depends also on the particular pulse-shape function. In practice, however, experimentalists rarely know the intensity accurately and, hence, a simplified normalization procedure can normally be used.
- **Vector potential of a single pulse:** The interaction of the electrons with the electric field of the incident pulse of frequency  $\omega$ , duration  $T$ , carrier envelope phase  $\phi$  and with linear polarization along  $\mathbf{e}_p$  is often described in terms of the vector potential

$$\mathbf{A}(t) = A_o \sin^2\left(\frac{\pi t}{T}\right) \sin(\omega t + \phi) \mathbf{e}_p, \quad A_o = \frac{1}{\omega} \sqrt{\frac{I}{I_o}},$$

and where  $I_o = 3.5 \cdot 10^{16} \text{ W/cm}^2$ .

### Intensity and pulse geometry:

- The atomic unit of electric field is  $m_e^2 e^5 / \hbar^4 = 5.1422 \cdot 10^9 \text{ V/cm}$ . From this we have:  $E_0 [a.u.] = 5.34 \cdot 10^{-9} \sqrt{I [W/cm^2]}$ .

### 5.4.d. Bichromatic laser fields

#### Bichromatic laser fields:

- **Bichromatic laser fields:** Of some special interests in light-atom interaction studies are fields with two components of commensurate frequencies; for instance, the fundamental component  $\omega$  and one of its low harmonics  $2\omega$  or  $3\omega$ . Moreover, these two components are in general out of phase by some angle  $\phi$ .
- **Linearly-polarized bichromatic fields:** For such a field, the electric field can be written in a quite general form as

$$E(t) = F(t) \left[ \cos(\omega t + \phi_1^{(\text{cep})}) + \eta \cos(2\omega t + \phi_2^{(\text{cep})}) \right]$$

with frequencies  $\omega$  of the fundamental radiation and  $2\omega$  due to the second harmonic. Here, the same envelope function  $F(t)$  is applied for both, the fundamental and the second harmonic, while the ratio of the corresponding amplitudes is specified by the real parameter  $\eta$  ( $\eta > 0$ ). The carrier-envelope phases (CEP) are here denoted by  $\phi_1^{(\text{cep})}$  and  $\phi_2^{(\text{cep})}$ , respectively.

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- **Time-dependent electric field in two-color experiments:** In two-color experiments, the field is often approximated by (DiFraia *et al.*, 2019)

$$\mathcal{E}(t) = \sqrt{I_\omega(t)} \cos \omega t + \sqrt{I_{2\omega}(t)} \cos(2\omega t - \phi), \quad \mathcal{E}(t) = \mathcal{E}(t) \mathbf{e}_z,$$

and where  $I_\omega(t)$ ,  $I_{2\omega}(t)$  are the envelopes of the two pulses and  $\phi$  the relative phase between the  $\omega - 2\omega$  pulses. In this definition, the larger  $\phi$  as more the  $2\omega$  pulse is delayed.

## 5.5. Elements from modern optics

### Singular optics:

- **Singular optics:** This field of modern optics makes use of wavefront dislocations and phase singularities.
- **Singular optics:** The subject of singular optics are light fields with an intricate knot structure in their field line, fields with optical vortices and (so-called) C-lines as well as light fields with spirals, umbilics, ribbons and Möbius strips in their polarization. These light fields give rise to many different phenomena if they are coupled with space-dependent birefringent elements.



## 6. Atomic amplitudes

### 6.1. In JAC implemented amplitudes

#### 6.1.a. Dipole amplitudes (MultipoleMoment)

##### Amplitude, notations & application:

- **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{D} \parallel \alpha_i \mathbb{J}_i \rangle = \langle \alpha_f \mathbb{J}_f \parallel \sum_i \mathbf{r}_i \parallel \alpha_i \mathbb{J}_i \rangle$  for  $P_f \neq P_i$
- Note that the full dipole operator is often defined by:  $\mathbb{D}' = -|e| \mathbb{D}$ .
- Using JAC: Call `MultipoleMoment.dipoleAmplitude(level_f::Level, level_i::Level)` or `(level_f::Level, level_i::Level; display=true)`, if the value of the amplitude needs to be printed to screen.

#### 6.1.b. Electro-magnetic multipole transition amplitudes (MultipoleMoment, Radiative)

##### Amplitude, notations & application:

- **Formal quantum notation:**

$$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{emission})}(\omega) \parallel \alpha_i \mathbb{J}_i \rangle = \left\langle \alpha_i \mathbb{J}_i \left\| \sum_{k=1}^N \boldsymbol{\alpha}_k a_{k,L}^p \right\| \alpha_f \mathbb{J}_f \right\rangle^* \equiv \langle \alpha_i \mathbb{J}_i \parallel \mathbb{O}^{(\mathbb{M}, \text{absorption})}(\omega) \parallel \alpha_f \mathbb{J}_f \rangle^*$$

$$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{T}^{(\mathbb{M}, \text{absorption})}(\omega) \parallel \alpha_i \mathbb{J}_i \rangle$$

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which retains the **right order of the initial and final levels with regard to absorption or emission** and which can be obtained from `Jac.Radiative.amplitude()`; cf. section 5.3.c.

- Using JAC: Call `Radiative.amplitude("absorption", Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level)` or `("absorption", Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level; display=true)`, if the value of the amplitude needs to be printed to screen.
- Using JAC: Call `MultipoleMoment.transitionAmplitude(Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level)` or `(Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level; display=true)`, if the value of the amplitude needs to be printed to screen.

### Further remarks:

- A multipole  $\mathbb{M} \equiv (L, p) \equiv (L, \text{electric/magnetic}) = E1, M1, E2, \dots$  hereby contains all information about its multipolarity (angular momentum)  $L$  and type *magnetic* ( $p = 0$ ) or *electric* ( $p = 1$ ), respectively.
- In the module **Radiative**, the multipole-transition amplitudes can be calculated in one of the gauge = {Coulomb, Babushkin, Magnetic} as appropriate for electric- and magnetic-multipole transitions.
- **Johnson's multipole-transition operators:** Following Johnson (2007), the electron-photon interaction with the multipole fields ( $\mathbb{M}$ ) can be expressed in terms of a dimensionless **multipole-transition operator**  $\mathbb{T}_M^{(\mathbb{M})}(\omega) = \sum_j \mathbb{t}_M^{(\mathbb{M})}(\mathbf{r}_j; \omega)$ , an irreducible tensor operator, whose reduced (single-electron) matrix elements are given in Section 5.3.b. The amplitudes to these operators always describe the absorption of a photon with a given multipolarity.
- Johnson's (2007) multipole-transition amplitudes can be calculated in one of the gauge = {Velocity, Length, Magnetic} as appropriate for electric- and magnetic-multipole transitions.

### 6.1.c. Electro-magnetic multipole-moment amplitudes (MultipoleMoment)

#### Amplitude, notations & application:

- **Formal quantum notation:**

$$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{Q}^{(\mathbb{M})}(\omega) \parallel \alpha_i \mathbb{J}_i \rangle$$

- Using JAC: Call `MultipoleMoment.amplitude(Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level)` or `(Mp::Multipole, gauge::EmGauge, omega::Float64, level_f::Level, level_i::Level; display=true)`, if the value of the amplitude needs to be printed to screen.

### Further remarks:

- **Johnson's multipole-moment operator:** Johnson (2007) also defines a **frequency-dependent (irreducible tensor) multipole-moment operator**

$$\mathbb{Q}_M^{(\mathbb{M})}(\omega) = \sum_j \mathbb{Q}_M^{(\mathbb{M})}(\mathbf{r}_j; \omega) \equiv \frac{(2L+1)!!}{(\omega/c)^L} \sum_j \mathbb{t}_M^{(\mathbb{M})}(\mathbf{r}_j; \omega)$$

- These amplitudes are calculated by a call to (Johnson's) multipole-transition amplitudes from above [cf. section 6.1.b] but by taking the frequency-dependence into account.
- Electric multipole-moment amplitudes can be calculated in one of the gauge = {**Velocity**, **Length**, **Magnetic**} as appropriate for electric- and magnetic-multipole transitions.

### 6.1.d. Momentum transfer amplitudes (FormFactor)

#### Amplitude, notations & application:

- **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f \parallel \sum_j \exp(i \mathbf{q} \cdot \mathbf{r}_j) \parallel \alpha_i \mathbb{J}_i \rangle = \text{selection rules}$
- Using JAC: Call `FormFactor.amplitude(level_f::Level, level_i::Level, ...)` or `(level_f::Level, level_i::Level, ...; display=true)`, if the value of the amplitude needs to be printed to screen.

### Further remarks:

- The (single-electron) **momentum transfer amplitude** help describe inelastic scattering processs and is closely related also to the (so-called) **generalized oscillator strength**.

## 6. Atomic amplitudes

- The (one-electron) momentum-transfer operator  $\mathbb{T}^{(1)}(\mathbf{q}) = \sum_{j=1}^N \exp(i \mathbf{q} \cdot \mathbf{r}_j)$  can be utilized in order to express the standard form factor for an atom in a given sublevel  $|\alpha \mathbb{J} M\rangle$  in terms of an (many-electron) expectation value; cf. 7.1.d.

## 6.2. In JAC partly-implemented amplitudes

### 6.2.a. Parity non-conservation amplitudes (ParityNonConservation)

#### Amplitude, notations & application:

- **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f || \mathbb{H}^{(\text{weak}-\text{charge})} || \alpha_i \mathbb{J}_i \rangle$
- **Using JAC:** Call `ParityNonConservation.weakChargeAmplitude(level_f::Level, level_i::Level, model::Nuclear.Model)` or `(level_f::Level, level_i::Level, model::Nuclear.Model; display=true)`, if the value of the amplitude needs to be printed to screen.

#### Further remarks:

- Parity non-conservation (PNC) effects arises in atoms mainly because of the exchange of  $Z^0$ -bosons between atomic electrons and the nucleus. Various observables due to this parity non-conserving interactions can be described in terms of a **nuclear-spin independent Hamiltonian**  $\mathbb{H}^{(\text{weak}-\text{charge})}$ , an effective single-electron operator, if non-relativistic nucleons can be assumed, cf. section 3.9.b.
- Especially, if the **proton and neutron densities coincide**,  $\rho_p = \rho_n = \rho$ , the general nuclear-spin independent Hamiltonian simplifies and can be described in terms of a single nuclear- weak charge  $Q_W$ ,

$$\mathbb{H}^{(\text{weak}-\text{charge})} = -\frac{G}{2\sqrt{2}} Q_W \sum_j \gamma_{5,j} \rho(r_j),$$

where  $G = 2.22 \cdot 10^{-14}$  a.u. is the Fermi constant,  $\rho(r)$  is the normalized nuclear density with  $\int dV \rho(\mathbf{r}) = 1$ , and  $Q_W \approx -N + Z (1 - 4 \sin^2 \theta_W)$  is the nuclear weak charge with  $\theta_W$  being the Weinberg angle.

### 6.2.b. Schiff-moment amplitudes (ParityNonConservation)

#### Amplitude, notations & application:

- **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{Schiff-moment})} \parallel \alpha_i \mathbb{J}_i \rangle = \langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{Schiff-moment})} \parallel \alpha_i \mathbb{J}_i \rangle \delta_{J_f, J_i} \quad P_f \neq P_i$
- Using JAC: Call `ParityNonConservation.schiffMomentAmplitude(level_f::Level, level_i::Level, model::Nuclear.Model)` or `(level_f::Level, level_i::Level, model::Nuclear.Model; display=true)`, if the value of the amplitude needs to be printed to screen.

#### Further remarks:

- **Nuclear electric-dipole (Schiff) moments:** If  $\mathbf{S}$  is the P-odd and T-odd nuclear Schiff moment, the associated P-odd and T-odd Hamiltonian is given by (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{Schiff-moment})} = -e \phi^{(\text{Schiff-moment})} = -4\pi e \mathbf{S} \cdot \nabla \delta(r) = -\frac{3 S^{(\text{SM})} (\mathbf{I}/I) \cdot \mathbf{r}}{R} \rho(r)$$

where  $S^{(\text{SM})} (\mathbf{I}/I)$  is the Schiff-moment vector, i.e. the product of the coupling constant  $S^{(\text{SM})}$  and the nuclear spin  $\mathbf{I}$ , and  $R = \int_0^\infty dr r^4 \rho(r)$ . Moreover,  $\phi^{(\text{Schiff-moment})}$  is the electrostatic potential of the nucleus corresponding to a P-odd and T-odd charge distribution; cf. section 3.9.c.

## 6.3. Further amplitudes, not yet considered in JAC

### 6.3.a. Anapole-moment amplitudes (ParityNonConservation)

#### Amplitude, notations & application:

➤ Formal quantum notation:  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{anapole-moment})} \parallel \alpha_i \mathbb{J}_i \rangle$

#### Further remarks:

- A **P-odd, T-even anapole moment** of the nucleus was first introduced by Zel'dovich and arises due to the presence of a parity-violating weak interaction between nucleons, cf. section 3.9.b. The anapole moment is directed along the nuclear spin  $\mathbf{I}$ , gives typically the **dominant nuclear-spin dependent electron-nucleus interaction** and manifests itself in terms of a slightly modified electro-magnetic interaction between the nucleus and the atomic electrons.
- **Hamiltonian for the interaction of the electrons with the nuclear anapole moment:** This Hamiltonian has the form (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{anapole-moment})} = \frac{G}{\sqrt{2}} (I + 1/2) (-1)^{I+1/2-\ell_N} \kappa_{\text{AM}} \sum_j \frac{\mathbf{I} \cdot \boldsymbol{\alpha}_j}{I(I+1)} \rho(r_j),$$

where  $G = 2.22 \cdot 10^{-14}$  a.u. is the Fermi constant,  $I$  is the nuclear spin,  $\ell_N$  the orbital angular momentum of the outermost nucleon and  $\kappa_{\text{AM}}$  is a dimensionless coupling constants for ...

### 6.3.b. Scalar-pseudo-scalar amplitudes

#### Amplitude, notations & application:

➤ Formal quantum notation:  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{scalar-pseudo-scalar})} \parallel \alpha_i \mathbb{J}_i \rangle$

### Further remarks:

- **Hamiltonian for the P-odd, T-odd scalar-pseudo-scalar interaction:** In coordinate representation, this Hamiltonian can be written as (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{scalar-pseudo-scalar})} = -\frac{G}{\sqrt{2}} \frac{1}{2m_p c} C_s \sum_j \left[ \gamma_0 \frac{d\rho(r)}{dr} \right]_j$$

where  $G$  is the Fermi constant,  $m_p$  is the nucleon mass,  $C_s$  is a (isotope and) nuclear-state dependent constant, and where  $\left[ \gamma_0 \frac{d\rho(r)}{dr} \right]$  is a scalar term that arises from the scalar product of the  $\nabla$ -vector with an particularly averaged spin-vector of the nucleus.

### 6.3.c. Tensor-pseudo-tensor amplitudes

#### Amplitude, notations & application:

- **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{tensor-pseudo-tensor})} \parallel \alpha_i \mathbb{J}_i \rangle$

### Further remarks:

- **Hamiltonian for the P-odd, T-odd tensor-pseudo-tensor interaction:** In coordinate representation, this Hamiltonian can be written as (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{tensor-pseudo-tensor})} = i \sqrt{2} G C_t \sum_j [\gamma \rho(r)]_j$$

where  $G$  is the Fermi constant,  $C_t$  is a (isotope and) nuclear-state dependent constant, and where  $[\gamma \rho(r)]$  is a scalar term that arises from the scalar product of the  $\gamma$ -vector with an averaged spin-vector of the nucleus.

- **Total P-odd, T-odd electron-nucleus interaction Hamiltonian:**  $\mathbb{H}^{(\text{P-odd, T-odd electron-nucleus})} = \mathbb{H}^{(\text{tensor-pseudo-tensor})} + \mathbb{H}^{(\text{tensor-pseudo-tensor})}$

### 6.3.d. Nuclear magnetic-quadrupole-moment amplitudes due to internal $B$ -field

#### Amplitude, notations & application:

➤ **Formal quantum notation:**  $\langle \alpha_f \mathbb{J}_f \parallel \mathbb{H}^{(\text{nuclear-MQM})} \parallel \alpha_i \mathbb{J}_i \rangle$

#### Further remarks:

- This interaction (Hamiltonian) arise from the interaction of the electron EDM  $d_e$  with the electro-magnetic fields of the nucleus as seen by the electron. If the treatment is restricted to second order, only the interaction of the electron EDM with the magnetic field  $\mathbf{B}$ , which is created by the nuclear magnetic-dipole moment, need to be taken into account.
- **Nuclear-MQM Hamiltonian:** In coordinate representation, this Hamiltonian can be written as (Dzuba *et al.*, 2009)

$$\mathbb{H}^{(\text{nuclear-MQM})} = -i d_e \boldsymbol{\gamma} \cdot \mathbf{B} = -i d_e \sum_j \boldsymbol{\gamma}_j \cdot \left[ \nabla_j \times \frac{\mathbf{M} \times \mathbf{r}_j}{r_{>,j}^3} + \dots \right]$$



## 6.4. Composed many-electron amplitudes, not yet considered in JAC

### 6.4.a. Parity-violating (non-diagonal, second-order) amplitudes

#### Amplitude, notations & application:

- **Parity violation:** The (effective) parity-violating interaction is caused by the exchange of  $Z_o$  bosons between the atomic electrons and the nucleus. The parity-violating interaction typically results in non-vanishing off-diagonal electric-dipole matrix element between two atomic states of the same parity; cf. section 3.9.b.

### 6.4.b. Charge-parity-violating (diagonal, second-order) amplitudes

#### Amplitude, notations & application:

- **Charge-parity violation:** An intrinsic electron electric dipole moment  $d_e$  leads to CP-violation in atoms and also induces an **atomic electric dipole moment**. cf. section 3.9.d.

### 6.4.c. Electric-dipole moment enhancement factor

#### Amplitude, notations & application:

- An intrinsic electric-dipole moment (EDM) of the electron can enhanced the EDM of the atom. In heavy atoms, in particular, an induced atomic EDM can be strongly enhanced, when compared to the electron EDM itself.
- A typical goal is to find the atomic EDM  $d_{\text{atom}} = |\mathbf{d}_{\text{atom}}| \equiv d_{\text{atom}} |\mathbf{F}/F|$ , where  $\mathbf{F} = \mathbf{I} + \mathbf{J}$  is the total angular momentum of an atomic (hyperfine) level.
- The value of the atomic EDM, compared to the electron EDM, is expressed by means of an enhancement factor  $K = d_{\text{atom}}/d_e$ , and which increases with nuclear charge  $Z$  faster than  $Z^3$ .



## 7. Atomic properties

### 7.1. In JAC implemented level properties

#### 7.1.a. Transition probabilities for a single multiplet (Einstein)

##### Properties, notations & application:

- **Photon emission:** from an atom or ion  $A^* \longrightarrow A^{(*)} + \hbar\omega$
- **Formal quantum notation:**  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega$
- Using JAC: Perform an `Atomic.Computation(..., properties=[EinsteinX, ...], configs=[...], einsteinSettings=Einstein.Settings(...), ...)` or call directly functions from the module `Einstein`.
- In the JAC program, the transition probabilities, oscillator strength (in emission) and radiative lifetimes are calculated and tabulated by default for all selected transitions from a given single multiplet (i.e. list of configurations). Apart from the multipoles, the user can also specify an overall shift in the photon energies as well as a minimum and maximum transition energy, for which transitions are taken into account.
- In the `Einstein` module, the emission (transition) amplitudes  $\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{emission})} || \alpha_i \mathbb{J}_i \rangle$  or absorption amplitudes  $\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{absorption})} || \alpha_i \mathbb{J}_i \rangle$  can be obtained directly by call of the function `Jac.Einstein.amplitude()`.

##### Further remarks:

- Einstein  $A$  and  $B$  coefficients and oscillator strength for levels  $(\alpha \mathbb{J})$  from a single multiplet are frequently needed for various applications and in different contexts.

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- Although these coefficients are *no* (single) level property, the **Einstein** module still supports the computation of these coefficients for **levels from a single multiplet**, and which is generated by a single CSF basis.
- Although the **Einstein** module does not allow to include relaxation effects, this module helps obtain either a quick estimate of the Einstein coefficients between levels from just a few configurations or to deal with cascade computations.
- **JAC's standard multipole amplitudes for photon emission:** Although **all (one- and many-electron) matrix elements are always evaluated in absorption** within the JAC toolbox, we keep the intuitive description of the matrix elements as *final-state – operator – initial-state*, cf. section 5.3.c.

### 7.1.b. Hyperfine parameters and hyperfine representations (Hfs)

#### Properties, notations & application:

- **Hyperfine splitting** of an atomic level into hyperfine (sub-) levels:  $|\alpha\mathbb{J}\rangle \longrightarrow |\alpha(J)\mathbb{F}\rangle, \quad F = |I - J|, \dots, I + J - 1, I + J$ .
- **Formal quantum notation:**  $|\alpha\mathbb{J}\rangle \longrightarrow |\alpha\mathbb{F}\rangle \equiv |(I, \alpha'\mathbb{J})\mathbb{F}\rangle \equiv |\alpha(I\mathbb{J})\mathbb{F}\rangle \equiv |\alpha(IJP)\mathbb{F}\rangle$  or  $|\alpha\mathbb{J}M_J\rangle \longrightarrow |\alpha\mathbb{F}M\rangle \equiv |(I, \alpha'\mathbb{J})\mathbb{F}M\rangle \equiv |\alpha(I\mathbb{J})\mathbb{F}M\rangle \equiv |\alpha(IJP)\mathbb{F}M\rangle$ .
- Using JAC: Perform an `Atomic.Computation(.., properties=[HFS, ..], configs=[..], hfsSettings=Hfs.Settings(..), ..)` or call directly functions from the module `Hfs`. The Boolean values `calcT1` and `calcT2` in `Hfs.Settings` determine which parts of the hyperfine Hamiltonian are taken into account into the computations.
- In the JAC program, the hyperfine *A* and *B* coefficients as well as the (electric) hyperfine amplitudes  $\langle \alpha\mathbb{J} || \mathbb{T}^{(1)} || \alpha\mathbb{J} \rangle, \langle \alpha\mathbb{J} || \mathbb{T}^{(2)} || \alpha\mathbb{J} \rangle$  are calculated and tabulated by default for all selected levels together with the energy shifts  $\Delta E_F$  of the hyperfine levels with regard to the (electronic) level energy  $E_{\alpha\mathbb{J}}$ .
- In JAC, the hyperfine amplitudes  $\langle \beta_r\mathbb{J}_r || \mathbb{T}^{(1)} || \beta_s\mathbb{J}_s \rangle$  and  $\langle \beta_r\mathbb{J}_r || \mathbb{T}^{(2)} || \beta_s\mathbb{J}_s \rangle$  can be obtained from the function `Jac.Hfs.amplitude()`.
- In JAC, moreover, an explicit representation of a hyperfine multiplet is obtained by diagonalizing the Hamiltonian  $\mathbb{H} = \mathbb{H}^{(\text{DCB})} + \mathbb{H}^{(\text{hfs})}$  within the atomic hyperfine *IJF*-coupled basis if `calcIJFexpansion=true` is set in `Hfs.Settings`.
- In JAC, all the (hyperfine) level energies  $E_{\alpha\mathbb{F}}$  and the energies relative to the lowest (hyperfine) level are tabulated if `printDeltaEF=true` in `Hfs.Settings`.

- In JAC, all (diagonal and nondiagonal) hyperfine amplitudes are calculated and tabulated explicitly if `calcNondiagonal=true` in `Hfs.Settings`.

### Further remarks:

- For a nucleus with *non-zero* spin  $I > 0$ , a hyperfine splitting of (all) atomic levels generally occurs since each atomic electron also interacts with the electric and magnetic (multipole) fields of the nucleus. This is sometimes described also as the interaction of the magnetic moments of the electrons and nucleus.
- In atomic physics, this interaction is better known as ‘*hyperfine interaction*’ whose two dominant contributions arise from the nuclear magnetic-dipole field  $\mathbf{A} = \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3}$  and the electric-quadrupole field  $\Phi(r) = \sum_{ij} \frac{r_i r_j}{2r^5} Q_{ij}$ , respectively. In these expressions,  $\boldsymbol{\mu}$  is the nuclear magnetic moment operator and  $Q_{ij}$ ,  $i, j = 1..3$  are the Cartesian components of the nuclear quadrupole operator.
- Apart from the hyperfine parameters  $A(\alpha \mathbb{J})$  and  $B(\alpha \mathbb{J})$ , we also provide in JAC a *representation of the atomic hyperfine levels* that can be utilized, for instance, to compute *hyperfine quenched transitions probabilities*.

### Hyperfine interaction Hamiltonian:

- *Relativistic hyperfine interaction Hamiltonian:* For many-electron systems, this Hamiltonian can be written as

$$H^{(\text{hfs})} = \sum_K \mathbb{W}^{(K)} \cdot \mathbb{T}^{(K)}$$

where  $\mathbb{W}^{(K)}$  and  $\mathbb{T}^{(K)}$  represent the *spherical tensor operators of rank  $K$  that occur in the nucleonic and electronic sectors*, respectively.

- *Reduced nuclear matrix elements:* These matrix elements are determined geometrically by

$$\langle I \| \mathbb{W}^{(1)} \| I \rangle = \mu_I \sqrt{\frac{I+1}{I}}, \quad \langle I \| \mathbb{W}^{(2)} \| I \rangle = \frac{Q}{2} \sqrt{\frac{(I+1)(2I+3)}{I(2I-1)}},$$

while, in contrast, the corresponding *electronic amplitudes require detailed atomic structure calculations*.

- Values of nuclear magnetic dipole and electric quadrupole moments can be found in the compilation by Stone (2005).

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- **Electronic tensor operators:** For an  $N$ -electron atom or ion, these tensor operators are given by (Andersson and Jönsson, 2008)

$$\mathbb{T}^{(1)} = \sum_j^N \mathbb{t}^{(1)}(j) = \sum_j^N -i\sqrt{2}\alpha \frac{(\alpha_j \mathbb{C}^{(1)}(j))^{(1)}}{r_j^2} \quad \text{interaction with the magnetic – dipole field}$$

$$\mathbb{T}^{(2)} = \sum_j^N \mathbb{t}^{(2)}(j) = \sum_j^N -\frac{\mathbb{C}^{(2)}(j)}{r_j^3} \quad \text{interaction with the electric – quadrupole field,}$$

and where  $\alpha$  is the fine-structure constant,  $\alpha_j$  the vector of Dirac matrices of the  $j$ -th electron, and the  $\mathbb{C}^{(K)}$  are (normalized) spherical tensors as before.

- **Empirical hyperfine-interaction Hamiltonian:** From an empirical viewpoint, the hyperfine-interaction Hamiltonian can be parametrized in terms of the hyperfine constants  $A^{(\text{hfs})}$ ,  $B^{(\text{hfs})}$  as well as the total nuclear and electronic angular momenta as

$$\mathbb{H}^{(\text{hfs})} = \hbar A^{(\text{hfs})} \mathbf{I} \cdot \mathbf{J} + \hbar B^{(\text{hfs})} \frac{6(\mathbf{I} \cdot \mathbf{J})^2 + 3\mathbf{I} \cdot \mathbf{J} - 2\mathbf{I}^2 \mathbf{J}^2}{2I(2I-1)2J(2J-1)}.$$

Here, of course, the hyperfine constants  $A^{(\text{hfs})}$ ,  $B^{(\text{hfs})}$  depend on the atomic level of interest. Moreover, this empirical Hamiltonian neglects the coupling of hyperfine levels from different (fine-structure) levels with some total angular momenta  $\mathbf{J}$ .

- **Diagonal matrix elements of  $\mathbb{H}^{(\text{hfs})}$  in a hyperfine-coupled basis:** Obviously, the empirical Hamiltonian  $\mathbb{H}^{(\text{hfs})}$  is diagonal with regard to  $F$ ,  $M_f$  in a hyperfine-coupled basis  $\{|\alpha(IJ)FM_F\rangle\}$ , and these diagonal matrix elements are given by

$$\langle \alpha(IJ)FM_F | \mathbb{H}^{(\text{hfs})} | \alpha(IJ)FM_F \rangle = \frac{\hbar}{2} A^{(\text{hfs})} G + \hbar B^{(\text{hfs})} \frac{3/2 G(G+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}$$

$$G = F(F+1) - I(I+1) - J(J+1).$$

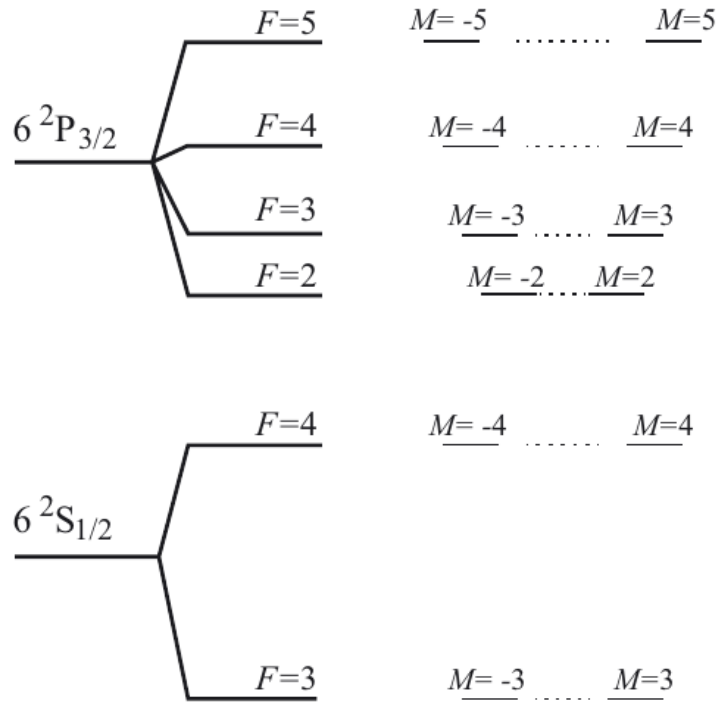


Figure 7.1.: Fine-structure and hyperfine-structure (energy) levels as associated with the  $6s\ 2S_{1/2} - 6p\ 2P_{3/2}$   $D_2$  line of atomic cesium; taken from Kien *et al.* (2013).

### Atomic (hyperfine) $IJF$ -coupled basis:

➤ This (geometrically fixed) basis is obtained by the standard coupling of the nuclear states  $|IM_I\rangle$  and the ASF  $|\alpha \mathbb{J}M_J\rangle$

$$|\alpha(I, J) \mathbb{F}M\rangle \equiv |(I, \alpha' \mathbb{J}) \mathbb{F}M\rangle = \sum_{M_I M_J} |IM_I\rangle |\alpha' \mathbb{J}M_J\rangle \langle IM_I, JM_J | \mathbb{F}M\rangle.$$

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- The atomic (hyperfine)  $IJF$ -coupled basis, also called the  $IJF$ -coupled ASF basis, is applied internally to represent all hyperfine levels, see below.

### Atomic hyperfine amplitudes and levels:

- **Atomic hyperfine levels:** For the combined system ‘nucleus+electrons’, the atomic hyperfine states (magnetic sub-levels) can be formed as linear combination

$$|\alpha \mathbb{F} M\rangle = \sum_{r=1} \tilde{c}_r(\alpha) |(I, \beta_r \mathbb{J}_r) \mathbb{F} M\rangle$$

of hyperfine (basis) states  $|(I, \beta_r \mathbb{J}_r) \mathbb{F} M\rangle$  of the same total angular momentum  $F$  and (the same electronic) parity  $P$ , and where  $\{\tilde{c}_r(\alpha)\}$  denotes the representation of these states in the **atomic hyperfine-coupled basis** (Johnson, 2010).

- Analogue as for the ASF  $|\alpha \mathbb{J}\rangle$  in the standard MCDF ansatz, the representation  $\{\tilde{c}_r(\alpha)\}$  of an atomic hyperfine state is obtained by diagonalizing the Hamiltonian  $\mathbb{H} = \mathbb{H}^{(\text{DFB})} + \mathbb{H}^{(\text{hfs})}$  of the combined system ‘nucleus+electrons’ in either the  $IJF$ -coupled CSF or ASF basis.
- In the  $IJF$ -coupled ASF basis, we can make use of  $\mathbb{H}^{(\text{DFB})} |(I, \beta_r \mathbb{J}_r) \mathbb{F} M\rangle = E(\beta_r \mathbb{J}_r) |(I, \beta_r \mathbb{J}_r) \mathbb{F} M\rangle \equiv E_{\beta_r \mathbb{J}_r} |(I, \beta_r \mathbb{J}_r) \mathbb{F} M\rangle$ .
- For the hyperfine part of the Hamiltonian, the (reduced) matrix elements can be written after some standard angular momentum algebra as

$$\begin{aligned} \langle (I, \beta_r \mathbb{J}_r) \mathbb{F} M | H^{(\text{hfs})} | (I, \beta_s \mathbb{J}_s) \mathbb{F}' M' \rangle &= \delta_{MM'} \langle (I, \beta_r \mathbb{J}_r) \mathbb{F} | H^{(\text{hfs})} | (I, \beta_s \mathbb{J}_s) \mathbb{F}' \rangle \\ &= \delta_{MM'} \delta_{\mathbb{F}\mathbb{F}'} (-1)^{I+J_r+F} \sum_K \begin{Bmatrix} I & J_r & F \\ J_s & I & K \end{Bmatrix} \langle \beta_r \mathbb{J}_r || \mathbb{T}^{(K)} || \beta_s \mathbb{J}_s \rangle \langle I || \mathbb{W}^{(K)} || I \rangle, \end{aligned}$$

with  $\delta_{\mathbb{F}\mathbb{F}'} = \delta_{PP'} \delta_{FF'}$ , and if all nuclear excitations are ignored right from the beginning.

- **Hyperfine amplitudes:** These amplitudes refer to the (reduced) electronic matrix elements  $\langle \beta_r \mathbb{J}_r || \mathbb{T}^{(K)} || \beta_s \mathbb{J}_s \rangle$ . In the JAC program, we compute the **hyperfine amplitudes for both, the magnetic-dipole and the electric-quadrupole operators** of the electron-nucleus interaction.
- These hyperfine amplitudes are utilized to set-up and diagonalize the Hamiltonian matrix within the **atomic  $IJF$ -coupled basis** for  $\mathbb{H} = \mathbb{H}^{(\text{DCB})} + \mathbb{H}^{(\text{hfs})}$  in order to determine the representation  $\{\tilde{c}_r(\alpha)\}$  of the atomic hyperfine states.



### Hyperfine energies and interaction constants:

- **Hyperfine interaction constants:** Usually the hyperfine splitting is considered independently for each atomic level  $(\alpha\mathbb{J})$  and without the need to specify all the hyperfine level energies  $E_{\alpha\mathbb{F}}$  explicitly. Instead, the energy splitting of an atomic level  $(\alpha\mathbb{J})$  into hyperfine levels  $(\alpha\mathbb{F})$  can be expressed conveniently in terms of the (hyperfine interaction) constants

$$A(\alpha\mathbb{J}) = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)}} \langle \alpha\mathbb{J} \| \mathbb{T}^{(1)} \| \alpha\mathbb{J} \rangle, \quad B(\alpha\mathbb{J}) = 2Q \sqrt{\frac{J(2J-1)}{(J+1)(2J+3)}} \langle \alpha\mathbb{J} \| \mathbb{T}^{(2)} \| \alpha\mathbb{J} \rangle$$

- **Hyperfine energy splitting:** With these constants, the hyperfine energy shifts with regard to the electronic level energy  $E(\alpha\mathbb{J})$  is given by

$$\Delta E_F = \frac{A(\alpha\mathbb{J}) C}{2} + B(\alpha\mathbb{J}) \frac{3/4 C(C+1) - I(I+1) J(J+1)}{2I(2I-1) J(2J-1)}, \quad C = F(F+1) - J(J+1) - I(I+1).$$

### 7.1.c. Isotope-shift parameters (IsotopeShift)

#### Properties, notations & application:

- **Isotope shift** of an atomic level for two isotopes  $A, A'$  with nuclear masses  $M < M'$ :  $E(\alpha\mathbb{J}; A) \longrightarrow E(\alpha\mathbb{J}; A')$ .
- **Formal quantum notation:**  $\Delta E(\alpha\mathbb{J}; A, A') / h = \frac{M' - M}{M M'} K^{(\text{MS})} + F \delta \langle r^2 \rangle$ .
- **Using JAC:** Perform an `Atomic.Computation(..., properties=[Isotope, ...], configs=[...], isotopeSettings=IsotopeShift.Settings(...), ...)` with `calcNMS=true`, `calcNMS=true` or `calcF=true` and/or call directly functions from the module `IsotopeShift` in order to include the various contribution of the recoil Hamiltonian.
- In JAC, we calculate and tabulate by default the (relativistic) mass-shift parameters  $K^{(\text{MS})}$ ,  $K^{(\text{NMS})}$ ,  $K^{(\text{SMS})}$  and the field-shift parameter  $F$  for all selected levels.

## Further remarks

- **Isotope shift of atomic transitions:** Similar to the level energies, the isotope shift of the observed transition (emission) energy  $E(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f, A) = E(\alpha_i \mathbb{J}_i, A) - E(\alpha_f \mathbb{J}_f, A)$  for two isotopes with masses  $A, A'$  can be readily parametrized by

$$\begin{aligned} \Delta E^{(\text{IS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') &= E(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A) - E(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A') \\ &= \Delta E^{(\text{IS})}(\alpha_i \mathbb{J}_i; A, A') - \Delta E^{(\text{IS})}(\alpha_f \mathbb{J}_f; A, A') = \Delta E^{(\text{MS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') + \Delta E^{(\text{FS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') \end{aligned}$$

This isotope shift is called **normal**, if the transition energy is larger for the heavier isotope,  $\Delta E^{(\text{IS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') > 0$  for  $A > A'$ , and this convention is usually made if isotope shifts are presented and discussed. However, not all the observed isotope shifts are ‘normal’ in this sense but also  $\Delta E^{(\text{IS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') < 0$  have been observed for selected atomic transitions.

- Owing to the conservation of the total momentum, the (total non-relativistic) mass shift is a sum of two parts, the (so-called) **normal mass shift (NMS)** and the **specific mass shift (SMS)**:

$$\mathbb{H}^{(\text{MS}, \text{nr})} = \mathbb{H}^{(\text{NMS}, \text{nr})} + \mathbb{H}^{(\text{SMS}, \text{nr})} = \frac{1}{2M} \sum_j \mathbf{p}_j^2 + \frac{1}{2M} \sum_{i \neq j} \mathbf{p}_i \cdot \mathbf{p}_j$$

While the normal mass shift operator is obviously a one-particle operator, the specific mass shift is a two-particle operator. The sum of these two parts is known also as the **total recoil operator within the nonrelativistic theory**.

- **Importance of different contributions to the isotope shift:** Different isotope-shift contributions dominate for different elements and charge states: While the mass-shift contribution is most relevant for low- $Z$  ions, heavy elements are dominated by the field-shift contributions due to the finite nuclear size.
- **Standard parametrization of the isotope (energy) shift of an atomic level ( $\alpha \mathbb{J}$ ) for isotope  $A$ :** The standard parametrization just distinguishes between the *mass shift* and *field shift* of any atomic level ( $\alpha \mathbb{J}$ ) due to the omitted recoil of the (overall) ion and changes in the nuclear (atomic) potential if additional neutrons are *added* to some reference isotope  $A_o$  with mass  $M_o$ :

$$\Delta E^{(\text{IS})}(A; \text{nuclear model}; \alpha \mathbb{J}) = \frac{m}{M} K(\text{nuclear model}; \alpha \mathbb{J}) + \frac{R}{[\text{fm}]} F(\text{nuclear model}; \alpha \mathbb{J}) \quad \Delta E^{(\text{IS})}(A_o) \equiv 0$$

Here  $R = \sqrt{\langle r^2 \rangle}$  is the root-mean-square nuclear radius as determined by different nuclear techniques and communicated within the literature. Since most isotope-shift computations are carried out in atomic units, one could re-normalize the root-mean-square radius to the Bohr radius  $a_o$ , although this may cause again confusion. Almost all nuclear radii are tabulated in Fermi instead. With this definition, the isotope-shift parameters are defined in energy units, in contrast to what is often used in laser spectroscopy.

### Relativistic recoil (Hamilton) operator:

- **Recoil Hamiltonian:** Within the lowest-order relativistic approximation ( $\sim v^2/c^2$ ) and in first order of  $m/M$  for a nucleus with mass  $M$ , the recoil corrections are given by means of the (recoil) Hamiltonian (Tupitsyn *et al.*, 2003):

$$\mathbb{H}^{(\text{recoil})}(M) = \frac{1}{2M} \sum_{ij} \left[ \mathbf{p}_i \cdot \mathbf{p}_j - \frac{\alpha Z}{r_i} \left( \boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_i) \mathbf{r}_i}{r_i^2} \right) \cdot \mathbf{p}_j \right]$$

- The expectation value of  $\mathbb{H}^{(\text{recoil})}(M)$  with regard to the relativistic wave function from  $\mathbb{H}^{(\text{DCB})}$  gives the **recoil correction to the energy of the atomic energy ( $\alpha\mathbb{J}$ ) in first order of  $m/M$** .
- **Decomposition of the relativistic recoil Hamiltonian:** Similar as in the non-relativistic theory, the (relativistic) recoil operator above can be written as (Tupitsyn *et al.*, 2003; Gaidamauskas *et al.*, 2011)

$$\begin{aligned} \mathbb{H}^{(\text{recoil})}(M) &= \mathbb{H}^{(\text{NMS, relativistic})} + \mathbb{H}^{(\text{SMS, relativistic})} \\ &= \frac{1}{2M} \sum_i \left[ \mathbf{p}_i^2 - \frac{\alpha Z}{r_i} \left( \boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_i) \mathbf{r}_i}{r_i^2} \right) \cdot \mathbf{p}_i \right] + \frac{1}{2M} \sum_{i \neq j} \left[ \mathbf{p}_i \cdot \mathbf{p}_j - \frac{\alpha Z}{r_i} \left( \boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_i) \mathbf{r}_i}{r_i^2} \right) \cdot \mathbf{p}_j \right] \\ &= \frac{1}{2M} \sum_i \left[ \mathbf{p}_i^2 - \frac{\alpha Z}{r_i} \boldsymbol{\alpha}_i \cdot \mathbf{p}_i - \frac{\alpha Z}{r_i} (\boldsymbol{\alpha}_i \cdot \mathbb{C}_i^{(1)}) \mathbb{C}_i^{(1)} \cdot \mathbf{p}_i \right] + \frac{1}{2M} \sum_{i \neq j} \left[ \mathbf{p}_i \cdot \mathbf{p}_j - \frac{\alpha Z}{r_i} \boldsymbol{\alpha}_i \cdot \mathbf{p}_j - \frac{\alpha Z}{r_i} (\boldsymbol{\alpha}_i \cdot \mathbb{C}_i^{(1)}) \mathbb{C}_i^{(1)} \cdot \mathbf{p}_j \right] \\ &= \mathbb{H}^{(\text{NMS})} + \mathbb{H}^{(\text{SMS, A})} + \mathbb{H}^{(\text{SMS, B})} + \mathbb{H}^{(\text{SMS, C})} \end{aligned}$$

- The relativistic correction to the recoil effect is typically strongly overestimated if the nonrelativistic recoil operator is applied just together with relativistic wave functions.

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- The full relativistic theory of the nuclear recoil effect can be formulated only within the framework of quantum electrodynamics. Such a theory was first formulated by Shabaev (1985), where the complete  $\alpha Z$ -dependence of the recoil corrections to an energy level ( $\alpha \mathbb{J}$ ) was derived in first order of  $m/M$ .

### Reduced one-electron matrix elements of the recoil (Hamilton) operator:

- **Recoil Hamiltonian:** While the normal mass-shift Hamiltonian is a one-particle operator, the specific mass-shift is a (symmetric) two-particle operator

$$\mathbb{H}^{(\text{NMS})} = \sum_j \mathbb{h}^{(\text{NMS})}(\mathbf{r}_j), \quad \mathbb{H}^{(\text{SMS}, k)} = \sum_{i \neq j} \mathbb{h}^{(\text{SMS}, k)}(\mathbf{r}_i, \mathbf{r}_j) = \sum_{i \neq j} g(r_i, k) g(r_j, k) \left( \mathbb{T}_i^{(1)} \cdot \mathbb{T}_j^{(1)} \right), \quad k = A, B, C$$

The particular tensorial structure of the two-particle specific mass-shift Hamiltonian ensures that the reduced (one-electron) matrix elements can be expressed in terms of the **first-rank effective interaction strength**  $X^{(1; \text{SMS}, k)}$  that are specified below for  $k = A, B, C$ .

- **Reduced one-electron matrix element for the normal mass-shift:** With the definition of the angular coefficients in GRASP, this one-electron matrix element is given with  $P' = \frac{\partial P}{\partial r}$  (Gaidamauskas *et al.*, 2011)

$$\begin{aligned} \langle a || \mathbb{h}^{(\text{NMS})} || b \rangle &= \delta_{\kappa_a, \kappa_b} \frac{1}{2M} \int_0^\infty dr \left( P'_a P'_b + Q'_a Q'_b + \frac{\ell_b (\ell_b + 1) P_a P_b + (2j_b - 1) 2j_b Q_a Q_b}{r^2} \right. \\ &\quad \left. - (2\alpha Z) \frac{Q_a P'_b + Q_b P'_a}{r} - (\alpha Z) \left( \frac{\kappa_b - 1}{r^2} \right) (Q_a P_b + Q_b P_a) \right) \end{aligned}$$

### Parametrization of the isotope shift:

- **Mass shift  $\Delta E^{(\text{MS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A')$  of atomic transitions for a pair  $(A, A')$  of isotopes:** The mass shift of an atomic emission line  $i \rightarrow f$  is typically expressed in terms of the mass-shift parameters of the upper and lower level by

$$\begin{aligned} \Delta E^{(\text{MS})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; A, A') &= \left( \frac{M' - M}{M M'} \right) (K^{(\text{MS})}(\alpha_i \mathbb{J}_i) - K^{(\text{MS})}(\alpha_f \mathbb{J}_f)) \\ &= \left( \frac{M' - M}{M M'} \right) (K^{(\text{NMS})}(\alpha_i \mathbb{J}_i) - K^{(\text{NMS})}(\alpha_f \mathbb{J}_f) + K^{(\text{SMS})}(\alpha_i \mathbb{J}_i) - K^{(\text{SMS})}(\alpha_f \mathbb{J}_f)). \end{aligned}$$

- **Mass shift of two isotopes:** Within lowest order of  $m/M$ , the **(isotope) mass shift** for an atomic level  $(\alpha \mathbb{J})$  is determined by the difference of the expectation values of  $\mathbb{H}^{(\text{recoil})}(M)$  for two different isotopes:

$$\Delta E^{(\text{MS})}(M, M') = \langle \alpha \mathbb{J} | \mathbb{H}^{(\text{recoil})}(M) - \mathbb{H}^{(\text{recoil})}(M') | \alpha \mathbb{J} \rangle = \frac{M' - M}{M M'} K^{(\text{MS})}$$

$$\frac{K^{(\text{MS})}}{M} = \langle \alpha \mathbb{J} | \mathbb{H}^{(\text{recoil})}(M) | \alpha \mathbb{J} \rangle = \langle \alpha \mathbb{J} || \mathbb{H}^{(\text{recoil})}(M) || \alpha \mathbb{J} \rangle,$$

and where the Wigner-Eckardt theorem is used here in a special form that is consistent with GRASP and that is utilized for the implementation of corresponding angular coefficients.

- The **conversion factor between the mass-shift parameters  $K^{(\text{MS})}$  in the frequently applied units** is:  
 $K^{(\text{MS})}/[\text{GHz u}] = 3609.4824 K^{(\text{MS})}/[\text{a.u.}]$ .

- **Field shift of two isotopes:** is caused by their different nuclear charge distributions and can be parametrized by:

$$\Delta E^{(\text{FS})}(M, M') = - \left\langle \alpha \mathbb{J} \left| \sum_{j=1}^N (\mathbb{V}^{(\text{nuc})}(r_j; R') - \mathbb{V}^{(\text{nuc})}(r_j; R)) \right| \alpha \mathbb{J} \right\rangle = \left\langle \alpha \mathbb{J} \left\| \sum_{j=1}^N \delta \mathbb{V}^{(\text{nuc})}(r_j; R', R) \right\| \right\rangle = -F \delta \langle r^2 \rangle$$

$$F = \frac{\left\langle \alpha \mathbb{J} \left| \sum_j (\mathbb{V}^{(\text{nuc})}(r_j; R') - \mathbb{V}^{(\text{nuc})}(r_j; R)) \right| \alpha \mathbb{J} \right\rangle}{R' - R}$$

where  $\delta \langle r^2 \rangle = R' - R$  is the difference of the *root-mean-square* (rms) charge radii of the two isotopes with masses  $M'$ ,  $M$ .

- **Field shift  $\Delta E^{(\text{FS})}(\alpha \mathbb{J}; A, A')$  of an atomic level  $(\alpha \mathbb{J}, A, A')$  for a pair  $(A, A')$  of isotopes:** Since the field shift arises from the different nuclear charge distributions of the isotopes  $A, A'$ , it can be simply obtained as difference of the total energies of two separate SCF computations. However, these shifts are quite small, when compared to the total level energies, and such differences are therefore very sensitive to the numerical implementation of the total energies as well as to the parametrization of the nuclear charge distributions. As alternative to this difference, the field shifts can be obtained from first-order perturbation theory by

$$\Delta E^{(\text{FS})}(\alpha \mathbb{J}; A, A') = - \int d^3 \mathbf{r} \rho(\mathbf{r}; \alpha \mathbb{J}) [V^{(\text{nuc})}(\mathbf{r}; A) - V^{(\text{nuc})}(\mathbf{r}; A')],$$

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where  $\rho(\mathbf{r}; \alpha\mathbb{J})$  is the *electronic density of level*  $(\alpha\mathbb{J})$  for either the (reference) isotope  $A$  or  $A'$ , and  $V^{(\text{nuc})}(\mathbf{r}; A)$ ,  $V^{(\text{nuc})}(\mathbf{r}; A')$  are the (nuclear) potentials that arise from the nuclear charge distributions of the isotopes  $A$ ,  $A'$ . If the electronic density depends moreover on the magnetic quantum number  $M$ ,  $\rho(\mathbf{r}; \alpha\mathbb{J})$  as, for instance, for deformed nuclei,  $\rho(\mathbf{r}; \alpha\mathbb{J})$  refers to the averaged electron density over the magnetic components  $M$  of the magnetic substates  $(\alpha\mathbb{J}M)$ .

- **Electronic density of level  $(\alpha\mathbb{J})$  near the origin:** Near to the origin ( $r \rightarrow 0$ ), the electronic density is spherical symmetric to a very good approximation and can be expressed as a even-polynomial function (Ekman *et al.*, 2019)

$$\rho(\mathbf{r}; \alpha\mathbb{J}) \approx b(r) = \sum_{k=0,2,4,6} b_k(\alpha\mathbb{J}) r^k = b_0(\alpha\mathbb{J}) + b_2(\alpha\mathbb{J}) r^2 + b_4(\alpha\mathbb{J}) r^4 + b_6(\alpha\mathbb{J}) r^6,$$

due to the decomposition of the many-electron wave function into (orthonormal) orbitals. Here, the restriction to  $k_{\text{max}} = 6$  is made for practical purposes and because of the (spherical) approximation, the numerical stability as well as, to a very large extent, the accuracy of the experimental data that are available for such field shifts.

- **Field-shift parameters of level  $(\alpha\mathbb{J})$ :** The expansion of the electronic density for  $r \rightarrow 0$  can be substituted into the first-order perturbative expression for  $\Delta E^{(\text{FS})}(\alpha\mathbb{J}; A, A')$  and the terms sorted due to powers of  $r^k$  as (Ekman *et al.*, 2019)

$$\Delta E^{(\text{FS})}(\alpha\mathbb{J}, A, A') \approx \sum_{k=0,2,4,6} F_k(\alpha\mathbb{J}) \left( \langle r^{k+2} \rangle^A - \langle r^{k+2} \rangle^{A'} \right) \equiv \sum_{k=0,2,4,6} F_k(\alpha\mathbb{J}) \langle r^{k+2} \rangle^{A, A'}$$

$$F_k(\alpha\mathbb{J}) = \frac{4\pi Z b_k(\alpha\mathbb{J})}{(k+2)(k+3)}, \quad \langle r^{k+2} \rangle^A = \frac{1}{Z} \int d^3 \mathbf{r} r^{k+2} \rho^{(\text{nuc})}(r; A).$$

Here, the  $F_k(\alpha\mathbb{J})$  are the field-shift parameters of level  $(\alpha\mathbb{J})$ , and the nuclear charge  $Z$  arise in the nuclear moments due to the normalization of the nuclear density  $\int d^3 \mathbf{r} \rho^{(\text{nuc})} = 1$ . Of course, analogous relations for the field-shift energies  $\Delta E^{(\text{FS})}(\alpha_i\mathbb{J}_i \rightarrow \alpha_f\mathbb{J}_f; A, A')$  and field-shift parameter  $F_k(\alpha_i\mathbb{J}_i \rightarrow \alpha_f\mathbb{J}_f)$  in terms of modified expansion coefficients  $b_k(\alpha_i\mathbb{J}_i \rightarrow \alpha_f\mathbb{J}_f)$  can be formulated for atomic (emission) lines  $(\alpha_i\mathbb{J}_i \rightarrow \alpha_f\mathbb{J}_f)$  by just taking the according differences, although this makes the notation more cumbersome.

The parametrization of the field shift applies for all spherically-symmetric nuclear potentials  $V^{(\text{nuc})}(\mathbf{r}; A)$  and, hence, **for all spherically-symmetric nuclear charge densities**  $\rho^{(\text{nuc})} = \rho^{(\text{nuc})}(r; A)$  as well as for **deformed nuclei with total spin  $I = 0$** . Moreover, this parametrization is expected to work even for *deformed* nuclei with  $I \neq 0$ , since the electronic density depends only weakly on small deformations of the nuclear density.

- **Modified field-shift parameter of level  $(\alpha\mathbb{J})$ :** A single electron-density coefficient  $b_0(\alpha\mathbb{J})$  occurs for a *constant* electronic density inside of the nuclear charge distribution. All other coefficients  $b_k(\alpha\mathbb{J})$ ,  $k > 0$  therefore describe (more or less) small variations of the electronic

density *within* the nucleus. The different relevance of these coefficients therefore suggests a slightly modified parametrization

$$\begin{aligned} \Delta E^{(\text{FS})}(\alpha\mathbb{J}; A, A') & \approx F_0(\alpha\mathbb{J}) \delta \langle r^2 \rangle^{A,A'} + F_2(\alpha\mathbb{J}) \delta \langle r^4 \rangle^{A,A'} + F_4(\alpha\mathbb{J}) \delta \langle r^6 \rangle^{A,A'} + F_6(\alpha\mathbb{J}) \delta \langle r^8 \rangle^{A,A'} \\ & = \delta \langle r^2 \rangle^{A,A'} \left( F_0(\alpha\mathbb{J}) + F_2(\alpha\mathbb{J}) \frac{\delta \langle r^4 \rangle^{A,A'}}{\delta \langle r^2 \rangle^{A,A'}} + F_4(\alpha\mathbb{J}) \frac{\delta \langle r^6 \rangle^{A,A'}}{\delta \langle r^2 \rangle^{A,A'}} + F_6(\alpha\mathbb{J}) \frac{\delta \langle r^8 \rangle^{A,A'}}{\delta \langle r^2 \rangle^{A,A'}} \right) \equiv F_{\text{mod}}(\alpha\mathbb{J}) \delta \langle r^2 \rangle^{A,A'}. \end{aligned}$$

- **Electronic-density coefficients  $b_k(\alpha\mathbb{J})$ :** Since these coefficients refer to a spherically-symmetric electronic charge density, they can be readily obtained by either calculating the mean occupation numbers of all CSF, which are involved in the wave function expansion of level  $((\alpha\mathbb{J}))$  *or*, equivalently by calculating the expectation value  $\langle \alpha\mathbb{J} | \delta^{(\text{N-electron})}(\mathbf{r}) | \alpha\mathbb{J} \rangle$  of the zero-rank operator  $\delta^{(\text{N-electron})}(\mathbf{r})$  and by making use of the corresponding angular coefficients. Indeed, these zero-rank coefficients are the same as they occur also in the computation of the normal mass shift (matrix elements).

### Boson-field (isotope) shift parameters:

- **Scalar-boson-field Hamiltonian:** In quantum-field theory, an additional contribution to the electron-nucleus interaction may arise from massive (hypothetical) boson particles of mass  $m_\phi$ . This additional interaction can be expressed in terms of the mass  $A$  and nuclear charge  $Z$  of the isotope by means of the (many-electron) Hamiltonian (Surzhykov 2020)

$$\mathbb{H}^{(\text{boson field})} = \sum_i^N -\alpha^{(\text{boson field})} (A - Z) \hbar c \frac{e^{-m_\phi r_i c/\hbar}}{r_i}$$

In this definition of  $\mathbb{H}^{(\text{boson field})}$ , the (new-physics) **boson-field coupling constant is dimensionless**, and the proper dimension of the Hamiltonian arise from  $\left[\frac{\hbar c}{r}\right] = \left[\frac{\text{kg}\cdot\text{m}}{\text{s}^2}\right] = [\text{J}]$ .

### Non-linear King plots:

- **King plots:** The standard parametrization of isotope shifts assumes that the isotope-shift parameter  $K(\text{nuclear model}; \alpha\mathbb{J})$  and  $F(\text{nuclear model}; \alpha\mathbb{J})$  do neither depend on the mass number nor on the nuclear model. Then, the dependence on the atomic level can be eliminated by taking the ratio of this parametrization for two atomic transitions. With this assumption in mind, this ratio refer to

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a linear dependence, i.e. the King plot is by definition *linear*. — How come non-linearities into play for the King plot ?? ... Explain in further details how such King plots are constructed in detail.

### 7.1.d. Atomic form factors (FormFactor)

#### Properties, notations & application:

- **Form factor**  $F(q; \alpha \mathbb{J})$  of an atom in level  $(\alpha \mathbb{J})$  with an (assumed) spherical-symmetric charge distribution:.
- **Formal quantum notation:**  $F^{(\text{standard})}(q; \alpha \mathbb{J}), F^{(\text{modified})}(q; \alpha \mathbb{J})$ .
- Using JAC: Perform an `Atomic.Computation(.., properties=[FormF, ..], configs=[..], formSettings=FormFactor.Settings(..), ..)` or call directly functions from the module `FormFactor`.
- In JAC, the standard and modified form factors are calculated and tabulated by default for all selected levels in `FormFactor.Settings` and for all specified  $q$ -values [in a.u.]; the default values of the momentum transfer are  $q = 0.1, 1.0, 10.0$  a.u.
- **Atomic form factor:** In atomic physics, the form factors are generally taken as a **fast approximation to the (scattering) amplitude in forward direction at  $\vartheta \simeq 0$  if an incident quantum wave is scattered by an isolated atom with spherical-symmetric charge distribution.**
- In practice, of course, the definition of the atomic form factor depends on both, the particular scattering (elastic or inelastic) as well as the type of incident radiation, such as photons, electrons or neutrons. As usual, we here restrict ourselves to the **atomic form factor for the elastic (x-ray) scattering of photons.**
- **Momentum transfer:** Most easily, the atomic form factor can be written as function of the momentum transfer  $q = |\mathbf{q}|$ , that is closely related also to the scattering angle:  $\hbar q = 2k \sin(\vartheta/2) = \frac{2}{\lambda} \sin(\vartheta/2)$ .
- **Momentum-transfer variable:** Instead of the momentum transfer  $q$ , some tabulations of x-ray scattering amplitude make use also of the (so-called) momentum-transfer variable  $x = [\sin(\vartheta/2)] / \lambda [\text{\AA}]$  with  $\lambda [\text{\AA}] = 12.398520/E [\text{keV}]$ .
- **Application of form factors:** The elastic scattering of photons by atoms, ions or molecules has been found important in many fields of physics, such as crystallography, plasma physics and astrophysics. For high-photon energies well above the K-shell threshold energy of the atom or ion, both the standard form factor (FF) or the modified form factor (MFF) approximations are widely applied and were found moderately successful in estimating the scattering cross sections. However, **both form factor approximations typically fail for small photon energies.**



### Definition of atomic form factors:

- **Standard atomic form factor:** For an atom in level  $(\alpha \mathbb{J})$  with a spherically-symmetric charge distribution  $\rho(r)$ , the standard atomic form factor is given by

$$F^{(\text{standard})}(q; \alpha \mathbb{J}) = 4\pi \int dr r^2 \rho(r) \frac{\sin(qr)}{qr} = \frac{1}{2J+1} \sum_M \langle \alpha \mathbb{J} M | \mathbb{T}^{(1-\text{particle})}(\mathbf{q}) | \alpha \mathbb{J} M \rangle.$$

It is equal to the Fourier transform of the charge density  $\rho(r)$ , if the charge density is just normalized to the number of bound electrons:  $4\pi \int dr r^2 \rho(r) = N$ . The second equivalence still need to be worked out in detail since  $\mathbb{T}^{(1-\text{particle})}(\mathbf{q})$  is a general (symmetric) one-particle operator but without definite rank.

- As seen from above, this standard form factor can be expressed also as (averaged many-electron) expectation value of the single-electron momentum-transfer operator  $\mathbb{T}^{(1-\text{particle})}(\mathbf{q}) = \sum_{j=1}^N \exp(i \mathbf{q} \cdot \mathbf{r}_j)$  for a given sublevel  $|\alpha \mathbb{J} M = 0\rangle$ .
- **Modified atomic form factor:** For an atom or ion with a spherically-symmetric charge distribution, a modified atomic form factor can be defined via the charge distributions of the individual (sub-) shells of the element

$$F^{(\text{modified})}(q; \alpha \mathbb{J}) = 4\pi \sum_{i=1}^N \int dr r^2 \rho_i(r) \frac{\sin(qr)}{qr} \frac{mc^2}{\varepsilon'_i - V(r)},$$

and where  $\rho_i(r)$  is the charge density of the  $i$ -th electron,  $\varepsilon'_i = \varepsilon_i + mc^2$  its energy (including the rest mass), and  $V(r)$  the (full atomic) potential of the  $i$ -th electron as seen at position  $r$ . Here, the summation is taken over all electrons, and the charge distribution must fullfill again the constraint that  $4\pi \sum_i \int dr r^2 \rho_i(r) = N$  is equal to the number of bound electrons.

- **Generalized atomic form factor:** A generalized form factor can be defined for any pair of states; it is often calculated for the ground state  $|\alpha_o \mathbb{J}_o M_o\rangle$  and some excited state  $|\alpha_e \mathbb{J}_e M_e\rangle$  by:

$$F^{(\text{generalized})}(q; \alpha_e \mathbb{J}_e M_e; \alpha_o \mathbb{J}_o M_o) = \langle \alpha_e \mathbb{J}_e M_e | \mathbb{T}^{(1)}(\mathbf{q}) | \alpha_o \mathbb{J}_o M_o \rangle.$$

This generalized atomic form factor help describe also inelastic scattering processs and is closely related to the **generalized oscillator strength**, cf. Section 8.3.o.

### 7.1.e. Energy shifts in plasma environments (PlasmaShift)

#### Properties, notations & application:

- **Plasma shift** of an atomic level:  $E(\alpha\mathbb{J}) \longrightarrow E(\alpha\mathbb{J}; \text{plasma model and parameters})$  .
- **Formal quantum notation:**  $\Delta E^{(\text{plasma})}(\alpha\mathbb{J}) = E(\alpha\mathbb{J}; \text{plasma model and parameters}) - E(\alpha\mathbb{J}; \text{unperturbed})$  .
- **Spectral line shifts:** The interaction between the plasma and the bound electrons of an ion embedded into the plasma alters the ionic structure and transition properties. Therefore, **a plasma environment generally results in spectral line shifts, line broadening and changes in the line shapes**, when compared with the free ion.
- For realistic plasma conditions, the number of bound states of the ions often becomes finite and the electrons less tightly bound by the nucleus, if the plasma coupling parameter increases.
- Using JAC: Perform an `Atomic.Computation(.., properties=[Plasma, ..], configs=[..], plasmaSettings=PlasmaShift.Settings(..), ..)` or call directly functions from the module `PlasmaShift`.
- In JAC, the plasma (energy) shifts are calculated and tabulated by default for a Debye-Hückel plasma model with screening parameter  $\lambda = 0.25$ . Hereby, the Debye-Hückel interaction is incorporated only in first-order perturbation theory within the CI matrix.

#### High-density plasma:

- Relativistic corrections to the plasma screening may become necessary for a detailed analysis of atomic spectra, especially if lines of multiply-charged ions are used in some spectral analysis.
- **Collisional-radiative model:** The effects of the plasma-environment can be further taken into account also by kinetic *or* collisional-radiative models, and where the energy shifts are often introduced by semi-empirically formulas, such as the formula by Stewart and Pyatt.
- **Application of simple plasma models:** Apart from plasma diagnostics, a **proper treatment of a (plasma) screening potential** has been found useful also in other areas of physics, such as nuclear and elementary particle physics, solid state physics, or even the design of nanostructures.
- **Strongly-coupled plasma:** For a **strongly-coupled dense plasma**, the (averaged) electrostatic energy between neighbouring particles in the plasma exceeds their thermal energy. The coupling parameter  $\Gamma = q^2/4\pi\epsilon_0 R_0 kT > 1$  is used in order to characterize such a strongly-coupled plasma. This **coupling parameter  $\Gamma$**  simply describes the ratio of the electrostatic and the thermal energy of the plasma particles, and where  $R_o = (3/4 \pi n_e)^{1/3}$ .

- **Laser-induced plasma with  $\Gamma \gg 1$ :** Strongly-coupled plasma obeys generally classical statistics and has been observed for a large number of experimental and astrophysical conditions. In the laboratory, for instance, laser-induced plasma with  $\Gamma \gg 1$  has been investigated in high-compression fusion experiments. Such a laser-produced plasma provides a very typical example of a high-density, strongly-coupled plasma with electronic densities well beyond  $10^{24} \text{ cm}^{-3}$ .
- Theoretical (plasma) models for hot and dense plasma are necessary to simulate its properties, such as the equation of state, radiative transfer coefficients or the conduction coefficients in plasma. These properties are relevant for inertial confinement fusion and astrophysics.
- **Average-atom (AA) model:** The AA model has been utilized to describe the electronic structure of hot and dense plasmas. This model was developed in order to describe **bound electrons in terms of the (atomic) shell model, and to deal with the free electrons within the Thomas-Fermi statistical model.**
- **Plasma models:** Plasma screening effects have been investigated extensively by employing various analytical models, such as the ion sphere, Debye-Hückel, Stewart-Pyatt as well as Ecker-Kröll models.

### Frequently applied plasma models in atomic structure calculations:

- **Debye-Hückel model:** This model has been commonly used in order to incorporate plasma effects into atomic structure calculations. However, the **validity of this model remains rather questionable** because it is valid only when the *correlation* time of the ion is much longer than the lifetime of excited atomic states. Therefore, **this perturbative approach is at best valid for weakly-coupled plasmas and should not be applied for modeling of high-density plasmas.**
- **Coulomb interaction in the Debye-Hückel model:** In this model, the (pairwise) Coulomb interaction among the charged particles is modified (screened) for an ion with nuclear charge  $Z$  to

$$V^{(\text{DH})}(r, \lambda) = - \sum_i^N \frac{Z e^{-\lambda r_i}}{r_i} + \sum_{i>j}^N \frac{e^{-\lambda r_{ij}}}{r_{ij}} = \sum_i^N V^{(\text{e-n, DH})}(r_i, \lambda) + \sum_{i>j}^N V^{(\text{e-e, DH})}(r_{ij}, \lambda).$$

Here,  $N$  is the number of bound electrons in the ion,  $r_i$  is the distance of the  $i$ -th electron from the nucleus, and  $r_{ij}$  the distance between the electrons  $i$  and  $j$ .

- **Plasma screening parameter  $\lambda$ :** This parameter is the inverse of the Debye shielding length for a certain plasma environment and can be readily expressed in terms of the electron density  $n_e$  and the temperature  $T_e$  of the plasma by:

$$\lambda = \left[ \frac{4\pi n_e}{k T_e} \right]^{\frac{1}{2}}.$$

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- **Debye-Hückel model:** To obtain the modified two-particle integrals due the plasma screening, we can write

$$V^{(e-e, \text{DH})}(r_{ij}, \lambda) = -\lambda \sum_{l=0}^{\infty} (2l+1) j_l(i\lambda r_{<}) h_l^1(i\lambda r_{>}) P_l(\cos\theta)$$

in terms of the *larger* ( $r_{>} = \max(r_i, r_j)$ ) and *smaller* radii ( $r_{<} = \min(r_i, r_j)$ ) of the one-particle radii  $r_i$  and  $r_j$ , respectively, and where  $j_l$  denotes a spherical Bessel function and  $h_l^1$  a Hankel function of the first kind.

- **Nonrelativistic functions  $Y^k(r; ab)$  and  $Z^k(r; ab)$  for a Debye-Hückel potential:** Jiao *et al.* (2019) reformulated the frequently-applied  $Z^k(r; ab)$  and  $Y^k(r; ab)$  for atoms and ions in a Debye-Hückel potential, i.e. for weakly-coupled plasmas. In this reformulation, use is made of the Gegenbauer expansion in order to decompose the screened interelectronic Coulomb potential.
- **Electron-electron interaction in a Debye-Hückel plasma:** For atoms in a screened Debye-Hückel plasma, the Coulomb operator  $\mathbb{V}^{(\text{Coulomb})}$  has to be replaced by (Jiao *et al.*, 2019)

$$\mathbb{V}^{(e-e, \text{DH})} = \frac{e^{-\lambda r_{12}}}{r_{12}} = \sum_{k=0}^{\infty} (2k+1) \frac{I_{k+\frac{1}{2}}(\lambda r_{<})}{\sqrt{r_{<}}} \frac{K_{k+\frac{1}{2}}(\lambda r_{>})}{\sqrt{r_{>}}} P_k(\cos \vartheta_{12}),$$

where  $\lambda$  is the screening parameter and  $I_\alpha$  and  $K_\alpha$  are the modified (but not spherical) Bessel functions of the first and second kind.

- **Solutions of the  $Y^k(r; ab)$  and  $Z^k(r; ab)$  functions:** For atoms in a screened Debye-Hückel potential, the pair of differential equations can be written (Jiao *et al.*, 2019)

$$\begin{aligned} \frac{d}{dr} Z^k(r; \lambda, ab) &= \left[ \frac{k+1}{r} - \lambda \frac{K_{k+3/2}(\lambda r)}{K_{k+\frac{1}{2}}(\lambda r)} \right] Z^k(r; \lambda, ab) + (2k+1) I_{k+\frac{1}{2}}(\lambda r) K_{k+\frac{1}{2}}(\lambda r) P_a(r) P_b(r), \\ \frac{d}{dr} Y^k(r; \lambda, ab) &= \left[ \frac{k+1}{r} - \lambda \frac{K_{k+3/2}(\lambda r)}{K_{k+\frac{1}{2}}(\lambda r)} \right] Y^k(r; \lambda, ab) - \lambda \left[ \frac{I_{k+3/2}(\lambda r)}{I_{k+\frac{1}{2}}(\lambda r)} + \frac{K_{k+3/2}(\lambda r)}{K_{k+\frac{1}{2}}(\lambda r)} \right] Z^k(r; \lambda, ab) \end{aligned}$$

and with the same boundary conditions  $Z^k(0; \lambda, ab) = 0$ ,  $Y^k(r \rightarrow \infty; ab) = Z^k(r \rightarrow \infty; ab)$  for all finite  $\lambda$ . It is therefore convenient to calculate  $Z^k(r; \lambda, ab)$  by an outward integration from  $r = 0$  and then to obtain  $Y^k(r; \lambda, ab)$  by an inward integration from  $r \approx \infty$ .

- **Debye-Hückel model:** While the Debye-Hückel screening of the electron-nucleus interaction usually destabilizes the binding of the electron, the screening of the electron-electron repulsion counteracts this trend.

- Saha and Fritzsche (2006) demonstrated for beryllium-like ions that the Debye-Hückel screening (if applicable) should be incorporated into both, the electron-nucleus and electron-electron interaction in order to obtain reliable results for the plasma shifts.
- **Ion-sphere model:** In this model, the ion is typically enclosed in a spherically symmetric cell that contains the exact number of electrons in order to ensure neutrality. In the ion-sphere model, one needs to define an electron-density distribution that either obeys self-consistency equations or need to make some simple hypothesis, such as an uniform density within the cell.

### Plasma in oscillating electric fields:

- **Plasma in oscillating electric fields:** The collective movement of plasma particles, such as the electron plasma waves (Langmuir oscillations) or ion plasma waves, is mainly determined by the plasma creation and/or heating device but lead also to quite significant fields (Peyrusse 1977).

### Free-electron distributions in plasma:

- In a plasma, the free-electron (radial) density  $n_e(r)$  can follow different distributions:
- **Maxwell-Boltzmann distribution:** The Maxwell-Boltzmann statistics has been often applied to describe the free-electron distribution but is **not well justified for high-density or low-temperature plasma**.
- **Fermi-Dirac distribution:** This distribution is preferable if the free electrons are degenerate

$$n_e(r) = \frac{4}{\sqrt{\pi}} \int_{r_o}^{\infty} dr \frac{\sqrt{r}}{e^{r-r_o - \mu/kT_e} + 1} = 2 \lambda_{th}^{-3} \mathcal{F}_{1/2} \left( -\frac{V(r)}{kT_e} + \frac{\mu}{kT_e}; -\frac{V(r)}{kT_e} \right).$$

Here  $\mu$  is the chemical potential of the plasma,  $\mathcal{F}_{1/2}(x, y)$  the incomplete Fermi-Dirac integral and  $\lambda_{th} = \sqrt{2\pi/kT_e}$  the thermal de-Broglie thermal wavelength.

- **Uniform electron-gas distribution:** This distribution considers a sphere of radius  $R_o = (3/4\pi n_e)^{1/3}$  around the ion with  $N_b$  bound electrons, in which the ionic charge is completely neutralized by the additional  $N_f = Z - N_b$  free electrons. Although all electrons inside of the sphere will strongly interact with the embedded ion, the free electrons are here assumed to be distributed uniformly. With this assumption in mind, the electrostatic potential for the bound electrons with radial coordinate  $r$  is given by

$$V^{(IS)}(\mathbf{r}; \mathbf{R}_0) = \begin{cases} -\frac{Z}{r} + \frac{Z-N_b}{2R_0} \left[ 3 - \left( \frac{r}{R_0} \right)^2 \right] & \text{for } \mathbf{r} \leq \mathbf{R}_0 \\ 0 & \text{for } \mathbf{r} > \mathbf{R}_0. \end{cases}$$

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In this potential above, the first term describes the interaction of the bound electron with the nucleus, while the second (repulsive) term arises from the plasma background and always causes a shift of all the level energies towards the continuum.

- **Collision-induced localization:** The plasma environment typically leads to a broadening of the momentum distribution of free electrons and partly also to its localization. Indeed, random collisions of the continuum electron with particles from the plasma environment may results in a loss of coherence of the outgoing, photoionized electrons when leaving the parent ions. Such a collision-induced localization resembles the Anderson localization of randomly scattered electrons in solids as well as the dynamical localization of Rydberg electrons in plasma.
- **Collision-induced localization:** The collision-induced energy and momentum broadening of stationary states can reduce also the lifetime of the bound states. At a given plasma temperature, the momentum broadening increases with the plasma density or, in other words, the electron localization is more pronounced in a dense plasma.

### Gordon-Kim theory:

- In the Gordon-Kim theory (1972), the total energy of the system consists out of the direct Coulomb potential energy, the exchange Coulomb potential energy, the kinetic energy as well as the correlation energy. The direct Coulomb potential energy is calculated by integrating the Coulomb potential for the (approximated) electron density, while the other contributions to the total energy were calculated by using a temperature-dependent local density functional (LDA) approach.

#### 7.1.f. Level-dependent fluorescence and Auger yields (DecayYield)

### Properties, notations & application:

- **Fluorescence versus Auger decay** of an (excited) atomic level:  $A^{q+*} \longrightarrow \begin{bmatrix} A^{q+(*)} + \hbar\omega \\ A^{(q+1)+(*)} + e_a^- \\ \dots \end{bmatrix}.$

The corresponding level-specific or configuration-averaged fluorescence and Auger yields just describe the fraction of atoms in a particular level or configuration that decay either by fluorescence or Auger electron emission.

- **Formal quantum notation:**  $|\alpha\mathbb{J}\rangle \longrightarrow \begin{bmatrix} \{ |\alpha_r\mathbb{J}_r\rangle + \hbar\omega(\{\mathbb{M}\}) \} \\ \{ |\alpha_a\mathbb{J}_a\rangle + |\varepsilon\kappa\rangle \} \\ \dots \end{bmatrix}.$
- Using JAC: Perform an `Atomic.Computation(..., properties=[Yields, ...], configs=[...], yieldSettings=DecayYield.Settings(...), ...)` or call directly functions from the module `DecayYield`.
- In JAC, we calculate and tabulate by default the fluorescence yields  $\omega_r(\alpha\mathbb{J})$  and Auger yields  $\omega_a(\alpha\mathbb{J})$  for all selected levels.
- In JAC, the computation of all fluorescence and Auger yields is always traced back to single-step cascade computations. Therefore, the same (cascade) approaches `{ AverageSCA, SCA, ... }` can be applied as in cascade computations, cf. section 9.1. The particular approach, that is to be applied in the given computation above, need to be specified however as `String` in the `DecayYield.Settings("AverageSCA", ...)`.
- In JAC, the explicit settings of the underlying `Cascade.Computation` can be overwritten in the function `Cascade.determineSteps()`; no attempt has been made so far to support such control features directly by means of the `DecayYield.Settings(...)`.
- **Fluorescence yields  $\omega_r(\alpha\mathbb{J})$ :** This yield typically represents the probability of an inner-shell (core) hole to be filled under photon emission, in contrast and competition with other nonradiative processes.
- **Auger yields  $\omega_a(\alpha\mathbb{J})$ :** This yield describes the (complementary) probability for an inner-shell hole level to decay by electron emission, hence:  $\omega_r(\alpha\mathbb{J}) + \omega_a(\alpha\mathbb{J}) = 1$ . The Auger yield is sometimes further partitioned into an Auger and Coster-Kronig yield:  $\omega_a(\alpha\mathbb{J}) = \omega^{(\text{Auger})}(\alpha\mathbb{J}) + \omega^{(\text{Coster-Kronig})}(\alpha\mathbb{J})$ .
- If not explicitly overwritten within the code [cf. the module `Cascade`], only the electric-dipole (E1) transitions and the **Coulomb interaction  $\mathbb{V}^{(\text{Coulomb})}$**  are taken into account in the evaluation of all Auger and radiative transition amplitudes and rates.
- More often than not, the fluorescence and Auger yields are computed and analyzed for either *K* - or *L* -shell (holes) states, and for which usually no distinction need to be made for the different fine-structure levels ( $\alpha\mathbb{J}$ ) that arise only due to the couplings of the valence shells.
- **Typically, it is completely sufficient to include only electric-dipole decay channels**, although other multipoles could be incorporated explicitly in the computations, as far this is supported by the underlying cascade approach, or invoked explicitly within the code.

## 7.2. In JAC partly-implemented level properties

### 7.2.a. Radial electron density distribution & natural orbitals (ElectronDensity)

#### Properties, notations & application:

- **Radial electron density distribution:** The electron density can also be obtained from the  $N$ -electron wave function as expectation value of the  $\delta(\mathbf{r})$  operator

$$\rho(\mathbf{r}) = N \int d\mathbf{q}_1 d\mathbf{q}_2 \dots d\mathbf{q}_N \Psi(\mathbf{q}_1, \dots, \mathbf{q}_N) \delta^{(N-\text{electron})}(\mathbf{r}) \Psi^*(\mathbf{q}'_1, \dots, \mathbf{q}'_N).$$

- **Many-electron  $\delta^{(N-\text{electron})}(\mathbf{r})$  operator:** This operator probes whether all electrons are at a given position  $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  in space and can be written in terms of the single-electron operators

$$\delta(\mathbf{r} - \mathbf{r}_j) = \frac{1}{r^2 \sin \vartheta} \delta(r - r_j) \delta(\vartheta - \vartheta_j) \delta(\varphi - \varphi_j) = \frac{1}{r^2} \delta(r - r_j) \sum_{\ell m} Y_{\ell m}(\vartheta, \varphi) Y_{\ell m}^*(\vartheta_j, \varphi_j)$$

$$\delta(\mathbf{r})^{(N-\text{electron})} = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) = \frac{1}{r^2} \sum_{j=1}^N \delta(r - r_j) \sum_{\ell m} Y_{\ell m}(\vartheta, \varphi) Y_{\ell m}^*(\vartheta_j, \varphi_j).$$

- **Many-electron  $\delta^{(N-\text{electron})}(\mathbf{r})$  operator in second quantization:** This operator can be written also in second quantization by means of the creation and annihilation operators of electrons in well-defined relativistic subshells  $(n\kappa)$

$$\delta(\mathbf{r} - \mathbf{r}_j) = \sum_{\kappa} \sqrt{2j+1} \sum_{ab} [a_{n_a\kappa}^+ a_{n_b\kappa}]^{(0)} [P_{n_a\kappa}(r) P_{n_b\kappa}(r) + Q_{n_a\kappa}(r) Q_{n_b\kappa}(r)].$$

- **Radial electron-density distribution for single configurations:** This distribution represents the probability to find an electron in the interval  $[r, r + dr]$  from the nucleus, averaged over all directions:

$$D(r) \equiv r^2 \rho(r) = \sum_a q_a (P_a^2(r) + Q_a^2(r)), \quad \int_0^\infty dr D(r) = \int_0^\infty dr r^2 \rho(r) = \sum_a q_a = N.$$



- **Radial electron-density distribution for MCDHF wave functions:** In general, this representation can be written for a given level  $(\alpha\mathbb{J})$  in terms of the CSF mixing coefficients as (Borgoo *et al.*, 2010)

$$D(r) \equiv r^2 \rho(r, \alpha\mathbb{J}) = \sum_{ij} c_i^* D_{ij}(r) c_j = \sum_{ij} c_i^* \left[ \sum_{\kappa, n\kappa'} u_{ij}(n\kappa, n'\kappa) I_\rho(n'\kappa, n\kappa) \right] c_j = \sum_{\kappa, n\kappa'} \rho_{n'n}^{(\kappa)} I_\rho(n'\kappa, n\kappa)$$

$$\rho_{n'n}^{(\kappa)} = \sum_{ij} c_i^* u_{ij}(n\kappa, n'\kappa) c_j,$$

and where  $u_{ij}(n\kappa, n'\kappa)$  are the angular coefficients for a zero-rank one-electron operator,  $I_\rho(n'\kappa, n\kappa) = (P_{n'\kappa} P_{n\kappa} + Q_{n'\kappa} Q_{n\kappa})$  radial functions, and where the summation over  $ij$  runs over all CSF in the wave function expansion.

- **Natural orbitals:** These orbitals are defined as the one-electron orbital functions that diagonalize the block-diagonal (first-order) density matrix  $\mathbf{C}^+ \boldsymbol{\rho}_{n'n}^{(\kappa)} \mathbf{C} = \tilde{\boldsymbol{\rho}}$ . The natural orbitals are then obtained as linear combination (Borgoo *et al.*, 2010):

$$\tilde{R}_{n\ell}(r) = C_{n',n}^{(\kappa)} R_{n'\kappa}(r),$$

and the eigenvalue  $\tilde{\boldsymbol{\rho}}_{nn} = \tilde{q}_{n\kappa}$  is interpreted as the occupation numbers of the natural orbital  $(n\kappa)$ .

## 7.2.b. Scattering amplitudes and scattering factors (FormFactor)

### Properties, notations & application:

- Scattering amplitude  $S(q; \alpha \mathbb{J})$  of an atomic level with supposed spherical-symmetric charge distribution:.
- Formal quantum notation: .

### Anomalous scattering factors:

- Coherent Rayleigh scattering factor: This scattering factor characterizes the (complex) scattering amplitude in forward direction and is obtained by:

$$\frac{1}{2} \sum_{\varepsilon_i, \varepsilon_f} M(\varepsilon_i, \mathbf{k}_i, \varepsilon_f, \mathbf{k}_f = \mathbf{k}_i),$$

i.e. as average over the polarization (states) of the incident photon and by a summation over the polarization of the scattered photon.

- Using the modified form factor for describing the scattering in forward-scattering angle  $\vartheta \approx 0$ , the real  $g'(\omega)$  and imaginary  $g''(\omega)$  anomalous scattering factors can be approximately defined in terms of the photoionization cross sections and oscillator strength (Zhou *et al.*, 1990). This formally requires a summation over the complete spectrum of the atom, although the major contributions arise from just a few resonances.
- Anomalous scattering factor: The real  $g'(\omega)$  and imaginary  $g''(\omega)$  anomalous scattering factors are frequently employed in order to express the coherent (Rayleigh) scattering factor  $G(\omega)$  for incident photons with energy  $\hbar\omega$ .
- Coherent Rayleigh scattering factor: For incident photons with energies  $\hbar\omega$ , the coherent (Rayleigh) scattering factor in forward direction has been written as (Zhou *et al.*, 1990)

$$G(\omega) = F(0) + g'(\omega) + i g''(\omega),$$

where  $F(0) = N$  is the atomic form factor. Therefore, the (Rayleigh) scattering amplitude and scattering factor can be expressed also in terms of the standard (atomic) form factor (FF) or the modified form factor (MFF).

### Incoherent scattering function $S(\mathbf{q})$ :

- Incoherent scattering function:
- Incoherent scattering function: This scattering function can be expressed in terms of the generalized atomic form factor

$$S(\mathbf{q}; \alpha_o \mathbb{J}_o M_o) = \sum_{e \neq o} |F^{(\text{generalized})}(q; \alpha_e \mathbb{J}_e M_e; \alpha_o \mathbb{J}_o M_o)|^2 = \langle \alpha_o \mathbb{J}_o | \mathbb{T}^{(2)}(\mathbf{q}) | \alpha_o \mathbb{J}_o \rangle - |F^{(\text{standard})}(q; \alpha_o \mathbb{J}_o)|^2.$$

but where the summation over  $e$  includes all discrete levels as well as an integration over the continuum. In the second equivalence, the two-electron momentum-transfer operator  $\mathbb{T}^{(2)}(\mathbf{q}) = \sum_{m,n=1}^N \exp[i \mathbf{q} \cdot (\mathbf{r}_m - \mathbf{r}_n)]$  occurs, but then just requires to compute the expectation value of this operator with regard for the ground state  $|\alpha_o \mathbb{J}_o M_o\rangle$ .

### 7.2.c. Lande $g_J$ factors and Zeeman splitting of fine-structure levels (LandeZeeman)

#### Properties, notations & application (not yet fully implemented):

- Zeeman splitting of an atomic level into Zeeman (sub-) levels:  $|\alpha \mathbb{J}\rangle \longrightarrow |\alpha \mathbb{J} M\rangle, \quad M = -J, \dots, J-1, +J$ .
- Formal quantum notation:  $|\alpha \mathbb{J} M\rangle$ .
- Using JAC: Perform an `Atomic.Computation(..., properties=[LandeJ, ...], configs=[...], zeemanSettings=LandeZeeman.Settings(...), ...)` with `calcLandeJ=true` or call directly functions from the module `LandeZeeman`.
- In JAC, we calculate and tabulate by default the Lande  $g_J \equiv g(\alpha \mathbb{J})$  factors for the selected fine-structure levels.
- In the JAC program, the Zeeman amplitudes  $\langle \beta_r \mathbb{J}_r || \mathbb{N}^{(1)} || \beta_s \mathbb{J}_s \rangle$  and  $\langle \beta_r \mathbb{J}_r || \Delta \mathbb{N}^{(1)} || \beta_s \mathbb{J}_s \rangle$  can be obtained from the function `Jac.LandeZeeman.amplitude()`.

#### Further remarks:

- The Zeeman effect describes the (level) splitting of an atomic level  $(\alpha \mathbb{J})$  into its sub-levels  $|\alpha \mathbb{J} M\rangle$  in the presence of a static magnetic field.

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- The various components  $|\alpha JM\rangle$  of a Zeeman-split line usually have different intensities, and with some of them possibly even forbidden within the dipole approximation.
- The energy splitting of the Zeeman sub-levels depends of course on the magnetic field strength. — Therefore, the **Zeeman effect has been applied for measuring magnetic field strengths**, e.g. in astrophysics at the surface of the Sun or in laboratory plasmas.

### Zeeman Hamiltonian $\mathbb{H}^{(\text{mag})}$ :

- If the  $z$ -axis is chosen along the magnetic field  $\mathbf{B} \parallel \mathbf{e}_z$  and if we neglect diamagnetic contributions, the **magnetic (Zeeman) Hamiltonian** can be written in terms of spherical tensors (Andersson and Jönsson, 2008)

$$\mathbb{H}^{(\text{mag})} = \left( \mathbb{N}_0^{(1)} + \Delta \mathbb{N}_0^{(1, \text{QED})} \right) B$$

$$\mathbb{N}^{(1)} = \sum_j^N \mathfrak{n}^{(1)}(j) = \sum_j^N -i \frac{\sqrt{2}}{2\alpha} r_j (\boldsymbol{\alpha}_j \mathbb{C}^{(1)}(j))^{(1)}$$

$$\Delta \mathbb{N}^{(1)} = \sum_j^N \Delta \mathfrak{n}^{(1)}(j) = \sum_j^N \frac{g_s - 2}{2} \beta_j \boldsymbol{\Sigma}_j, \quad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix},$$

and where the second term in the magnetic Hamiltonian above is (so-called) Schwinger's QED correction. Here,  $g_s = 2.00232$  is the  $g$ -factor of the electron, including some leading QED corrections.

- **Total Hamiltonian:** For a moderate magnetic  $\mathcal{B}$ -field, one considers the total Hamiltonian  $\mathbb{H}^{(\text{DC})} + \mathbb{H}^{(\text{mag})}$  whose matrix is diagonal in  $P, M$  but no longer in the total angular momentum quantum number  $J$ . In practice, one usually starts from a given ASF basis, in which  $\mathbb{H}^{(\text{DC})}$  is already diagonal, and then diagonalized the total Hamiltonian matrix in very moderate basis of atomic state functions. For a non-zero nuclear spin, however, the hyperfine and Zeeman splitting is often comparable and the Hamiltonian  $\mathbb{H}^{(\text{DC})} + \mathbb{H}^{(\text{mag})} + \mathbb{H}^{(\text{hfs})}$  need then to be diagonalized in some given ASF basis. In this case, only the parity and  $M_F$  are diagonal, i.e. good quantum numbers.

### Lande factor $g_J \equiv g(\alpha\mathbb{J})$ and Zeeman splitting of an electronic level $(\alpha\mathbb{J})$ :

- **$g$ -factors of atomic fine and hyperfine levels:** In the classical vector coupling model, the  $g$ -factors simply follow from the coupling rules of the angular momenta and are given by:

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I \frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)},$$

and where the second relation can be used to obtain  $g_I$ , provided that  $g_J$  and  $g_F$  is known.

- **Zeeman splitting of an atomic level  $(\alpha\mathbb{J})$  :** If the energy splitting due to the magnetic field is small, when compared with the fine-structure splitting, it can be expressed in first-order perturbation theory by

$$\begin{aligned} \Delta E^{(\text{mag})}(\alpha\mathbb{J}M) &= E(\alpha\mathbb{J}M) - E(\alpha\mathbb{J}, M=0) \\ &= \left\langle \alpha\mathbb{J}M \left| \mathbb{N}_0^{(1)} + \Delta \mathbb{N}_0^{(1, \text{QED})} \right| \alpha\mathbb{J}M \right\rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \sqrt{2J+1} \left\langle \alpha\mathbb{J} \left\| \mathbb{N}^{(1)} + \Delta \mathbb{N}^{(1, \text{QED})} \right\| \alpha\mathbb{J} \right\rangle B \\ &= \frac{M}{\sqrt{J(J+1)}} \left\langle \alpha\mathbb{J} \left\| \mathbb{N}^{(1)} + \Delta \mathbb{N}^{(1, \text{QED})} \right\| \alpha\mathbb{J} \right\rangle B \end{aligned}$$

and with regard to the unperturbed energy  $E(\alpha\mathbb{J}, M=0) = E(\alpha\mathbb{J}, B=0)$ .

- **Lande  $g_J$  factor of an atomic level  $(\alpha\mathbb{J})$  :** Usually, the dependence on the  $M$  quantum number is factored out and the energy splitting is expressed for a single level  $(\alpha\mathbb{J})$  in terms of its Lande factor  $g_J \equiv g(\alpha\mathbb{J})$

$$\Delta E^{(\text{mag})}(\alpha\mathbb{J}M) = g(\alpha\mathbb{J}) M \frac{B}{2}, \quad g(\alpha\mathbb{J}) \equiv g_J = 2 \frac{\left\langle \alpha\mathbb{J} \left\| \mathbb{N}^{(1)} + \Delta \mathbb{N}^{(1, \text{QED})} \right\| \alpha\mathbb{J} \right\rangle}{\sqrt{J(J+1)}}$$

### 7.2.d. Lande $g_F$ factors and Zeeman splitting of hyperfine levels (LandeZeeman)

#### Properties, notations & application (not yet fully implemented):

- Zeeman splitting of an atomic hyperfine level into Zeeman (sub-) levels:  $|\alpha(J)\mathbb{F}\rangle \longrightarrow |\alpha(J)\mathbb{F}M\rangle, \quad M = -F, \dots, F-1, +F$ .
- Formal quantum notation:  $|\alpha(J)\mathbb{F}M\rangle$ .
- Using JAC: Perform an `Atomic.Computation(.., properties=[LandeJ, ..], configs=[..], zeemanSettings=LandeZeeman.Settings(..), ..)` with `calcLandeF=true` or call directly functions from the module `LandeZeeman`.
- In JAC, we calculate and tabulate by default the Lande  $g_F \equiv g(\alpha\mathbb{F})$  factors for the selected hyperfine-structure levels.

#### Further remarks:

- The Lande  $g$ -factor (also known as  $g$  value or dimensionless magnetic moment) is a dimensionless entity that characterizes the gyromagnetic ratio of an atomic or hyperfine level. The Lande  $g$ -factor is basically a proportionality constant how efficient a particle, spin or quantum state with given total angular momentum  $s$  contributes to the splitting in an external magnetic field  $B$ .

#### Lande factor $g_F \equiv g(\alpha\mathbb{F})$ of an hyperfine level $(\alpha\mathbb{F})$ :

- Zeeman splitting of an hyperfine level  $(\alpha\mathbb{F})$  : If the energy splitting due to the magnetic field is small, when compared with the hyperfine-

splitting, it can be expressed in first-order perturbation theory in terms of the reduced electronic Zeeman amplitudes by

$$\begin{aligned}
\Delta E^{(\text{mag})}(\alpha \mathbb{F} M) &= E(\alpha \mathbb{F} M) - E(\alpha \mathbb{F}, M = 0) \\
&= \left\langle (I, \alpha \mathbb{J}) F M \left| \mathbb{N}_0^{(1)} + \Delta \mathbb{N}_0^{(1, \text{QED})} \right| (I, \alpha \mathbb{J}) F M \right\rangle \\
&= M \frac{F(F+1) + J(J+1) - I(I+1)}{2 F(F+1)} \frac{\left\langle \alpha \mathbb{J} \left| \mathbb{N}_0^{(1)} + \Delta \mathbb{N}_0^{(1, \text{QED})} \right| \alpha \mathbb{J} \right\rangle}{\sqrt{J(J+1)}} \\
&= M \frac{F(F+1) + J(J+1) - I(I+1)}{2 F(F+1)} g(\alpha \mathbb{J}) \frac{B}{2},
\end{aligned}$$

and expressed with regard to the unperturbed hyperfine energy  $E(\alpha \mathbb{F}, M = 0) = E(\alpha \mathbb{F}, B = 0)$ .

➤ Lande factor  $g_F \equiv g(\alpha \mathbb{F})$  and Zeeman energy splitting of an hyperfine level  $(\alpha \mathbb{F})$  :

$$g(\alpha \mathbb{F}) = \frac{F(F+1) + J(J+1) - I(I+1)}{2 F(F+1)} g(\alpha \mathbb{J}) \quad \implies \quad \Delta E^{(\text{mag})}(\alpha \mathbb{F} M) = g(\alpha \mathbb{F}) M \frac{B}{2}$$

### 7.2.e. Sensitivity of level energies with regard to variations of $\alpha$ (AlphaVariation)

#### Properties, notations & application (not yet fully implemented):

➤ Differential sensitivity parameter  $\Delta q(\delta\alpha; \beta \mathbb{J})$  of an atomic level: For an atomic level  $(\beta \mathbb{J})$ , the level energy depends of course on the fine-structure constant  $\alpha$ . Therefore, an energy shift arises for any variation  $\delta\alpha = \alpha - \alpha_o$  of the fine-structure constant and for a non-zero differential sensitivity parameter  $\Delta q(\delta\alpha; \beta \mathbb{J})$  :

$$\Delta E(\delta\alpha; \beta \mathbb{J}) = \Delta q(\delta\alpha; \beta \mathbb{J}) \left[ \left( \frac{\alpha}{\alpha_o} \right)^2 - 1 \right],$$

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and where  $\alpha_o$  is the (current) reference value of the fine-structure constant.

- **Formal quantum notation:**  $\Delta E(\delta\alpha; \beta\mathbb{J}), \quad \Delta q(\delta\alpha; \beta\mathbb{J}), \quad K(\beta\mathbb{J})$  .
- **Using JAC:** Perform an `Atomic.Computation(..., properties=[AlphaVar, ...], configs=[...], alphaSettings=AlphaVariation.Settings(...), ...)` or call directly functions from the module `AlphaVariation`.
- In JAC, we calculate and tabulate by default the differential sensitivity parameter  $\Delta q(\delta\alpha; \beta\mathbb{J})$  and the enhancement factor  $K(\beta\mathbb{J})$  for all selected levels.

### Further remarks:

- **Fine-structure constant  $\alpha$ :** The dimensionless constant  $\alpha$  becomes dynamical, i.e. explicitly time-dependent, in a number of (quantum-field) theories that go beyond the standard model and general relativity.
- **Search for variations of fundamental constants:** This search is closely related to several, so-far still unexplained phenomena of the Universe, such as the nature of dark matter.
- From the individual level-dependent sensitivity parameters  $\Delta q(\delta\alpha; \beta\mathbb{J})$  and enhancement factors  $K(\beta\mathbb{J})$ , the analogue values for any atomic transition can be simply obtained by taking the sum of the corresponding level parameters.
- Experimentally, a variation of  $\alpha$  are currently measured by monitoring for two ions the ratio of (two) clock frequencies with quite different values of  $K$  .
- **Current limits on the time variation of  $\alpha$ :** Currently, the best laboratory limit of  $\dot{\alpha}$  was obtained from a comparison of the frequency ratio  $\text{Al}^+ / \text{Hg}^+$  over the course of *one* year. This ratio is sensitive to variations in  $\alpha$  because these two optical transitions have quite different sensitivity coefficients with regard to time-variations in the ‘current’ value of the fine-structure constant  $\alpha_o$  (Berengut *et al.*, 2012)

$$q = \left. \frac{d\omega}{dx} \right|_{x=0}, \quad x = \frac{\alpha^2}{\alpha_o^2} - 1,$$

- **Limits on the time variation of  $\alpha$ :** Various proposals have been made in the literature to limit the time variations of  $\alpha$  more tightly, provided that the frequency ratio can be measured with similar accuracy as for  $\text{Al}^+ / \text{Hg}^+$  clock transitions. This is possible for clock transitions with a much higher sensitivity  $q$ , as expected for the optical transitions of the  $\text{Tl}^+$  clock, for multiply-charged Te, Po, and Ce ions as well as for the  $^{229}\text{Th}$  nuclear clock, which all have a rather large sensitivity to the variation of  $\alpha$ .



### Enhancement and sensitivity of atomic levels with regard to variations of $\delta\alpha$ :

- **Enhancement of energy shifts due to  $\delta\alpha$  variations:** The sensitivity of an atomic level energy  $E(\beta\mathbb{J}; \alpha)$  on  $\delta\alpha$  can be re-written also in terms of the dimensionless enhancement factor  $K = 2 \Delta q / \Delta E$  as:

$$\frac{E(\beta\mathbb{J}; \alpha) - E(\beta\mathbb{J}; \alpha_o)}{E(\beta\mathbb{J}; \alpha_o)} = K \frac{\alpha - \alpha_o}{\alpha_o} = K \frac{\delta\alpha}{\alpha_o}$$

- The reasons for  $\delta\alpha$  variations can be of different type, such as temporal, spatial, slow drift, or of oscillatory nature, and it can depend on the gravity-potential or others reasons. The theoretical reasoning about such changes is typically outside of atomic theory.

## 7.3. Further properties, not yet considered in JAC

### 7.3.a. Electron localization function (ELF)

#### Remarks & notations:

- **Electron localization function (ELF):** Becke and Edgecombe (1990) derived a simple *localization function* in order to reveal the atomic shell structure as well as the core, binding and lone electron pairs in simple molecules. **This localization function is an orbital-independent measure and based on the Hartree-Fock pair probability.** Such a concept of localized electron groups is quite different from the typically delocalized Hartree-Fock orbitals; it supports a descriptive chemistry and may thus help identify and distinguish, for instance, between  $\sigma$ - and  $\pi$ -electrons systems.
- **Localization versus Hartree-Fock theory:** The canonical HF orbitals can be transformed unitarily due to different prescriptions and by leaving the total HF energy unchanged. However, these **transformations are generally not unique** and can even result in qualitatively different ‘bondings’ of the electrons. In fact, Hartree-Fock theory is defined by its single-electron density matrices, which are invariant with regard to unitary orbital transformations. Therefore, any meaningful definition of electron localization must be sought in the (two-electron) density matrix itself and not in the orbitals (Becke and Edgecombe, 1990).
- **Electron localization function (ELF):** The ELF depends on the total electronic density, its gradient as well as the kinetic energy density. For all noble gases, this function completely reveals their expected shell structure. The ELF is closely related also to density-functional theory which asserts the total electronic density as the fundamental variable of many-electron theory. Moreover, since the probability density  $\rho_\sigma$  is *nonnegative*, it can be shown that the spherically-averaged pair probability  $D_\sigma$  must vanish for one-electron systems as well as in multi-electron systems that is dominated by a single, localized spin orbital.
- **Electron localization function (ELF):** Becke and Edgecombe (1990) propose a localization function in terms of the spherically-averaged pair probability  $D_\sigma$  and an analogue density  $D_\sigma^o$  of a uniform electron gas with a spin density equal to the local value of  $\rho_\sigma(\mathbf{r})$

$$\text{ELF} = \left[ 1 + \left( \frac{D_\sigma}{D_\sigma^o} \right)^2 \right]^{-1}, \quad D_\sigma^o = \frac{3}{5} (6\pi^2)^{2/3} \rho_\sigma^{5/3}, \quad 0 \leq \text{ELF} \leq 1.$$

Of course, the ratio  $D_\sigma / D_\sigma^o$  refers to a dimension-less localization index that is calibrated with regard to the uniform-density electron gas. Here, the upper limit  $\text{ELF} = 1$  correspond to a perfect localization, while a value  $\text{ELF} = 1/2$  refers to a electron-gas like pair probability.

- **Electron localization function (ELF):** In (quantum) chemistry, the ELF has been found a valuable alternative in the description and interpretation of chemical bindings.

### 7.3.b. Photoemission in external magnetic fields (MagneticFieldInduced)

#### Remarks & notations:

- **Magnetic-field induced transitions (MIT):** These induced transitions occur when an external magnetic field mixes levels with different total angular momenta  $J$ .
- **Transition rates for magnetic-field & hyperfine-induced transitions:** These transition rates are calculated as a sum over (reduced, unperturbed and single-photon) emission amplitudes between fine- or hyperfine-structure levels, respectively, and weighted by the representation of the corresponding expansion coefficients. Special care has to be taken if the radiative widths of the (hyperfine) levels becomes comparable with the level splitting which, at least in principle, then requires a common treatment of both, the hyperfine and magnetic-field interactions. The corresponding changes in the line intensities is also known as radiation damping in the literature.
- **Application of MIT:** Hyperfine & magnetic-field induced transitions have been investigated for different atomic systems both, theoretically and experimentally. In plasma diagnostics, these transitions may help in the determination of electron densities, isotope compositions as well as magnetic fields. A proper implementation of these induced transitions also help analyze spectra from electron-beam ion trap (EBIT) sources as well as the spectra of magnetic stars.
- **Application of MIT:** MIT may help in plasma diagnostics in order to determine the local strength of magnetic fields in plasmas, especially if the transitions is otherwise a forbidden atomic line.

## Amplitudes and rates:

- **Magnetic-field induced transitions (MIT):** In an external magnetic field, the direction of the  $\mathcal{B}$ -field is typically chosen as quantization axis. For this particular choice, only states with the same parity and magnetic quantum number  $M_J$ , but with different total angular momentum  $J$  from different  $J$  will mix with each other

$$|\alpha PM; \mathcal{B}\rangle \equiv |\psi_\alpha(PM)\rangle = \sum_{\bar{\beta}=1} c_{\bar{\beta}}(\alpha; \mathcal{B}) |\bar{\beta} \mathbb{J}M, \mathcal{B}=0\rangle, \quad c_{\bar{\beta}}(\alpha; \mathcal{B}) = \frac{\langle \bar{\beta} PM; \mathcal{B}=0 | H^{(\mathcal{B}\text{-field})} | \alpha PM; \mathcal{B} \rangle}{E(\bar{\beta} PM; \mathcal{B}=0) - E(\alpha PM; \mathcal{B})}$$

and where  $\bar{\beta} = (\beta J_\beta)$  and the mixing coefficients  $c_{\bar{\beta}}(\alpha; \mathcal{B})$  are here given in first-order perturbation theory.

- **Oscillator strength for transitions between hyperfine levels:** If the (off-diagonal) hyperfine interaction is negligible between neighbored fine-structure levels  $(\alpha \mathbb{J})$ , the absorption oscillator strengths for the electric-dipole transitions between two hyperfine levels  $\alpha_i(IJ_i)\mathbb{F}_i \rightarrow \alpha_f(IJ_f)\mathbb{F}_f$  can be expressed in terms of the transition energy  $\Delta E = (E(\alpha_i(IJ_i)\mathbb{F}_i) - E(\alpha_f(IJ_f)\mathbb{F}_f))$  and the associated fine-structure amplitudes by

$$\begin{aligned} gf(\alpha_i(IJ_i)\mathbb{F}_i \rightarrow \alpha_f(IJ_f)\mathbb{F}_f) &= \frac{2}{3} \Delta E \left| \langle \alpha_f(IJ_f)\mathbb{F}_f \parallel \mathbb{O}^{(\text{E1, absorption})} \parallel \alpha_i(IJ_i)\mathbb{F}_i \rangle \right|^2 \\ &= \frac{2}{3} \Delta E (2F_i + 1) (2F_f + 1) \left\{ \begin{matrix} J_i & I & F_i \\ F_f & 1 & J_f \end{matrix} \right\} \left| \langle \alpha_i \mathbb{J}_i \parallel \mathbb{O}^{(\text{E1, absorption})} \parallel \alpha_f \mathbb{J}_f \rangle \right|^2. \end{aligned}$$

In this case, the distribution of the oscillator strength among the hyperfine-resolved transitions is just determined geometrically by the Wigner 6- $j$  symbol, i.e. due to the  $(IJ)F$  coupling of the nuclear spin and the total electronic angular momentum.

- **Oscillator strength for transitions between hyperfine levels:** If, more generally, the hyperfine coupling between neighbored fine-structure levels  $\{|\alpha \mathbb{J}\rangle\}$  is not negligible, the expansion coefficients  $c_{\bar{\beta}}(\alpha \mathcal{B})$  of the hyperfine levels in the given ASF basis need to be taken into account. Then, the absorption oscillator strength for the electric-dipole transitions between two hyperfine levels  $\alpha_i(IJ_i)\mathbb{F}_i \rightarrow \alpha_f(IJ_f)\mathbb{F}_f$

can still be written in terms of the associated fine-structure E1 transition amplitudes as (Andersson *et al.*, 2006)

$$\begin{aligned}
 gf(\alpha_i \mathbb{F}_i \rightarrow \alpha_f \mathbb{F}_f; \mathcal{B}) &= \frac{2}{3} \Delta E \left| \sum_{\bar{\beta}_i} \sum_{\bar{\beta}_f} c_{\bar{\beta}_i}(\alpha_i; \mathcal{B}) c_{\bar{\beta}_f}(\alpha_f; \mathcal{B}) \langle \beta_i(IJ_i) \mathbb{F}_i \| \mathbb{O}^{(\text{E1, absorption})} \| \beta_f(I, J_f) \mathbb{F}_f \rangle \right|^2 \\
 &= \frac{2}{3} \Delta E (2F_i + 1) (2F_f + 1) \left| \sum_{\beta_i J_i} \sum_{\beta_f J_f} c_{\bar{\beta}_i}(\alpha_i; \mathcal{B}) c_{\bar{\beta}_f}(\alpha_f; \mathcal{B}) \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix} \langle \beta_i \mathbb{J}_i \| \mathbb{O}^{(\text{E1, absorption})} \| \beta_f \mathbb{J}_f \rangle \right|^2.
 \end{aligned}$$

Here, the summation runs over all fine-structure levels in the representation of the initial and final hyperfine levels. Moreover, interferences occurs if different terms in this summation are of similar size, and this may lead to a sizeable redistribution of the oscillator strengths from the different fine-structure transitions, which can be formed between selected fine-structure levels in the ASF representations above.

### 7.3.c. Stark shifts and (dc) ionization rates in static electric fields

#### Remarks & notations:

- **Stark shift:** The Stark shift of an atomic level generally refers to the change of its level energy in an external electric field. Apart from the dc Stark shift in static fields, the frequency-dependent (ac) Stark shift in a monochromatic light field has attracted much recent attention. The dc Stark shift was first observed by Stark in 1913, and detailed measurements were restricted indeed for a rather long time (until ~ 1960s) to such static electric fields. The frequency-dependent (ac) Stark shift due to laser irradiation was first observed by Bonch-Bruевич and coworkers in 1969.
- **Static (dc) Stark shift:** When an atom or molecule is exposed to a (constant) external electric field  $\mathcal{E} \neq \mathcal{E}(t)$ , its discrete level spectrum turns into a **spectrum of resonances with complex energies**. These energies are the eigenvalues of a non-Hermitian Hamiltonian (Schrödinger equation), and whose eigenfunctions are asymptotically outgoing-waves. The shift and broadening of the (discrete) bound energies are also known as **LoSurdo-Stark effect** (Nicolaidis and Themelis, 1992).
- **Static (dc, electric-dipole) Stark Shift:** An atom in the level  $(\alpha JM)$  in a homogeneous static (dc) electric-dipole field  $\mathcal{E} = \mathcal{E} \mathbf{e}_z$

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experiences a shift due to the coupling to the induced electric-dipole moment

$$\Delta E^{(\text{dc Stark})}(\mathcal{E}; \alpha \mathbb{J} M) \propto -\frac{1}{2} \alpha^{(\text{static})}(\alpha \mathbb{J} M) \mathcal{E}^2 = -\frac{1}{2} \alpha^{(\text{ac E1})}(\omega = 0; \alpha \mathbb{J} M) \mathcal{E}^2,$$

and which is **quadratic in the electric field**. Here,  $\alpha^{(\text{static})}(\alpha \mathbb{J})$  is also called the **static electric-dipole polarizability**. Similarly, for an atom in the hyperfine level  $(\alpha(IJ) \mathbb{F})$ , the static (dc) Stark Shift is quadratic

$$\Delta E^{(\text{dc Stark})}(\mathcal{E}; \alpha \mathbb{F}) \propto -\frac{1}{2} \alpha^{(\text{ac E1})}(\omega = 0; \alpha \mathbb{F}) \mathcal{E}^2,$$

and is often briefly referred to as **quadratic Stark shift**.

- **Static (dc) Stark shift:** In a static external electric field  $\mathcal{E} \parallel \mathbf{e}_z$ , a degenerate level  $(\alpha \mathbb{J})$  with energy  $E_o$  generally splits into  $(2J + 1)$  states

$$E(\mathcal{E}; \alpha \mathbb{J}) = E_o + \Delta E^{(\text{dc Stark})}(\mathcal{E}; \alpha \mathbb{J} M)$$

since each magnetic sublevel may acquire a different energy shift  $\Delta E^{(\text{dc Stark})}(\mathcal{E}; \alpha \mathbb{J}_o M)$ . These shifts are quite small as all field strengths in the laboratory are typically small when compared to the atomic fields. Typical (dc) Stark shifts do not exceed 1 Kayser = 1/cm, although these shifts can be much larger ( $\sim 10^2 \dots 10^4$ ) than most natural line widths.

- **Perturbation expansions of the static (dc) Stark shift:** Since, even for an arbitrarily weak dc field, all atomic states become unstable with regard to *ionization*, **all perturbation (series) expansions are divergent**. In these expansions, in fact, the first terms in the series often decrease before they start to diverge; therefore, a summation should be done only up to the smallest term. At least for (non-relativistic) hydrogenic atoms, dc Stark shifts calculations are fairly well understood and are in good agreement with experiment, cf. Delone and Krainov (1999).
- **Static electric-quadrupole (dc) Stark shift & electric-quadrupole Hamiltonian:** A gradient of a static (external) electric field  $\mathcal{E}$  interacts of course with the (induced) quadrupole moment of the atom and gives rise to a static electric-quadrupole (dc) Stark shift. This interaction can be described by the Hamiltonian

$$\mathbb{H}^{(\text{dc EQM})} = (\nabla \mathcal{E})^{(2)} \cdot Q^{(2)} = \sum_{q=-2}^2 (-1)^q (\nabla \mathcal{E})_q^{(2)} Q_{-q}^{(2)},$$

where  $(\nabla \mathcal{E})^{(2)}$  is the vector gradient at the position of the atom (a second-rank tensor) and  $Q^{(2)}$  the quadrupole tensor of the atom. In the frame of the principal axis of the induced charge distribution (quadrupole tensor), the Hamiltonian  $\mathbb{H}^{(\text{dc EQM})}$  can be expressed in terms of just three spherical tensor components  $Q_2^{(2)}, Q_0^{(2)}, Q_{-2}^{(2)}$  or, equivalently, **two real parameters which characterize the strength and asymmetry of the field gradient**. The **static electric-quadrupole (dc) Stark shift**, or briefly electric-quadrupole shift, of an atomic fine-structure level  $|\alpha \mathbb{J} M\rangle$  or hyperfine level  $|\alpha(IJ) \mathbb{F} M\rangle$  is then obtained by

$$\langle \alpha \mathbb{J} M | \mathbb{H}^{(\text{dc EQM})} | \alpha \mathbb{J} M \rangle, \quad \langle \alpha(IJ) \mathbb{F} M | \mathbb{H}^{(\text{dc EQM})} | \alpha(IJ) \mathbb{F} M \rangle,$$

and can be really expressed in terms of the strength and asymmetry parameters of the Hamiltonian, the Euler angles to convert the principal-axis into the laboratory frame (that defines the quantization axis) as well as the reduced matrix elements  $\langle \alpha \mathbb{J} || Q^{(2)} || \alpha \mathbb{J} \rangle$  of the quadrupole tensor with regard to the level of interest.

- **Static (dc) Stark shift measurements:** In the laboratory, static electric fields are often limited to  $\lesssim 10^5$  V/cm and, hence, are much smaller than the inner-atomic fields  $\sim 10^9$  V/cm. Therefore, almost all (dc) Stark shifts refer to rather small corrections to the level energies and can be readily calculated perturbatively, if these corrections are considered at all in applications.
- **Relation between static (dc) and frequency-dependent (ac) polarizabilities:** The static (dc) and frequency-dependent (ac) — scalar, vector and tensor — polarizabilities are usually related to each other by the simple replacement

$$\frac{1}{\Delta E} \quad \longleftrightarrow \quad \frac{\Delta E}{(\Delta E)^2 - \omega^2}.$$

- **Static (dc) Stark shift *versus* ionization:** If the dc electric field is weak, when compared with the atomic field seen by the electrons, the **ionization width** (imaginary part of the total energy) is much smaller than the quadratic (dc) Stark shift. For such weak fields, therefore, a well-defined (dc) Stark shift is observed for all level energies. However, such a distinct (dc) Stark shift is no longer true if the dc field becomes comparable to field of the valence electrons, and which then leads to a rapid ionization. For hydrogenic ions with energy  $E_n = Z^2/n^2$ , the dc electric field become in a 1D ionization model equal to the Coulomb field for

$$\mathcal{E}(n) = \frac{E_n^2}{4Z} = \frac{Z^3}{16n^4}.$$

More generally, however, this critical field strength depends on both,  $n$  and  $\ell$ , in a more rigorous numerical treatment (for instance, in parabolic coordinates).

### Neutral atoms in static (dc) fields:

- **Complex-eigenvalue Schrödinger equation:** The system "neutral atom + static (dc) field" defines a rather complicated many-electron problem. Because of the (additional) time-independent field, the discrete spectrum of the atom changes into a resonance spectrum whose states are obtained as solutions of a complex-eigenvalue Schrödinger equation

$$(H - z_o) \psi = 0, \quad H = H^{(\text{atom})} + \sum_i \mathcal{E} \cdot \mathbf{r}_i, \quad z_o = E_o + \Delta(\mathcal{E}) - \frac{i}{2} \Gamma(\mathcal{E}).$$

- **Solution of the complex eigenvalue equation:** This equation can be solved in terms of square-integrable function spaces, if the transformation  $\rho = r e^{i\theta}$  is applied.
- This coordinate rotation for  $\rho$  has been applied to the Hamiltonian operators for the computation of the LoSurdo-Stark ground-state resonance of hydrogen atoms, and the solution was achieved by **direct diagonalization of the non-Hermitian Hamiltonian on a large square-integrable basis set**. However, such a direct diagonalization of the the non-Hermitian Hamiltonian matrix is quite unrealistic for the decaying states of many-electron atoms and molecules.

### Static (dc) Stark shifts for hydrogenic ions:

- **Static (dc) Stark shift for hydrogenic ions:** For non-relativistic hydrogenic ions, the quadratic (second-order, dc) Stark shift can be evaluated analytically in terms of the principal and orbital quantum numbers and are given by Delone and Krainov (1999) as

$$\Delta E^{(\text{dc Stark})}(\mathcal{E}; n\ell m) = -\frac{1}{2} \left[ \alpha^{(\text{scalar})}(n\ell) + \alpha^{(\text{tensor})}(n\ell) \frac{3m^2 - j(j+1)}{j(2j-1)} \right]$$

$$\alpha^{(\text{scalar})}(n\ell) = n^6 + \frac{7}{4} n^4 (\ell^2 + \ell + 2) \text{ a.u.}, \quad \alpha^{(\text{tensor})}(n\ell) = -\frac{1}{4/2\ell + 3} n^4 (3n^2 + 11\ell^2 + 11\ell - 9) \text{ a.u.}$$

Both, the scalar and tensor parts of the polarizabilities are of the same order, although the tensor part vanishes for  $\ell = 0$ .



### 7.3.d. Frequency-dependent (ac) Stark shifts (AcStarkShift)

#### Remarks & notations:

- **Frequency-dependent (ac) Stark shift:** The frequency-dependent, dynamic Stark shift is caused by the interaction of an atom with the electro-magnetic field; it can be induced by a laser pulses but also by a single-photon wave packet.
- **(ac) Stark shifts:** An intense light field also shifts the energy levels of the atom. In a time-harmonic laser field, these frequency-dependent (ac) Stark shifts generally depend on the frequency, intensity and polarization of the incident light as well as the atomic levels of interest.
- **Role of frequency-dependent (ac) Stark shifts:** Modern laser fields readily become comparable or even exceed the atomic field strength  $\sim 10^9$  V/cm. Therefore, the interaction with such lasers often leads to remarkable changes in the separation and sequence of levels and also requires to develop non-perturbative computational methods. Even for quite large (ac) Stark shifts, however, the level broadening often remains moderate and keeps the concept of atomic levels in many experiments alive.
- **Static (dc) versus frequency-dependent (ac) Stark shifts:** In general, the dc and ac Stark shifts of atomic levels differ quite drastically from each other. While a weak static field simply shifts the energy levels, (1) a time-harmonic (ac) field also splits even non-degenerate states into (quasi-) energy states that are shifted with regard to the unperturbed level and that are separated by the frequency of the light field (formation of side bands). Despite of these shifts, however, (2) some atomic transitions frequencies are apparently not shifted for a certain frequency and intensity of the incident light; these (so-called) magic wavelength (frequencies) usually occur for different pairs of hyperfine levels of an atomic bound-state transitions. (3) For short few-cycle pulses, both the concept of quasi-energy levels (sidebands) as well as a well-defined (ac) Stark shifts gets lost.
- **Frequency-dependent (ac) Stark shift of atomic levels:** For time-harmonic electro-magnetic fields with well-defined frequency  $\omega$  and field strength  $\mathcal{E}$ , each atomic level is shifted by the (ac) Stark shift  $\Delta E^{(\text{acStark})}(\omega; \alpha JM)$  to its quasi-energy and is accompanied by a spectrum of quasi-harmonics,  $E^{(\text{quasi-energy})} \pm k\omega$  (sidebands). Of course, this frequency-dependent (ac) Stark shift and the strength of the sidebands depend on the strength and frequency of the incident field. Therefore, there is a clear difference in the level structure of atoms for a static and time-harmonic electric field.
- **Frequency-dependent (ac) Stark shift of atoms in weak, high-frequency fields:** At high laser frequencies, e.g. for  $\hbar\omega \gg \Delta E_{\nu,\nu'}$  much larger than the separation energy to neighbored atomic states, only one quasi-harmonic ( $k = 0$ ) can be excited, and this simply leads to the observed (ac) Stark shift  $\Delta E^{(\text{acStark})}(\omega; \alpha JM)$  of atomic levels. To a very good approximation, this frequency-dependent (ac) Stark shift is proportional to the square of the field strength (amplitude),  $\Delta E^{(\text{acStark})}(\omega; \alpha JM) \propto \mathcal{E}^2$  and is equal also to the (classical vibrational) energy of a free electron for a harmonic and linearly-polarized electric field,  $E^{(\text{vibration})} = \mathcal{E}^2/(4\omega^2)$ . For such weak, high-frequency fields, indeed, the atomic level structure is similar to a static (dc) field. In such a weak field, moreover, most atoms experience a negative shift

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of their ground state energy, i.e. the ionization potential slightly increases or, in other words, the atoms are slightly stronger bound in a weak, high-frequency fields.

- **(ac) Stark shifts in intense laser fields:** The concept of well-defined (ac Stark) level shifts, however, get lost – more or less completely, when the oscillation amplitude of a (free) electron in a laser field,  $a = \mathcal{E}/\omega$ , becomes comparable or even larger than the size of the atom. For such fields, the known level structure of the atom breaks down and the **electron dynamics must be described by methods from strong-field theory, such as the strong-field approximation**. While this strong-field regime is nowadays easily reached for low, infrared laser frequencies, much less is known about this breakdown for optical frequencies and moderate-to-high laser intensities.
- **Magic wavelength:** In atom trapping, this concept refers to the search and use of a laser (field) with proper frequency and intensity, for which the ground and excited state of the trapped atom experience an equal frequency-dependent (ac) Stark shift. Such a laser then leaves the atomic transition basically unaffected. Obviously, such a **magic wavelength requires a proper choice of the frequency and intensity of the laser as well as a proper pair of magnetic sub-levels of the atom**.
- **Magic wavelength:** The ac Stark shift of a clock transition is mainly determined by the frequency-dependent (ac electric-dipole) polarizabilities of the clock states. The (so-called) **magic wavelengths** of a clock transition can be determined by finding the frequencies where the (ac E1) polarizabilities of the two clock states are the same.
- **Trapping of atoms:** For atom trapping, **far-off resonant laser fields are often applied** in order to ensure low scattering rates and, hence, rather long coherence times.
- **Application of frequency-dependent (ac) Stark shifts:** These shifts are required to efficiently encode, process and store quantum information in atomic systems by using resonant or near-resonant light. Since neutral atoms only weakly couple to their environments, the coherent manipulation of atomic states might be robust enough against external perturbations. In the past, however, most previous computations were performed only for static (dc) Stark shifts.
- **Importance of the frequency-dependent (ac) Stark shift for ionization processes:** The frequency-dependent (ac) Stark shift is relevant for different research fields in physics and beyond because of: (1) an increase of the ionization potential of *dressed* atoms, that may become comparable or even exceed the photon energy (of the external field) and that may strongly affect the tunnel ionization behaviour and rate; (2) the modified threshold intensity (barrier suppression) at which all atoms are basically ionized, although this ionization is often achieved already at the front of the laser pulse.

### Ionization regimes in time-varying electro-magnetic fields:

- **Keldish adiabacity parameter  $\gamma_K$ :** Different strong-field ionization mechanisms can be distinguished for different laser frequencies  $\omega_L$ , (electric) field strength  $\mathcal{E}_o = |\mathcal{E}_o|$  as well as atomic ionization potentials  $I_p$ . They are often distinguished by the **Keldish adiabacity parameter**,  $\gamma_K = \omega \sqrt{2I_p}/\mathcal{E}_o$ .
- **Multiphoton regime,  $\gamma_K \gg 1$ :** This regime is realized at high laser frequency and low or moderate field strength, and it gives rise to a power law for the ionization rate,  $\Gamma \propto \mathcal{E}_o^n$ .
- **Tunnel regime,  $\gamma_K \ll 1$ :** This regime occurs at low laser frequency and a high-field strength, and it gives rise to an **exponential dependence of  $\Gamma$  on  $\mathcal{E}_o$** . In the tunnel regime, the ionization is often considered as a quasi-static process due to the low frequency, and the total ionization yield is obtained as integral over the time-dependent field strength:

$$A = 1 - \exp \left[ 1 - \int_{-\infty}^{\infty} dt \Gamma(\mathcal{E}_o(t)) \right].$$

- **Atomic structure computations:** In the tunnel regime, atomic structure computation can provide reliable predictions for both, the Stark shifts in an (quasi-static) electric field as well as for the ionization rates.
- **Ammosov-Delone-Krainov (ADK) formula:** This formula for the ionization rate has often been used for many-electron atoms and has been extended also towards molecules.
- **Quasi-static regime:** For  $\gamma_K \ll 1$ , one often further distinguishes between the **tunnel ionization** and the **above-barrier ionization** due to the (semi-classical) field strength  $\mathcal{E}^{(\text{above-barrier})} = I_p^2/4$ . From a simplified classical viewpoint, the electron can leave the atom without tunneling for  $\mathcal{E}_o > E^{(\text{above-barrier})}$  owing to the suppression of the (atomic) Coulomb potential. In practice, however, this *barrier* is not sharp since an (scattered) outgoing electron is still partly reflected even for a classical suppressed barrier.
- **(Quasi-) Static ionization rates:** Within the tunneling regime, a variety of semiempirical expressions exist for the static ionization rates  $\Gamma(\mathcal{E}_o)$ . Many of them are based on Landau's seminal formula for the ionization rate of the hydrogen atom in its ground state, such as the ADK rule.
- **Limitations of the ADK rate:** A more rigorous treatment of the static ionization rates is often preferable, since the ADK and similar formulas neglect both, the exchange interaction and correlation effects, and **rather little is known so far how well these semi-empirical formulas work quantitatively**.

### Computation of second-order (ac) Stark shifts:

- **Perturbation expansions for the frequency-dependent (ac) Stark shift:** Most often, the frequency-dependent (ac) Stark shift of a level  $(\alpha\mathbb{J})$  with energy  $E_o$  is described in second-order perturbation theory and within the electric-dipole approximation due to the absorption and re-emission of a laser photon. A necessary condition for such a perturbative treatment can be given in terms of the laser frequency  $\omega$ , the field strength  $\mathcal{E}$ , the energy separation  $|E_o - E_\nu|$  from neighbored levels  $(\alpha_\nu\mathbb{J}_\nu)$  as well as the associated dipole matrix elements  $\langle \alpha_\nu\mathbb{J}_\nu | \mathbb{D} | \alpha\mathbb{J} \rangle$

$$| \langle \alpha_\nu\mathbb{J}_\nu | \mathbb{D} | \alpha\mathbb{J} \rangle | \mathcal{E} \ll | \omega - \omega_{nm} |, \quad \Longleftrightarrow \quad \begin{cases} | \langle \alpha_\nu\mathbb{J}_\nu | \mathbb{D} | \alpha\mathbb{J} \rangle | \mathcal{E} \ll \omega & \text{or} \\ | \langle \alpha_\nu\mathbb{J}_\nu | \mathbb{D} | \alpha\mathbb{J} \rangle | \mathcal{E} \ll |E_o - E_\nu|. \end{cases}$$

Obviously, the perturbation by the field (with strength  $\mathcal{E}$ ) must neither exceed the laser frequency nor the energy separation to neighbored levels.

- **Second-order (ac) Stark shift of a non-degenerate atomic state  $|\alpha\mathbb{J}M\rangle$ :** For a light field  $\mathcal{E}(t) = \mathcal{E} \mathbf{u}(t)$  with  $\mathcal{E} =$  (complex) constant far from resonance, the second-order (ac) Stark shift of a level  $|\alpha\mathbb{J}M\rangle$  with energy  $E_o$  is given in electric-dipole approximation by

$$\Delta E^{(\text{ac Stark})}(\omega; \alpha_o\mathbb{J}_oM_o) = -\frac{|\mathcal{E}|^2}{4} \sum_{\nu} \Re \left( \frac{|\langle \alpha_\nu\mathbb{J}_\nu M_\nu | \mathbf{u} \cdot \mathbb{D} | \alpha\mathbb{J}M \rangle|^2}{E_\nu - E_o - \omega - i\Gamma_{\nu o}/2} + \frac{|\langle \alpha\mathbb{J}M | \mathbf{u} \cdot \mathbb{D} | \alpha_\nu\mathbb{J}_\nu M_\nu \rangle|^2}{E_\nu - E_o + \omega + i\Gamma_{\nu o}/2} \right),$$

and where  $\Gamma_{\nu o} = \Gamma_\nu + \Gamma_o$  is the sum of the spontaneous decay widths of these two levels. The states  $|\alpha\mathbb{J}M\rangle$  and  $|\alpha_\nu\mathbb{J}_\nu M_\nu\rangle$  here refer to the *unperturbed* states with energies  $E_o$  and  $E_\nu$ , respectively. Here, the frequency-dependent (ac) Stark shift is given in the electric-dipole approximation due to the use of the dipole operator  $\mathbb{D}$ .

- **Second-order (ac) Stark shift of a hyperfine state  $|\alpha(IJ)\mathbb{F}M\rangle$ :** The (ac) Stark shift of a hyperfine state  $|\alpha(IJ)\mathbb{F}M\rangle$  can be expressed in terms of the reduced tensorial (frequency-dependent, ac) polarizabilities as

$$\Delta E^{(\text{ac Stark})}(\omega; \alpha(IJ)\mathbb{F}M) = \frac{|\mathcal{E}|^2}{4} \sum_{K=0,1,2} (-1)^K [\mathbf{u}^* \otimes \mathbf{u}]_0^{(K)} (-1)^{F-M} \begin{pmatrix} F & K & F \\ -M & 0 & M \end{pmatrix} \alpha^{(K)}(\omega; \alpha(IJ)\mathbb{F}).$$

Here, the *scalar* (character of the) energy shift is ensured by the Wigner 3- $j$  symbol which selects the  $q = 0$  components of the three tensor products due to  $-M + q + M = 0$ . Moreover, the  $\alpha^{(K)}$  are referred to also as reduced tensorial (ac) polarizabilities.

- **Second-order (ac) Stark shift of hyperfine state  $|\alpha(IJ)\mathbb{F}M\rangle$  :** For a given geometry of the wave vector  $\mathbf{k}$  and polarization vectors as well as a given quantization axis ( $z$ -axis), the frequency-dependent (ac) Stark shift can be parametrized in terms of the (conventional) scalar, vector and tensor (frequency-dependent) polarizabilities of a given hyperfine level  $(\alpha(IJ)\mathbb{F})$

$$\begin{aligned}\Delta E^{(\text{ac Stark})}(\omega; \alpha(IJ)\mathbb{F}M) &= \frac{\mathcal{E}^2}{4} \left[ \alpha^{(\text{scalar})}(\alpha(IJ_o)\mathbb{F}) + P_3 \cos \vartheta_k \frac{M}{2F} \alpha^{(\text{vector})}(\omega; \alpha(IJ)\mathbb{F}) \right. \\ &\quad \left. + \left( \frac{3 \cos^2 \vartheta_p - 1}{2} \right) \frac{3M^2 - F(F+1)}{F(2F-1)} \alpha^{(\text{tensor})}(\omega; \alpha(IJ)\mathbb{F}) \right] \\ &= \frac{\mathcal{E}^2}{4} \alpha^{(\text{ac E1})}(\omega; \alpha(IJ)\mathbb{F}M)\end{aligned}$$

$$\begin{aligned}\alpha^{(\text{ac E1})}(\omega; \alpha(IJ)\mathbb{F}M) &= \alpha^{(\text{scalar})}(\omega; \alpha(IJ)\mathbb{F}) + P_3 \cos \vartheta_k \frac{M}{2F} \alpha^{(\text{vector})}(\omega; \alpha(IJ)\mathbb{F}) \\ &\quad + \left( \frac{3 \cos^2 \vartheta_p - 1}{2} \right) \frac{3M^2 - F(F+1)}{F(2F-1)} \alpha^{(\text{tensor})}(\omega; \alpha(IJ)\mathbb{F}).\end{aligned}$$

However, these expressions only apply if  $J$  is a good quantum number for the hyperfine levels under consideration. The same relation remains valid, if the scalar, vector and tensor polarizabilities contains 3rd and higher-order contributions in the perturbative treatment of the (ac) Stark shift, for instance, due to the hyperfine interaction to the polarizabilities, cf section 7.3.f.

- **Frequency-dependent (ac) clock shift:** For a clock (absorption) transition  $\alpha_i F_i M_i \rightarrow \alpha_f F_f M_f$  between two hyperfine magnetic substates, the total (frequency-dependent, ac) Stark shift is simply the difference of the individual shifts and is given by

$$\Delta \nu = \frac{1}{\pi} [\Delta E^{(\text{ac Stark})}(\omega; \alpha_f F_f M_f) - \Delta E^{(\text{ac Stark})}(\omega; \alpha_i F_i M_i)] = \frac{1}{\pi} \frac{|\mathcal{E}|^2}{4} [\alpha^{(\text{ac E1})}(\omega; \alpha_f F_f M_f) - \alpha^{(\text{ac E1})}(\omega; \alpha_i F_i M_i)]$$

- **Comparison of polarizabilities & (ac) Stark shifts:** Since both, the frequency-dependent polarizabilities & (ac) Stark shifts depend on the fine-structure level or hyperfine levels as well as the frequency and polarization of the incident light, great care has to be taken to compare such data from the literature. In many numerical computations, moreover, the resonance wavelengths and reduced matrix elements are often taken from different sources. Missing information about the underlying formalism as well as the application of semi-empirical data often hamper a direct comparison of the underlying polarizabilities.

### (ac) Stark shift Hamiltonian:

- **Second-order (ac) Hamiltonian shift operator in electric-dipole approximation:** The (ac) Stark shift of a non-degenerate atomic state  $|\alpha \mathbb{J} M\rangle$  with unperturbed energy  $E_o$  can be expressed also as expectation value of an (ac) Stark shift Hamiltonian

$$\mathbb{H}^{(\text{ac Stark})} = \frac{|\mathcal{E}|^2}{4} [(\mathbf{u}^* \cdot \text{op}D) \mathbb{R}_+ (\mathbf{u} \cdot \mathbb{D}) + (\mathbf{u} \cdot \mathbb{D}) \mathbb{R}_- (\mathbf{u}^* \cdot \mathbb{D})], \quad \Delta E^{(\text{ac Stark})}(\omega, \alpha \mathbb{J} M) = \langle \alpha \mathbb{J} M | \mathbb{H}^{(\text{ac Stark})} | \alpha \mathbb{J} M \rangle$$

$$\mathbb{R}_+ = - \sum_{\nu} \Re \left( \frac{1}{E_{\nu} - E_o - \omega - i \Gamma_{\nu o}/2} \right) |\alpha_{\nu} \mathbb{J}_{\nu} M_{\nu}\rangle \langle \alpha_{\nu} \mathbb{J}_{\nu} M_{\nu}|$$

$$\mathbb{R}_- = - \sum_{\nu} \Re \left( \frac{1}{E_{\nu} - E_o + \omega + i \Gamma_{\nu o}/2} \right) |\alpha_{\nu} \mathbb{J}_{\nu} M_{\nu}\rangle \langle \alpha_{\nu} \mathbb{J}_{\nu} M_{\nu}|.$$

Although this (ac) Stark shift Hamiltonian is adopted from the shift of a nondegenerate level, **it is often assumed that  $\mathbb{H}^{(\text{ac Stark})}$  can be applied generally**, i.e. for degenerate levels as well as for the interaction among nondegenerate and degenerate levels. This assumption is consistent with the expression that is obtained in second-order perturbation theory with the perturbation  $\mathbb{H}^{(\text{E1})}$  for the electric-field interaction.

- **Relation between reduced tensorial and conventional tensorial polarizabilities:** The diagonal matrix elements of  $\mathbb{H}^{(\text{ac Stark})}$  of a given fine-structure level  $(\alpha \mathbb{J})$  can be expressed also in terms of the (cartesian) vector products of the polarization and total angular momentum operators as well as the **conventional frequency-dependent scalar, vector and tensor polarizabilities** of the given fine-structure level by (cf. Kien *et al.*, 2013)

$$\begin{aligned} & \langle \alpha \mathbb{J} | \mathbb{H}^{(\text{ac Stark})} | \alpha \mathbb{J} \rangle \\ &= \frac{|\mathcal{E}|^2}{4} \left( \alpha^{(\text{scalar})}(\omega; \alpha \mathbb{J}) - i \alpha^{(\text{vector})}(\omega; \alpha \mathbb{J}) \frac{[\mathbf{u}^* \times \mathbf{u}] \cdot \mathbf{J}}{2J} + \alpha^{(\text{tensor})}(\omega; \alpha \mathbb{J}) \frac{3[(\mathbf{u}^* \cdot \mathbf{J})(\mathbf{u} \cdot \mathbf{J}) + (\mathbf{u} \cdot \mathbf{J})(\mathbf{u}^* \cdot \mathbf{J}) - 2\mathbf{J}^2]}{2J(2J-1)} \right) \end{aligned}$$

$$\alpha^{(\text{scalar})}(\omega; \alpha\mathbb{J}) = \frac{1}{\sqrt{3(2J+1)}} \alpha^{(0)}(\omega; \alpha\mathbb{J}),$$

$$\alpha^{(\text{vector})}(\omega; \alpha\mathbb{J}) = -\sqrt{\frac{2J}{(J+1)(2J+1)}} \alpha^{(1)}(\omega; \alpha\mathbb{J})$$

$$\alpha^{(\text{tensor})}(\omega; \alpha\mathbb{J}) = \sqrt{\frac{2J(2J-1)}{3(J+1)(2J+1)(2J+3)}} \alpha^{(2)}(\omega; \alpha\mathbb{J}).$$

Here, the  $\alpha^{(K)}(\omega; \alpha\mathbb{J})$  are referred to as the reduced tensorial polarizability of the fine-structure level  $(\alpha\mathbb{J})$ .

- **Combined hyperfine and (ac) Stark shift interaction:** For a non-zero nuclear spin  $I$ , each (fine-structure) state  $|\alpha\mathbb{J}M\rangle$  is disturbed by both, the hyperfine interaction with the nucleus and the classical light field of the laser. This can be described perturbatively by the **combined interaction Hamiltonian**

$$\mathbb{H}^{(\text{hfs} + \text{Stark})} = \mathbb{H}^{(\text{hfs})} + \mathbb{H}^{(\text{ac Stark})},$$

and for which the Hamiltonian matrix can be calculated and diagonalized in the (unperturbed) hyperfine basis  $\{|\alpha(IJ)FM_F\rangle\}$ .

- **Matrix elements of  $\mathbb{H}^{(\text{ac Stark})}$  in an (unperturbed) hyperfine basis:** In an (unperturbed) hyperfine basis  $\{|\alpha FM\rangle \equiv |\alpha(IJ)FM\rangle\}$  of an electronic level  $(\alpha\mathbb{J})$ , these matrix elements are given by (Kien *et al.*, 2013)

$$\begin{aligned} & \langle \alpha FM | \mathbb{H}^{(\text{ac Stark})} | \alpha' F' M' \rangle \\ &= \frac{|\mathcal{E}|^2}{4} \sum_{K=0,1,2,q} [\alpha^{(K)}(\omega; \alpha\mathbb{J})] [\mathbf{u}^* \otimes \mathbf{u}]_q^{(K)} (-1)^{J+I+K+q-M} \sqrt{(2F+1)(2F'+1)} \begin{pmatrix} F & K & F' \\ M & q & -M' \end{pmatrix} \begin{Bmatrix} F & K & F' \\ J & I & J \end{Bmatrix}, \end{aligned}$$

and where  $\alpha^{(K)}(\omega; \alpha\mathbb{J})$  is referred to as the **reduced tensorial and frequency-dependent (or dynamical) polarizabilities of the atom in its fine-structure level  $(\alpha\mathbb{J})$** . These tensorial polarizabilities comprise the reduced scalar ( $K=0$ ), vector ( $K=1$ ) and tensor ( $K=2$ ) polarizabilities, and these reduced polarizabilities also just represent the real parts of the complex polarizability. The corresponding **imaginary parts of the polarizability are related to the (Rayleigh) scattering rate** of an atom in its fine-structure level  $(\alpha\mathbb{J})$ .

- **Matrix elements of  $\mathbb{H}^{(\text{hfs} + \text{Stark})}$  in an (unperturbed) hyperfine basis:** In general,  $\mathbb{H}^{(\text{ac Stark})}$  is neither diagonal in  $F$  nor  $M$ . Therefore, the combined Hamiltonian  $\mathbb{H}^{(\text{hfs} + \text{Stark})}$  need to be diagonalized in order to determine the eigenvectors and energies of an atom in a hyperfine basis. However, if the (ac) Stark shift of the (hyperfine) levels is small, when compared to the hyperfine splitting, one can neglect the mixing

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with other hyperfine levels and just calculate the diagonal matrix element  $\langle \alpha FM | \mathbb{H}^{(\text{ac Stark})} | \alpha FM \rangle$  to estimate this frequency-dependent (ac) Stark shift.

### Rayleigh-Schrödinger expansion of ac-Stark shifted levels:

- **Atoms and ions in intense laser field:** The perturbative description of the ac Stark shift of atoms (atomic levels) in fields with intensity  $I \gtrsim 10^{13} \text{ W/cm}^2$  has found continuous interest. For such fields, it is usually not sufficient to restrict the perturbation theory to second order.
- **Perturbative description of multiphoton ionization experiments:** Although, perturbation theory is often considered inadequate for the analysis of multiphoton ionization experiments with atoms and ions, rather little is still known about the breakdown of perturbation theory. Therefore, a perturbative treatment of the many-electron atom in intense fields is still of interest for various scenarios and intensities.
- **$m$ -th order perturbation states of atoms + field:** For a given (electric-) field operator  $\mathcal{E}$ , the atom-field interaction is  $V = \mathbf{r} \cdot \mathbf{E}$ . The  $m$ -th order perturbed state of the overall system 'atom + field' is then a linear combination of product states with just  $N - k$  photons (Pan *et al.*, 1988)

$$|\psi_m\rangle = \sum_{k=-m}^m |\phi_{m,k}(\mathbf{r})| N - k \rangle .$$

Here,  $N$  is the occupation number of the photon field and  $k$  runs in steps of 2.

### 7.3.e. Intensity-dependent quasi-energies and dressed (Floquet) states in slowly varying laser fields

#### Remarks & notations:

- **Dressed atomic states:** In a laser pulse of slowly varying intensity, the dressed atomic states follow adiabatically the temporal evolution of the intensity during the passage of the pulse. The slow variation of the intensity then results into fairly slow changes in the (coefficients of the) superposition of the dressed states when compared with the optical period of the laser.
- **Dressed atomic states:** The dressed states of atoms in an (ac) field of constant intensity and frequency refer to particular quasi-stationary solutions of the time-dependent Schrödinger equation.



- **Quasi-stationary wave function of dressed states:** For sufficiently slow variations of the laser intensity, each dressed state can be written in the Floquet form, i.e. by means of a space-independent complex exponential *multiplied* by a time-harmonic function that oscillates with the same (optical) period as the incident field.
- **Floquet ansatz:** The Floquet ansatz generally enables one to adopt the (time-independent) *dressed-state approach to pulses with a sufficiently slowly varying field intensity*, and where the time-dependence is captured by slow changes in the coefficients of the superposition.
- **Floquet ansatz:** The Floquet ansatz and eigenvalue problem has been applied especially in order to calculate the quasi-energy spectrum of atomic hydrogen and of hydrogenic ions within the dipole approximation and by neglecting spontaneous decay.
- **Floquet ansatz:** This ansatz might not be suitable for long-range polarization potentials as well as for multi-electron systems (Potvliege, 1998).
- **Floquet equations:** If the incident field is expanded in terms of a Fourier series, the time-dependent Schrödinger equation can be decomposed and re-written as a system of time-independent equations, the (so-called) *Floquet equations*. For multi-photon ionization, this system should be solved together with the radiation (Siegert) boundary conditions.
- **Floquet equations:** The (complex) eigenvalues of the Floquet equations provide both, the *quasienergies of the dressed states and the resonance poles of the scattering amplitudes for laser-assisted scattering*.
- **Floquet approximation:** This approximation is typically adequate for infrared laser pulses as well as for atoms in either the ground or some Rydberg level. It has been found inappropriate for UV laser frequencies and for low-lying excited levels because of avoided crossings between the dressed levels and the large non-ponderomotive (ac) Stark shifts at such high frequencies.
- **Widths of quasi-energies:** The computation of the widths of quasi-energies often requires to go beyond first-order perturbation theory.
- **Moderately intense and time-varying laser pulses:** If the laser pulses are neither ultra-intense nor ultra-short, they can usually be modeled as a rapidly oscillating electric field, though with a well-defined and slowly varying envelope (field amplitude). For such quasi-constant ac-fields, the behaviour of atoms can be described in terms of *superpositions of dressed bound states that decay under the emission of photoelectrons*.

### 7.3.f. Atomic polarizabilities

#### Remarks & notations:

- **Atomic polarizabilities and hyperpolarizabilities:** The polarizability of an atom in level  $(\alpha\mathbb{J})$  generally describes its *response* to the radiation field in second-order perturbation theory, i.e. due to the absorption and re-emission of a laser photon. In contrast, the **hyperpolarizabilities refer to contributions from a perturbation expansion in third or higher order of the radiation field**. This counting of the number of ‘electron-field’ interactions need to be distinguished from these perturbation expansions in which either the hyperfine interaction and/or some magnetic field is incorporated, in addition to the radiation field in second order, and which are often also referred to as ‘third-order expansions’.
- **Frequency-dependent (ac) polarizabilities:** For a sufficiently weak time-harmonic (ac) electric field, the frequency-dependent (ac) polarizability of an atomic state  $|\alpha JM\rangle$  also depends on the magnetic quantum number  $M$ , although just in a geometrical manner. This  $M$ -dependent part is associated with the (so-called) **vector and tensor polarizability**, while the **scalar polarizability** just refers to the atomic level  $(\alpha\mathbb{J})$ . The simple analytical form of the  $M$ -dependent components of the polarizabilities results of course from the  $(JM)$  symmetry of the unperturbed levels; the vector component vanishes for  $J = 0$ , and the tensor component for  $J = 0, 1/2$ . The vector polarizability is sometimes also referred to as **axial (asymmetric) polarizability** and arises for ac fields with a circularly-polarized (field) component. In general, the ratio of the scalar, vector and tensor polarizabilities are also frequency-dependent, and a detailed analysis often requires rather lengthy computations.
- **Frequency-dependent (ac E1) polarizability  $\alpha^{(\text{ac E1})}(\omega)$ :** The frequency-dependent (ac E1) polarizability describes the response of an atoms or nanoobjects to an (external) electromagnetic disturbance, if this field is much weaker than the (internal) atomic field:  $E \ll E^{(\text{atomic})} = m^2 e^5 / \hbar^4 \approx 5.14 \cdot 10^9 \text{ V/cm}$ , and if the wavelength of the field is much larger than the size of the object (Astapenko 2013).
- **Methods for calculating atomic polarizabilities:** Three broad classes of methods have been used in the literature, in addition to various combinations of these methods: (1) *Ab-initio* calculations are typically based on the **summation over all relevant states of the (many-electron) spectrum**, and where each contribution is determined individually; (2) direct solution of some inhomogeneous Schrödinger equation that include the frequency-dependent electric field in an effective manner into its inhomogeneous parts, and for which quite a number of different strategies were developed; (3) use of experimentally determined oscillator strengths together with estimates from class (1).
- **Precise computations of atomic polarizabilities:** For many-electron atoms, precise computations of atomic polarizabilities require at least a careful treatment of valence-valence correlations as well as the — direct or implicit — summation over the whole many-electron spectrum that can be reached by electric-dipole transitions. Here, core-valence and core-core correlations may also contribute quite significantly.

- **Precise computations of atomic polarizabilities:** Valence-valence correlations are usually taken into account by the configuration interaction (CI) method, while core-valence and core-core correlations have been treated by a combined CI+MBPT method in order to construct an effective Hamiltonian for the CI computations in the valence space (Porsev *et al.* 2018).
- **Units of atomic polarizabilities:** In atomic units, the polarizabilities of an atomic level have the dimension of a volume and values of  $\alpha(\omega; \alpha\mathcal{J})$  are usually given in  $a_0^3$ . In measurements, the units  $\text{\AA}^3$ ,  $\text{kHz} / (\text{kV cm}^{-1})^2$ ,  $\text{cm}^3 / \text{mol}$  as well as the SI unit  $\text{C m}^2 / \text{N}$  have been applied in the literature.
- **Typical frequency-dependence of atomic polarizabilities:** Figure 7.3.f displays a typical dependence of the polarizability of atomic ground states on the frequency of the external (incident laser) field. Resonances in the (frequency-dependent, ac) polarizability occur especially near to the excitation energies of single-photon (electric-dipole) transitions to neighbored levels.

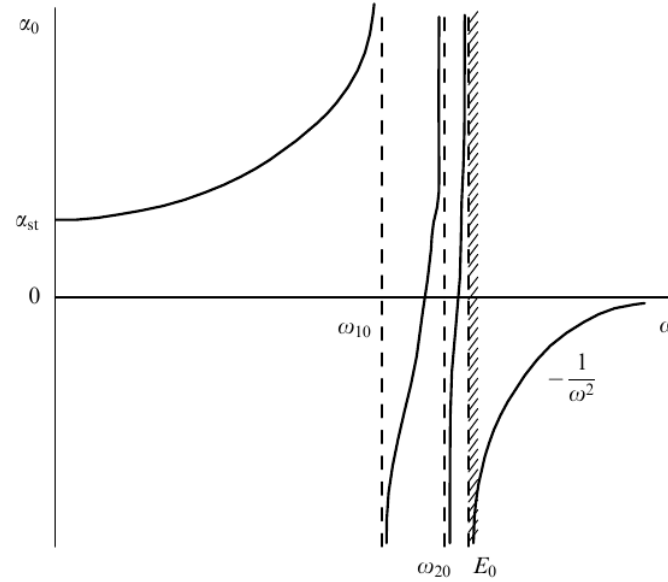


Figure 7.2.: Typical frequency dependence of the (ac) polarizability of atomic ground levels; from Krainov and Delone (1999).

- **Frequency-dependent (ac) polarizabilities at high laser frequencies:** At high frequencies of the incident light, the (bound) electrons of an atom can no longer follow the external field and, hence, their response (polarizability) decreases. From the second-order perturbation

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expansions, it can be readily seen that the scalar polarizability of an atomic level  $(\alpha\mathbb{J})$  in a linearly-polarized laser field decreases  $\sim \omega^{-2}$ , while the vector and tensor polarizabilities vanish even faster

$$\alpha^{(\text{scalar})}(\omega > E_o; \alpha\mathbb{J}) \longrightarrow -\frac{1}{\omega^2}, \quad \alpha^{(\text{vector})}(\omega > E_o; \alpha\mathbb{J}) \longrightarrow \frac{1}{\omega^k} \quad (k > 2), \quad \alpha^{(\text{tensor})}(\omega > E_o; \alpha\mathbb{J}) \longrightarrow \frac{1}{\omega^4}.$$

For the vector polarizabilities, moreover, the asymptotic behaviour for large  $\omega$  depends on the atomic state of interest.

- **Schiff theorem & atomic dipole moment:** Because of its spherical symmetry, the dipole moment of an atom is *zero* without an external field (Schiff theorem); therefore, any **induced dipole moment** is a direct measure for the disturbance of an atom by a field. For low-enough field strengths, this response of an atom to electromagnetic field can be simply characterized by its polarizability.
- **Induced dipole moment of an atom in an external field:** For an atom in an external field  $\mathcal{E} = \Re [\mathcal{E}_o e^{-i\omega t}] \mathbf{e}_z$ , the induced electric-dipole moment  $\mathbf{p}$  is related to its frequency-dependent polarizability by

$$\mathbf{p} = \frac{1}{2} (\alpha^{(\text{ac E1})}(\omega; \beta\mathbb{J}) \mathcal{E}_o e^{-i\omega t} + \alpha^{(\text{ac E1})*}(\omega; \beta\mathbb{J}) \mathcal{E}_o^* e^{i\omega t}).$$

- **Macroscopic view:** Mathematically, the dynamic polarizability  $\alpha(\omega)$  can be expressed by a second-rank tensor  $(\alpha_{ij})$  that connects the induced dipole moment  $\mathbf{d}$  of the atom with the strength of the external electric field  $\mathcal{E}$  at frequency  $\omega$ , and which, for spherically symmetrical systems, simplifies to a scalar

$$d_i = \sum_j \alpha_{ij} E_j(\omega), \quad \alpha_{ij}(\omega) = \alpha(\omega) \delta_{ij} \quad \longrightarrow \quad \mathbf{d}(\omega) = \alpha(\omega) \mathbf{E}.$$

- **Shielding of external fields:** For weak fields, the induced – electric or magnetic – dipole moments are proportional to the applied field and give rise to secondary fields with the same spatial symmetry as the externally applied field. Therefore, any applied multipole field is typically shielded (or enhanced) near to the nucleus by some factor that is specific for the given atom or ion.
- **Dielectric constant  $K$  of a gas:** An atomic or molecular gas is often characterized by its dielectric constant  $K$  which is closely related to the atomic number density  $N_d$  and (scalar electric-dipole) polarizability of the ground level  $(\beta\mathbb{J})$  of the atom

$$\alpha^{(\text{scalar E1})}(\beta\mathbb{J}) = \alpha^{(\text{scalar E1})}(\omega = 0; \beta\mathbb{J}) = \frac{K - 1}{4\pi N_d}.$$

This relation has also been applied in order to measure polarizabilities with relative uncertainties  $\sim 0.1\%$  for rare-gas atoms as well as for nitrogen and oxygen.

- **Clausius-Mossotti relation:** For a system embedded into a medium, the dynamic polarizability of atoms also defines the **dielectric permittivity**  $\varepsilon(\omega)$  of a medium with number density  $n_a$  of atoms, and if the medium just consists out of a single type of atoms

$$\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2} = \pi n_a \alpha(\omega) .$$

- **Frequency-dependent refractive index**  $n(\omega)$  of a gas: The refractive index  $n(\omega)$  of a gas with number density  $N_d$  is also related to the polarizability of the ground level ( $\beta\mathbb{J}$ ) by

$$\alpha^{(\text{scalar E1})}(\omega; \beta\mathbb{J}) = \frac{n(\omega) - 1}{2\pi N_d} .$$

- **Electric-dipole and magnetic-dipole susceptibility:** The susceptibility  $\chi^{(\text{electric, magnetic})}$  is generally a (dimensionless) proportionality constant that characterizes the induced polarization of a medium in response to an applied electric or magnetic field. The greater the susceptibility, the greater the response of the material to an applied field.
- **Electric susceptibility**  $\chi_e \equiv \chi^{(\text{electric})}$ : A proportionality **constant or tensor which relates the induced dielectric polarization density  $\mathbf{P}$  to the applied field** and which is very closely related to the (ground-state) atomic or molecular polarizability  $\alpha^{(\text{ac:E1})}(\beta\mathbb{J})$ :

$$\mathbf{P} = \varepsilon_o \chi_e \mathbf{E}, \quad \mathbf{p} = \varepsilon_o \alpha^{(\text{ac:E1})}(\beta\mathbb{J}) \mathbf{E}_{\text{local}}$$

Here  $\mathbf{p}$  refers to the induced atomic or molecular electric-dipole moment. Analogue expressions also exist for the magnetic susceptibility  $\chi^{(\text{magnetic})}$ , the magnetic field  $\mathbf{B}$  and the magnetization  $\mathbf{M}$  as well as for the magnetic-dipole moment  $\mathbf{m}$ .

- **Relation of frequency-dependent (ac) polarizabilities & Cauchy moments:** The static (dc) and frequency-dependent (ac) polarizabilities are related to each other by means of the Cauchy moments  $S(-q)$  by (Mitroy *et al.*, 2010)

$$\alpha^{(\text{scalar E1})}(\omega; \alpha_o\mathbb{J}_o) = \alpha^{(\text{scalar E1})}(\omega = 0; \alpha_o\mathbb{J}_o) + \omega^2 S(-4) + \omega^4 S(-6) + \dots$$

Moreover,  $S(-3)$  is related to the non-adiabatic polarizabilities.

- **Application of atomic polarizabilities:** Atomic polarizabilities are closely related to a number of **macroscopic properties of gases and materials, such as the dielectric constant and the refractive index**. At the microscopic scale, the formation of alkaline-earth anions and the

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(short term) binding of positrons by many-electron atoms can be largely explained by polarization-type interactions, i.e. in terms of atomic polarizabilities. Indeed, many textbooks of electro-magnetic theory study in quite detail the electrical polarizabilities of differently shaped macroscopic bodies, and for which only the (macroscopic) dielectric constant and the conductivity of the materials are then occur in the formalism.

- **Application of atomic polarizabilities:** Accurate atomic polarizabilities are needed also for quantum information processing as well as for precise optical cooling and trapping techniques.
- **Application of atomic polarizabilities for atomic clocks:** Precise estimates of atomic polarizabilities are needed especially for the next-generation of atomic clocks, and which will likely be based on optical transitions. Indeed, the uncertainties of atomic clocks are seriously limited by (unknown) atomic levels shifts due to (ac) Stark shifts and thermal (BBR) fluctuations of the environment. A more detailed theory of the **BBR shifts also need to relate the definition of the time unit to the thermodynamics of the radiation field.**

### Frequency-dependent (ac) polarizabilities of a fine-structure level $(\beta\mathbb{J})$ :

- **Frequency-dependent (ac) polarizability of an atomic state  $|\alpha\mathbb{J}M\rangle$  :** In a frequency-dependent (ac) electric field  $\mathcal{E}(t) = \mathcal{E}(t) \mathbf{e}_z$ , the (frequency-dependent, electric-dipole) polarizability of an atom in the state  $|\alpha\mathbb{J}M\rangle$  is given in terms of the electric-dipole matrix elements by

$$\alpha(\omega; \alpha\mathbb{J}M) = \sum_{\alpha\nu\mathbb{J}_\nu M_\nu} |\langle \alpha\nu\mathbb{J}_\nu m_\nu | \mathbb{D} | \alpha\mathbb{J}M \rangle|^2 \left[ \frac{1}{(E_n - E_k) + \omega} + \frac{1}{(E_n - E_k) - \omega} \right],$$

and where the summation is taken over all possible E1 transitions of the level  $|\alpha\mathbb{J}M\rangle$ .

- **Scalar *versus* vector and tensor polarizability:** For an effective closed-shell atom in the (ground) level  $(\beta\mathbb{J})$  with energy  $E_o$ , the **scalar atomic polarizability** can be expressed in terms of the absorption oscillator strength to any other level from the (many-electron) spectrum by (Mitroy *et al.*, 2010)

$$\alpha^{(\text{scalar E1})}(\omega; \beta\mathbb{J} = 0) = \sum_{\nu} \frac{f_{o\nu}}{(E_\nu - E_o)^2} = \sum_{\nu} \frac{2}{3(J+1)} \frac{|\langle \alpha\nu\mathbb{J}_\nu | \mathbb{O}^{(\text{E1, absorption})} | \beta\mathbb{J} \rangle|^2}{(E_\nu - E_o)}.$$

For an atom in a level with  $J > 0$ , the frequency-dependent polarizability also depends on the projection  $M$  by

$$\alpha^{(\text{E1})}(\omega; \beta\mathbb{J}M) = \alpha^{(\text{scalar E1})}(\omega; \beta\mathbb{J}M) + \alpha^{(\text{tensor E1})}(\omega; \alpha_o\mathbb{J}_o M_o) \frac{3M^2 - J(J+1)}{J(2J-1)},$$

The **tensor polarizability**  $\alpha^{(\text{tensor E1})}(\beta \mathbb{J} M) = \alpha^{(\text{tensor E1})}(\omega = 0; \beta \mathbb{J} M)$  is defined by

$$\alpha^{(\text{tensor E1})}(\beta \mathbb{J} M) = 4 \left( \frac{5J(2J-1)}{6(J+1)(2J+1)(2J+3)} \right)^{1/2} \sum_{\nu} (-1)^{J+J_{\nu}} \begin{Bmatrix} J & 1 & J_{\nu} \\ 1 & J & 2 \end{Bmatrix} \frac{|\langle \alpha_{\nu} \mathbb{J}_{\nu} | \mathbb{O}^{(\text{E1, absorption})} | \beta \mathbb{J} \rangle|^2}{(E_{\nu} - E_o)}.$$

The last expression shows that spherically-symmetric fine-structure levels with  $J \leq 1/2$  only have a scalar polarizability, while the corresponding hyperfine levels generally still depend on  $F, M_F$ . The relation between the polarizabilities for fine-structure and hyperfine levels depend on the size of the frequency-dependent (ac) Stark shifts relative to the hyperfine splitting, and accurate prediction may require theories of different sophistication (Mitroy *et al.*, 2010).

- **Non-relativistic limit of the frequency-dependent (ac) polarizability:** In the non-relativistic limit, the (ac) polarizability is simply related to the number of electrons  $N$  of the atom due to the Thomas-Reiche-Kuhn sum rule for the oscillator strengths

$$\alpha^{(\text{ac E1})}(i\omega, \beta \mathbb{J}) \sim \sum_{\nu} \frac{f(\alpha_{\nu} \mathbb{J}_{\nu} \rightarrow \beta \mathbb{J})}{\omega^2} = \frac{N}{\omega^2}.$$

### Frequency-dependent (ac) polarizabilities of a hyperfine level $(\beta(I\mathbb{J})\mathbb{F})$ :

- **Reduced tensorial (frequency-dependent, ac) polarizability of hyperfine level  $(\alpha(IJ)\mathbb{F})$  :** In second-order electric-dipole approximation, and if the (non-diagonal) hyperfine interaction is negligible, the reduced tensorial (frequency-dependent ac) polarizability of a hyperfine level  $(\alpha(IJ)\mathbb{F})$  with level energy  $E_o$  is given by (Beloy 2009)

$$\begin{aligned} \alpha^{(\text{K})}(\omega; \beta(IJ)\mathbb{F}) \\ = (-1)^{I-J+F} [F] [K]^{1/2} \begin{Bmatrix} F & K & F \\ J & I & J \end{Bmatrix} \sum_{\alpha_{\nu} \mathbb{J}_{\nu}} \begin{Bmatrix} J & K & J \\ 1 & J_{\nu} & 1 \end{Bmatrix} \langle \beta \mathbb{J} \| \mathbb{D} \| \alpha_{\nu} \mathbb{J}_{\nu} \rangle \langle \alpha_{\nu} \mathbb{J}_{\nu} \| \mathbb{D} \| \beta \mathbb{J} \rangle \left[ \frac{1}{E_o - E_{\nu} + \omega} + \frac{(-1)^K}{E_o - E_{\nu} - \omega} \right], \end{aligned}$$

and where  $\mathbb{D}$  denotes the electric-dipole operator.

- **Conventional scalar, vector and tensor (frequency-dependent, ac) polarizabilities of hyperfine level  $(\alpha(IJ)\mathbb{F})$  :** The conventional scalar, vector and tensor polarizabilities can be expressed in terms of the **reduced tensorial (frequency-dependent, ac) polarizability of a hyperfine**

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level  $(\beta(IJ) \mathbb{F})$  by

$$\begin{aligned}\alpha^{(\text{scalar})}(\omega; \beta(IJ) \mathbb{F}) &= \frac{1}{\sqrt{3(2F+1)}} \alpha^{(0)}(\omega; \beta(IJ) \mathbb{F}) \\ \alpha^{(\text{vector})}(\omega; \beta(IJ) \mathbb{F}) &= -\sqrt{\frac{2F}{(2F+1)(F+1)}} \alpha^{(1)}(\omega; \beta(IJ) \mathbb{F}) \\ \alpha^{(\text{tensor})}(\omega; \beta(IJ) \mathbb{F}) &= -\sqrt{\frac{2F(2F-1)}{3(2F+1)(F+1)(2F+3)}} \alpha^{(2)}(\omega; \beta(IJ) \mathbb{F}).\end{aligned}$$

### Frequency-dependent (ac) polarizabilities for hydrogenic ions:

- **Frequency-dependent polarizabilities for hydrogenic ions:** For non-relativistic hydrogenic ions, the frequency-dependent polarizabilities can be evaluated analytically in the low- and high-frequency limit, i.e. far from atomic resonances. A few such relations in terms of the principal and orbital quantum numbers are given by Delone and Krainov (1999)

$$\begin{aligned}\alpha^{(\text{scalar})}(\omega \ll E_n, n\ell) &= -\frac{n^6 \ell \omega}{8} (55n^2 + 26\ell^2 + 26\ell + 169) \text{ a.u.} \\ \alpha^{(\text{scalar})}(\omega \gg E_n, n, \ell = 0) &= -\frac{1}{\omega^2} - \frac{4}{3n^2 \omega^4} \text{ a.u.}, & \alpha^{(\text{scalar})}(\omega \gg E_n, n, \ell = 1) &= -\frac{1}{\omega^2} - \frac{2\sqrt{2}(n^2 - 1)}{9n^5 \omega^{11/2}} \text{ a.u.} \\ \alpha^{(\text{vector})}(\omega \gg E_n, n, \ell = 1) &= -\frac{2\sqrt{2}(n^2 - 1)}{9n^5 \omega^{11/2}} \text{ a.u.}, & \alpha^{(\text{vector})}(\omega \gg E_n, n, \ell \geq 2) &= -\frac{2\sqrt{2}(n^2 - 1)}{9n^5 \omega^{11/2}} \text{ a.u.} \\ \alpha^{(\text{tensor})}(\omega \gg E_n, n, \ell = 1) &= \frac{1}{\omega^2} - \frac{4}{15n^3 \omega^4} \text{ a.u.}, & \alpha^{(\text{tensor})}(\omega \gg E_n, n, \ell \geq 2) &= -\frac{4}{n^7 (\ell + 1) (2\ell + 1) (2\ell + 3) \omega^4} \text{ a.u.}\end{aligned}$$

Further relations of this kind can be found in this reference and in the literature; they mainly show that the corrections to the asymptotic values of the polarizabilities rapidly decrease as the principal quantum number (Rydberg states) or the frequency of the external field increases. Moreover, the scalar polarizabilities usually dominate for all hydrogenic ions.



### 7.3.g. Multipole polarizabilities (MultipolePolarizability)

#### Remarks & notations:

- **Frequency-dependent (ac  $2^L$ -multipole) polarizability:** For an atomic level  $(\beta\mathbb{J})$  with energy  $E_o$ , the frequency-dependent (ac  $2^L$ -multipole) polarizability is given by (Porsev *et al.*, 2018)

$$\alpha^{(\mathbb{M})}(\omega, \beta\mathbb{J}) = \frac{L+1}{L} \frac{2L+1}{[(2L+1)!!]^2} (\alpha\omega)^{2L-2} \sum_{\nu} \frac{(E_{\nu} - E_o) |\langle \alpha_{\nu}\mathbb{J}_{\nu} | \mathbb{T}^{(\mathbb{M})} | \beta\mathbb{J} \rangle|^2}{(E_{\nu} - E_o)^2 - \omega^2}$$

where  $\mathbb{T}^{(\mathbb{M})}$  is the corresponding multipole operator for E1, M1, ... transitions.

### 7.3.h. Hyperpolarizability

#### Remarks & notations:

- The **hyperpolarizability of atoms** describe a nonlinear-optical property of matter and is closely related to the second-order electric susceptibility (per unit volume).
- **Hyperpolarizability:** The hyperpolarizability of an atom or ions can be deduced experimentally, for instance, by observing the Kerr effect in gases. However, the experimental uncertainties in these measurements are often large.
- **Accuracy of static hyperpolarizabilities:** Any accurate calculation of the static hyperpolarizabilities of atoms in some state  $|\beta\mathbb{J}M\rangle$  is still a great challenge for atomic theory, and this even applies to the simplest atoms, such as lithium with only three electrons. As reported in the literature, both the choice of the basis set (grid) as well as the electronic correlations can have a large effects upon the (accuracy of the) computed hyperpolarizabilities.
- **Hyperpolarizability of closed-shell atoms:** For a neutral, closed-shell atom in its ground state  $|\beta^1S_0\rangle$ , the **energy (level) shift in the presence of a homogeneous static electric field of strength  $F$**  is given by (Kassimi and Thakkar, 1994)

$$E(F; \beta\mathbb{J}) - E_o = -\alpha \frac{F^2}{2!} - \gamma_2 \frac{F^4}{4!} - \gamma_4 \frac{F^6}{6!} - \gamma_6 \frac{F^8}{8!} - \dots,$$

where  $\alpha$  is the (static) dipole polarizability and  $\gamma_k$ ,  $k = 2, 4, \dots$  the hyperpolarizability parameters of the atom.

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- **Induced dipole moment  $d = |\mathbf{d}|$ :** In the same field static field  $F$ , the dipole moment is then given by

$$d(F; \beta\mathbb{J}) = \alpha F + \gamma_2 \frac{F^3}{3!} + \gamma_4 \frac{F^5}{5!} + \dots$$

- **Finite-field procedure:** In the computational procedure, the polarizabilities and hyperpolarizabilities are obtained from energy and/or dipole moment calculations of the atom in the presence of an electric fields of various strengths, and by using truncations of the given expansion above.

### 7.3.i. Black-body radiation shifts

#### Remarks & notations:

- **Black-body radiation (BBR) shift:** An atom at finite temperature interacts with (Planck's) black-body radiation background due to the virtual absorption and emission of photons with temperature-dependent wavelengths. This interaction leads to a (tiny) shift of the atomic levels, known as BBR shift. These BBR shifts have to be analyzed for atomic clocks in order to estimate, for instance, the influence of the cosmic microwave background radiation (CMBR) in various space missions. The uncertainties in the estimated BBR shifts contribute to the uncertainty budget of the present-day atomic clocks. The BBR shifts are typically estimated by applying a multipole expansion of the electro-magnetic background field and by just considering the E1 multipole component of the field. Other multipole components of the electro-magnetic field, such as the M1 and E2 multipole fields, are expected to become relevant for the next-generation atomic clocks.
- **CMBR:** Even in intergalactic space, an isolated atom is still subject to the cosmic microwave background. The uncertainties in the blackbody radiation shift may impose limits on the accuracy of the best atomic clocks.
- **Radiation studies:** From radiation studies it is known that object emit radiation whose wavelength depends on its temperature. At room temperature, objects emit radiation with wavelengths in the infrared region of the electro-magnetic spectrum.
- **Black-body radiation Hamiltonian  $\mathbb{H}^{(\text{BBR})}$ :** In Coulomb gauge, the interaction of the atomic electrons with the propagating background field with vector potential  $\mathbf{A}(\mathbf{r}, \omega)$  is described by the Hamiltonian

$$\mathbb{H}^{(\text{BBR})} = \sum_j -c \boldsymbol{\alpha}_j \cdot \mathbf{A}(\mathbf{r}_j, \omega) = \sum_j -c (\boldsymbol{\alpha}_j \cdot \mathbf{u}) e^{i \mathbf{k} \cdot \mathbf{r}_j},$$

and where  $\omega$ ,  $\mathbf{k}$  and  $\mathbf{u}$  are the frequency, wave vector and the polarization vector of the background field, respectively.

- **Black-body radiation (BBR) shift:** From the Hamiltonian  $\mathbb{H}^{(\text{BBR})}$ , the frequency shift of a level  $(\alpha\mathbb{J})$  with (unperturbed) energy  $E_o$  is given by

$$\Delta E^{(\text{BBR})}(T; \alpha\mathbb{J}) = \frac{1}{2} \sum_{\nu} \int d\omega \left| \langle \alpha_{\nu}\mathbb{J}_{\nu} | \mathbb{H}^{(\text{BBR})} | \alpha\mathbb{J} \rangle \right|^2 \left( \frac{E_o - E_{\nu}}{(E_o - E_{\nu})^2 - \omega^2} \right).$$

Here, the decomposition and evaluation of the matrix elements  $\langle \alpha_{\nu}\mathbb{J}_{\nu} | \mathbb{H}^{(\text{BBR})} | \alpha\mathbb{J} \rangle$  follows the standard decomposition of the interaction of electrons with the (plane-wave) radiation field but requires to include the spectral energy density from the background field.

- **Blackbody radiation (BBR) shift:** For a time-independent environment, the BBR shift is given at temperature  $T$  in terms of the polarizability  $\alpha_o$  by (Berengut *et al.*, 2012)

$$\delta E = -\frac{1}{2} (831.9 \text{ V/m})^2 \left[ \frac{T[\text{K}]}{300} \right]^4 \alpha_o (1 + \eta)$$

and where  $\eta$  refers to some dynamic correction due to the frequency distribution of the atom.

### 7.3.j. Dispersion coefficients

#### Remarks & notations:

- **Lennard-Jones model:** This model refers to a **mathematically simplified potential** for describing the interaction between a pair of neutral atoms or molecules at different distances. It was first proposed in 1924 by John Lennard-Jones. Especially, the long-range interactions between atoms and molecules play a prominent role in the **low-energy and low-temperature collision experiments**.
- **Dispersion coefficients  $C_n$ :** The interaction of atoms at large interatomic distances, for instance for cold gases in a cold traps, is usually described in terms of **dispersion (van der Waals) coefficients  $C_n$** .
- **Alkaline-earth dimers:** For two alkaline-earth atoms in their ground state, the long-range potential as function of the internuclear distance  $R$  can be written as (Porsev and Derivianko, 2006)

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots$$

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- **London's model of dispersion:** For two atoms at internuclear distance  $R$  and with given electron distributions, the dispersion arises from the interaction of the induced dipoles. For two (single-active) electrons with position  $\mathbf{r}_A$  at atom  $A$  and  $\mathbf{r}_B$  at atom  $B$ , the electron at  $\mathbf{r}_A$  causes multipole moments with respect to nucleus  $A$  and, similarly, the electron at  $\mathbf{r}_B$  multipole moments with respect to nucleus  $B$ . The energy shifts due to the interaction between these multipole moments can be evaluated by second-order perturbation theory and by using the *static* approximation. This approximation leads to the expansion above but with explicitly given dispersion coefficients (Johnson, 2011)

$$C_6(A, B) = \frac{\alpha_A \alpha_B \langle \mathbf{p}^2 \rangle_A \langle \mathbf{p}^2 \rangle_B}{\alpha_B \langle \mathbf{p}^2 \rangle_A + \alpha_A \langle \mathbf{p}^2 \rangle_B}$$

$$C_8(A, B) = \frac{3}{2} \frac{\alpha_A \alpha_B (\langle \mathbf{p}^2 \rangle_A \langle \mathbf{Q}^2 \rangle_B + \langle \mathbf{Q}^2 \rangle_A \langle \mathbf{p}^2 \rangle_B)}{\alpha_B \langle \mathbf{p}^2 \rangle_A + \alpha_A \langle \mathbf{p}^2 \rangle_B}$$

$$C_{10}(A, B) = 2 \frac{\alpha_A \alpha_B (\langle \mathbf{p}^2 \rangle_A \langle \mathbf{T}^2 \rangle_B + \langle \mathbf{T}^2 \rangle_A \langle \mathbf{p}^2 \rangle_B)}{\alpha_B \langle \mathbf{p}^2 \rangle_A + \alpha_A \langle \mathbf{p}^2 \rangle_B} + \frac{21}{5} \frac{\alpha_A \alpha_B \langle \mathbf{Q}^2 \rangle_A \langle \mathbf{Q}^2 \rangle_B}{\alpha_B \langle \mathbf{p}^2 \rangle_A + \alpha_A \langle \mathbf{p}^2 \rangle_B}$$

and where  $\langle \mathbf{p}^2 \rangle$ ,  $\langle \mathbf{Q}^2 \rangle$ ,  $\langle \mathbf{T}^2 \rangle$  are the expectation values of the squared dipole, quadrupole and octupole moments, respectively.

### Atomic computation of dispersion coefficients:

- **Atom-wall coefficient,  $C_3$ :** For an atom in a spherically-symmetric ground state  $|\beta \mathbb{J} M\rangle$ , the dispersion coefficient  $C_3$  of the Lennar-Jones interaction between an atom and a perfectly conducting wall is given by (Derivianko *et al.*, 1999)

$$C_3 = \frac{1}{4\pi} \int_0^\infty d\omega \alpha^{(\text{ac E1})}(i\omega; \beta \mathbb{J} M) = \frac{1}{12} \langle \beta \mathbb{J} M | \mathbf{R} \cdot \mathbf{R} | \beta \mathbb{J} M \rangle, \quad \mathbf{R} = \sum_{i=1}^N \mathbf{r}_i.$$

- **Van-der-Waals coefficient,  $C_6$ :** For an atom in a spherically-symmetric ground state  $|\beta \mathbb{J} M\rangle$ , the dispersion coefficient  $C_6$  of the Lennar-Jones interaction can be expressed as integral over the frequency-dependent (ac) electric-dipole polarizability (Derivianko *et al.*, 1999)

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega [\alpha^{(\text{ac E1})}(i\omega; \beta \mathbb{J} M)]^2.$$

- **Van-der-Waals coefficient,  $C_6$ :** Since the van-der-Waals coefficients  $C_6$  contains the electric-dipole matrix element upto fourth power, these dipole amplitudes must usually be calculated with high accuracy.
- **Long-range interaction of two atoms:** For two atoms  $a$  and  $b$  in spherical-symmetric ground states  $|\beta_a \mathbb{J}_a M_a\rangle$  and  $|\beta_b \mathbb{J}_b M_b\rangle$ , the long-range interaction can be written with  $k' = n - k - 1$  as (Porsev and Derivianko, 2006)

$$V(R) = - \sum_{n=3} \frac{C_{2n}^{ab}}{R^{2n}}, \quad C_{2n}^{ab} = \frac{(2n-2)!}{2\pi} \sum_{k=1}^{n-2} \frac{1}{(2k)!(2k')!} \int_0^\infty d\omega \alpha_k^{(\text{ac E1})}(i\omega; \beta_a \mathbb{J}_a M_a) \alpha_{k'}^{(\text{ac E1})}(i\omega; \beta_b \mathbb{J}_b M_b),$$

and where  $\alpha_k^{(\text{ac E1})}(i\omega; \alpha_c \mathbb{J}_c M_c)$  is the  $2^k$ -pole frequency-dependent (ac electric-dipole) polarizability of each atom  $a, b$ .

- **Dispersion coefficients  $C_n^{(AB)}$  of mixtures:** For mixed interactions of atomic pairs  $(AB)$ , a simple rule is often applied:

$$C_n^{(AB)} = \sqrt{C_n^{(A)} C_n^{(B)}}.$$

- **Van-der-Waals coefficients  $C_{12}$  and  $C_{14}$ :** The high-order dispersion coefficients, i.e. the van der Waals coefficients  $C_{12}$  and  $C_{14}$  are usually not so easily available for most systems of interest. They can be approximated from the low-order dispersion coefficients  $C_{12}$  and  $C_6, C_8, C_{10}$  by using certain dimensionless ratios of such coefficients as discussed for instance by Douketis *et al.* (1982).

## Dispersion coefficients in chemical computations:

- **Dispersion corrections to DFT calculations:** It has been found (very) important to incorporate dispersion corrections into (typical) DFT computations, especially if chemical processes and reaction pathes are to be considered. Different approaches to account for dispersion corrections include van-der-Waals functionals, dispersion-corrected effective-core potentials, the parameterization of meta-GGA functionals or, simply, the *posteriori* addition of a dispersion energy to the DFT energy (Johnson, 2011).
- **Grimme's DFT approaches to dispersion:** Several suggestions have been made by Grimme and coworkers to obtain dispersion coefficients for molecular environments from the ionization potentials, polarizabilities of the elements and some empirical constants. These suggestions are mainly motivated by the (so-called) **London model**. In a recent work of Grimme and coworkers, the dispersion coefficients were computed for each pair of atoms separately by using the Casimir-Polder formula for a number of reference molecules, and by adding some dependence on the coordination number. These dispersion coefficients then vary smoothly along a considered **reaction coordinate** and are sensitive also to changes in the hybridization, atomic volume as well as the atomic charge and oxidation state of the compound. Such dispersion models can then be combined with Hartree-Fock and/or exchange-correlation DFT calculations.

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- **Hirshfeld scaling of polarizabilities:** The effective atom-in-molecule polarizabilities of each atom  $\alpha_i$  are often evaluated by using the proportionality between the polarizability and volume as well as the free-atomic polarizabilities  $\alpha_i^{(\text{free})}$  from available tabulations:

$$\alpha_i = \left( \frac{\langle r^3 \rangle_i}{\langle r^3 \rangle_i^{(\text{free})}} \right) \alpha_i^{(\text{free})}.$$

While this Hirshfeld volume-based scaling is a reasonable approximation to determine the atom-in-molecule polarizabilities in various (neutral) molecular environments, the approach breaks down for ions. For instance, if the ionic polarizabilities are obtained from the neutral-atom values multiplied by a ratio of atomic volumes, the ionic  $C_6$  dispersion coefficients are drastically overestimated. In general, the volume-scaling approach overestimates the polarizability and dispersion coefficients of cations and underestimates these values for anions (Johnson, 2011).

### 7.3.k. Fano profiles of continuum-embedded resonances

#### Remarks & notations:

- **Fano resonances in physics:** In physics, a **Fano resonance generally refers to a resonant scattering process (phenomenon)** that gives rise to an asymmetric line-shape in the energy of scattered (emitted) particles due to the interference between a constant background and a resonant scattering amplitude. Fano-type resonances can be found across many areas of physics and engineering because resonant scattering is a rather ubiquitous wave phenomenon.
- **Fano resonances in atomic physics:** In atomic physics, the background amplitude often arise from the direct (ionization) amplitude of an electron to the continuum, while the resonant amplitude arise from the (indirect) coupling of the atom to a discrete, localized state that is embedded into the continuum.
- **Photoionization near to resonances:** The photoionization cross section near to an isolated resonance at energy  $E_r$  is best described by Fano's formula. In this formula, the resonant cross section is characterized by the resonance width  $\Gamma$ , the asymmetry parameter  $q$  and the non-resonant background cross section  $\sigma_b$ . Using this formula, the cross sections peaks at  $E_{\text{max}} = E_r + \frac{1}{2} \Gamma/q$  with  $\sigma_{\text{max}} = \sigma_b (1 + q^2)$  and reaches zero at  $E_r - \frac{1}{2} \Gamma q$ .

### 7.3.I. Stark splitting in crystal field

#### Remarks & notations:

- **Atomic line emission from ionic crystals:** Embedded rare-earth ions in ionic crystals, such as  $\text{Er}^{3+}$ , are known to exhibit very sharp absorption and emission lines. In selected cases, these lines can be as narrow as the lines of free ions, and quite in contrast to the rather broad spectra of most defects in crystals, such as nitrogen centers.
- **Application of doped erbium ions:** Apart from data communications, erbium oxides are considered also as primary candidate in nuclear fusion devices in order to reduce the tritium permeation barriers in the blanket system of tokamaks and stellarators.

#### Crystal-field Hamiltonian & splitting of atomic levels:

- **Crystal-field Hamiltonian  $\mathbb{H}^{(\text{crystal field})}$ :** If the  $N_c$  surrounding ions of the crystal are treated as point charges  $\{Z_c\}$  at given (fixed) positions  $\{\mathbf{R}_c = (R_c, \vartheta_c, \varphi_c)\}$ , the crystal-field interaction Hamiltonian of an embedded atom or ion of with  $N$  electrons can be written in atomic units in the form (Gaigalas and Kato, 2020)

$$\mathbb{H}^{(\text{crystal field})} = - \sum_{c=1}^{N_c} \sum_{j=1}^N \frac{Z_c}{|\mathbf{R}_c - \mathbf{r}_j|} = \sum_{c=1}^{N_c} \sum_{j=1}^N \sum_{k=0}^{\infty} \sum_{q=-k}^k (-1)^{q+1} \sqrt{\frac{4\pi}{2k+1}} B_k(r_j; R_c, Z_c) C_q^{(k)}(\vartheta_j, \varphi_j) Y_{k,-q}(\vartheta_c, \varphi_c)$$

$$B_k(r; R, Z) = Z \begin{cases} \frac{r^k}{R^{k+1}} & r \leq R \\ \frac{R^k}{r^{k+1}} & r > R. \end{cases}$$

The charges and positions of the surrounding ions are the physical parameters  $N_c$ ,  $Z_1$ ,  $\mathbf{R}_1 = (R_1, \vartheta_1, \varphi_1)$ ,  $Z_2$ ,  $\mathbf{R}_2 = (R_2, \vartheta_2, \varphi_2)$ , ... that determine the (additional) *crystal field*, and that must be given explicitly for each compound of interest.

- **Splitting of atomic levels in a crystal field:** For degenerate atomic levels with total angular momentum  $J \neq 0$ , the splitting in the electric

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(Stark) field of the crystal can be calculated in first-order perturbation theory from the matrix elements (Gaigalas and Kato, 2020)

$$\begin{aligned}
& \langle \alpha J M_J \parallel \mathbb{H}^{(\text{crystal field})} \parallel \alpha' J' M_J' \rangle \\
&= \sum_{c=1}^{N_c} \sum_{k=0}^{j_a+j_b} \sum_{q=-k}^k \sum_{rs} \sum_{ab} c_r c_s (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \sqrt{2J+1} d_{ab}^k(r, s) \langle \kappa_a \parallel C^{(k)} \parallel \kappa_b \rangle (-1)^{q+1} Z_c \sqrt{\frac{4\pi}{2k+1}} \\
&\quad \times Y_{k,-q}(\vartheta_c, \varphi_c) \left[ \int_0^{R_c} dr \frac{r^k}{R_c^{k+1}} (P_a P_b + Q_a Q_b) + \int_{R_c}^{\infty} dr \frac{R_c^k}{r^{k+1}} (P_a P_b + Q_a Q_b) \right] \\
&\langle \kappa_a \parallel C^{(k)} \parallel \kappa_b \rangle = (-1)^{j_a-1/2} \sqrt{2j_b+1} \begin{pmatrix} j_a & k & j_b \\ 1/2 & 0 & -1/2 \end{pmatrix} \pi(\ell_a, \ell_b, k).
\end{aligned}$$

Here  $P_a(r)$  and  $Q_a(r)$  are the large and small components of the relativistic one-electron radial wave function, and  $d_{ab}^k(r, s)$  the spin-angular coefficients due to the decomposition of the matrix elements of the rank-1 Hamiltonian  $\mathbb{H}^{(\text{crystal field})}$ .

- **Splitting of atomic levels in a crystal field:** In general, each degenerate level  $(\alpha \mathbb{J})$  splits into a number of sublevels, while  $J = 0$  levels are only shifted. The number of non-degenerate sublevels depend on the symmetry of the surrounding ions (crystal field) and follows directly from the diagonalization of the  $\mathbb{H}^{(\text{crystal field})}$  Hamiltonian matrix

$$|\beta\rangle = \sum_{r=1}^{N_{\text{csf}}} \sum_{-M_r}^{M_r} c_{r,M_r}(\beta) |\gamma_r J_r M_r\rangle.$$

These (sub-) levels of a multiplet in a crystal field have no longer a well-defined total angular momentum nor projection,  $J, M$ , although they can often be related to fine-structure levels of the free atom or ion.

### Classification and characterization of crystal fields:

- **Characterization of the crystal field:** While the ion of interest is always assumed to be at the origin of the coordinates, the position of the crystal atoms need to be specified in spherical coordinates  $\{\mathbf{R}_c = (R_c, \vartheta_c, \varphi_c)\}$ . These coordinates can be given explicitly as a list of point  $[(R_1, \vartheta_1, \varphi_1), (R_2, \vartheta_2, \varphi_2), \dots]$  or ...



## 7.4. Other topics closely related to atomic properties

### 7.4.a. Laser cooling, precision spectroscopy and quantum control

#### Quantum logic spectroscopy:

- **Quantum logic spectroscopy:** Quantum logic is typically implemented by a laser-induced coupling of the internal and external degrees of freedom of two ions, namely the **spectroscopy** and the **logic** ion. By making use of appropriate laser pulses, the **information about the internal state of the spectroscopic ion can then be transferred from the spectroscopic to the logic ion.**
- **Logic ion:** Simply speaking, the logic ion can be viewed as both, a remote control and a sensitive quantum sensor for the internal and external state of the spectroscopy ion.
- **Quantum-logic techniques:** Many limitations of precision spectroscopy can be overcome if simple quantum-logic techniques are used and **if the spectroscopic and logic ion is controlled together.** In this technique, especially, the readily-controllable logic ion provides sympathetic cooling, internal state preparation and detection of the ion with an interesting spectroscopic transition.
- **Realization of quantum logic spectroscopy:** Such a quantum-logical transfer scheme can be realized with two ions in a linear Paul trap.
- **Application of quantum logic spectroscopy:** Possible applications of quantum logic spectroscopy refer to the unprecedentedly high resolution spectroscopy of a wide range of sympathetically cooled atoms and molecules with special spectroscopic properties, such as an improved sensitivity to a variation of fundamental physics constants, or to tests of QED via precision spectroscopy.

#### Laser cooling and precision spectroscopy:

- **Laser-cooling techniques:** The recent development of laser-cooling techniques made cold and ultra-cold atomic samples available for optical spectroscopy. This development nowadays allows for long interrogation times and significantly reduced Doppler shifts; they give rise also to an unprecedented uncertainty in atomic clocks, exceeding one part in  $10^{-15}$ .
- **Coherent control of external and internal degrees of freedom:** In 1995, a controlled-NOT (CNOT) gate between a trapped atomic ion and its motional mode in the trap was first realized experimentally. Since then, the **coherent control over the internal and external degrees of freedom in an atomic system** has been demonstrated.
- **Coherent control of external and internal degrees of freedom:** Laser spectroscopy helped develop methods to simultaneously **control both, the internal electronic and the motional degrees of freedom of individual atoms, molecules and singly-charged ions in traps with high accuracy.**

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- **Precision spectroscopy of atoms and ions:** Most laser spectroscopy with clouds of trapped ions have explored a rather small class of atoms and atomic ions, including hydrogen, the alkali and alkaline-earth atoms and ions as well as few other species (Schmöger *et al.*, 2015). These atoms and ions usually have electronic transitions that are suited for laser cooling and that help localize the atoms for precision spectroscopy.
- **Application of precision spectroscopy:** In quantum information processing with trapped ions, precision spectroscopy has lead to new applications, such as teleportation, error-correction as well as the implementation of the Deutsch-Jozsa and semi-classical Fourier transformation algorithms.
- **Coulomb crystals:** A signature for trapped and well-localized ions is the formation of Coulomb crystals, i.e. **spatially ordered ensembles of mutually repelling ions that are confined in a common external trapping potential**. Such Coulomb crystals form when the thermal kinetic energy of the ions becomes (much) smaller than the ion-ion electrostatic energy.
- **Sympathetic cooling:** If atoms and ions do not have a direct cooling transition, **sympathetic cooling by use of co-trapped ions has been found a successful strategy in the past for singly and doubly charged atoms and molecules**.

### 7.4.b. Atomic clocks

#### Concepts and criteria of atomic clocks:

- **Atomic clock:** An atomic clock is typically based on an electron transition of either microwave, optical or ultraviolet frequency, and which serves as frequency standard for its time-keeping element.
- **Definition of the *second*:** The transition between the hyperfine levels of cesium in its  $[\text{Xe}] 6s\ ^2S_{1/2}$  ground level was first proposed by Essen and Parry for the definition of the time unit [sec]. As **primary frequency standard**, the second is today defined by 9,192,631,770 oscillations of a light pulse with  $6s\ ^2S_{1/2}\ F = 1/2 \rightarrow 3/2$  transition frequency of cesium. Standard atomic clocks must ensure this accuracy irrespective of their locations or the particular time of measurement. While the cesium clock is a microwave clock, **modern clocks are preferred to operate at optical frequencies**, i.e. at frequencies which are about five orders of magnitude higher and which are based on much narrower optical reference transitions.
- **Criteria for atomic clocks:** Three important criteria for an atomic clock refer to (1) a transition frequency that can be easily probed by some (rather) short-acting stable local oscillator; (2) a transition with a narrow natural linewidth; (3) a suitable technology for counting frequencies. Here, the suitability of a given atomic line is often characterized by a **quality factor**  $Q = \nu/\delta\nu$ , which should be large. Apart

from this quality factor of an atomic transition, however, one needs also to consider the limitations of the line with regard to reproducibility and stability. Here, the **stability of an atomic transition** measures the variability of the frequency standard as function of time. The three relevant factors of atomic clock transitions (accuracy, stability and reproducibility) generally depend also on the experimental set-up and the extent to which environmental perturbations can be controlled. **In the optical domain, frequency combs are applied as references to ensure high stability and accuracy of the optical clocks.**

- **Optical atomic clocks:** Recent developments in the **set-up and control of optical atomic clocks** has improved their precision by a factor of **1000** in less than two decades.
- **Challenges to atomic-clock developments:** The control of the thermal motions of the atoms and ions, trapped in some oscillating electro-magnetic field, often introduces the largest systematic uncertainties to the overall uncertainty budget. For clocks, which are operated at room temperature, the velocity distribution of the atoms causes **Doppler shifts due to the residual thermal or micromotion of the ions.**
- **Classes of systematic uncertainties:** (1) **Instrumental uncertainties** arise from the construction of the traps and instruments, while (2) **external uncertainties** are caused by the incomplete control of the external – electro-magnetic stray or gravitational – fields. The second class of uncertainties can be further controlled by both, a proper choice of the clock transitions and a detailed understanding how these transitions are affected by electro-magnetic fields. This control in terms of choosing the atomic clock transitions usually requires a detailed analysis of the trapping electric and magnetic fields as well as of all laser fields that act upon the trapped atoms or ions. This analysis must include also a careful treatment of the – linear and quadratic – Zeeman and (ac) Stark shifts.

### Shifts of atomic clock transitions:

- **Magic wavelength:** Often, the trap lasers of the optical lattice clock are operated at the (so-called) *magic* wavelength at which the electric-dipole polarizabilities of the (two) clock levels are the same in order to ensure a (nearly) zero ac Stark shift of the clock transition.
- **Magic wavelengths:** The need in precise (ac) polarizabilities arises especially from the study of atomic clocks and the search for **magic wavelengths** for developing optical frequency standards. At the magic wavelength (of some proper transition), the frequency-dependent polarizabilities of the lower and upper (atomic) state are the same and, hence, the (ac) Stark shift of the transition frequency just vanishes. Such magic wavelengths cannot be found for every atomic transitions, at least not for acceptable experimental conditions.
- **Light shifts for clock levels:** The frequency of an atomic clock can be affected by (i) the thermal bath of blackbody radiation (BBR), (ii) the electric-quadrupole coupling of the ions to the trapping field and with other residual electro-magnetic fields, (iii) by ambient magnetic fields as well as (iv) through various Stark shifts (Yudin *et al.*, 2014).
- **BBR shifts of clock transitions:** The probing of the clock transition by a laser leads to clock shifts due to the ac Stark effect. These shifts are proportional to the E1 polarizability like the BBR shift, but is strongly suppressed with  $\propto 1/\tilde{Z}^6$  for highly-charged ions.

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- **E1 versus M1 contributions to the BBR shift:** While the E1 contribution usually dominates the BBR shift of most atomic levels, M1 clock transitions are mainly affected by the thermal **B**-field fluctuations which couple to M1 transition moments (Yudin *et al.*, 2014).
- **Electric-quadrupole (E2) shift:** The gradients of the trapping and residual electric fields also couple to the quadrupole moments of the clock states. For  $J = 1/2$  clock states, the electric-quadrupole moment vanishes due to the angular selection rules.
- **Shifts of atomic clock transitions for HCl:** Taken from Berengut *et al.* (2012).

Contribution to the shift	Scaling
Second-order Stark shift	$\sim 1/(Z^{(\text{eff})})^4$
Blackbody shift	$\sim 1/(Z^{(\text{eff})})^4$
Second-order Zeeman shift	suppressed due to large energy denominators.
Electric-quadrupole shift	$\sim 1/(Z^{(\text{eff})})^2$
Fine structure	$\sim Z^2 (Z^{(\text{eff})})^2 / (Z_{\text{ion}} + 1)$
Hyperfine $A$ coefficient	$\sim Z (Z^{(\text{eff})})^2 / (Z_{\text{ion}} + 1)$

### Classes and realization of atomic clocks:

- **Classes of atomic clocks:** There are currently **two types of optical atomic clocks under development:** (i) **based on neutral atoms in optical lattices** or (ii) **based on a single trapped ion**. For both types, a similar uncertainty have been reached, namely:  $2.1 \times 10^{-18}$  for a Sr neutral atom clock (Nicholson *et al.*, 2015) and  $3.2 \times 10^{-18}$  for a  $\text{Yb}^+$  trapped ion clock (Huntemann *et al.*, 2016), that have been operated on a particular electric-octupole (E3) transition.
- **Classes of atomic clocks:** Modern optical clocks are either based on (1) neutral atoms, which are trapped and cooled in some magnetic-optical trap (MOT); or (2) singly- and multiply-charged ions in a Paul-type trap. There has been a remarkable progress (and competition) along both of these research lines, and it is undecided until now which particular scheme will become the primary frequency standard of the next-generation atomic clocks.
- **Accuracy and stability of optical atomic clocks:** The accuracy and stability of optical atomic clocks has been advanced significantly over the past ten years. The systematic uncertainty of the Sr optical lattice clock has been reduced to  $2.1 \times 10^{-18}$  in (so-called) fractional frequency units. A similar small (systematic) uncertainty of  $3.2 \times 10^{-18}$  was reported also for a single-trapped ion atomic clock, based on an electric-octupole transition in  $\text{Yb}^+$ .

- **Optical clocks:** Optical clocks that operate at an accuracy level of a few parts per  $10^{-18}$  will be sufficient to measure subtle relativistic effects and to become sensitive to the geodesic gravitational potential difference of Earth or to set upper limits on possible temporal or spatial variations of fundamental constants.
- **Single-ion optical clocks:** Because of limitations for having a proper spectroscopic transition, single-ion optical clocks, which are based on the isotopes of aluminium and boron, have not been realized in the past.
- **Single-ion mercury clock:** Recently, an optical clock, that is based on a forbidden transition in a single mercury ion, has achieved an uncertainty of  $7.2 \times 10^{17}$ . This clearly exceeds the performance of the best cesium fountain standards.
- **Atomic clocks based on singly-charged ions:** During the past two decades, detailed clock studies and developments have been performed for the ions:  $^{27}\text{Al}^+$ ,  $^{40}\text{Ca}^+$ ,  $^{43}\text{Ca}^+$ ,  $^{87}\text{Sr}^+$ ,  $^{88}\text{Sr}^+$ ,  $^{115}\text{In}^+$ ,  $^{171}\text{Yb}^+$ ,  $^{173}\text{Yb}^+$ ,  $^{199}\text{Hg}^+$ , and  $^{201}\text{Hg}^+$ , respectively.
- **Atomic clocks based on forbidden optical transitions:** Single-photon  $ns^2\ ^1S_0 - nsnp\ ^3P_0$  transitions among the low-lying levels of alkaline atoms are strictly forbidden because of selection rules. However, these lines can be readily quenched by weak electric and magnetic fields and may serve a reference transition for new frequency standards. Moreover, these transitions are ideal in the sense that their line widths can be perfectly tuned by the strength of the applied fields.
- **Proposals for a neutral Yb atomic clock:** The  $4f^{14}6s^2\ ^1S_0 - 4f^{14}6s6p\ ^3P_0$  transition in neutral Yb can be induced by hyperfine mixing in isotopes with nuclear spin  $I \neq 0$  and has served already as some frequency standard. However, neutral Yb has still another and very interesting  $4f^{14}6s6p\ ^3P_0 - 4f^{13}6s^25d\ (J=2)$  electric-quadrupole (E2) transition at an easily accessible wavelength of 1695 nm, which might be suitable as well for the development of another frequency standard in this atom (Safronova *et al.*, 2018).
- **$^{229\text{m}}\text{Th}$  nuclear clock:** Thorium has one exceptional nuclear state that is known for the last 40 years and that has a very low energy of presumably below 10 eV. The currently assumed excitation energy of this isomeric state is  $7.8 \pm 0.5$  eV, or correspondingly  $159 \pm 11$  nm or  $\sim 1900$  THz. This isomeric state conceptually allows for a direct laser excitation of the nucleus by using solid-state laser technology. This state has therefore been proposed for the development of a nuclear clock of extremely high stability owing to the expected high resilience against external influences and its radiative lifetime in the range of minutes to hours (von der Wense *et al.*, 2017).
- **$^{229\text{m}}\text{Th}$  nuclear clock:** Von der Wense *et al.* (2017) propose a different approach for the excitation of  $^{229\text{m}}\text{Th}$  that allows for a direct laser excitation of this transition without the prior request to know the transition energy accurately. This approach makes use of the fast (lifetime of  $\sim 10\ \mu\text{s}$ ) nonradiative internal conversion decay channel of neutral thorium for the isomer detection. The internal conversion transfers the nuclear excitation energy to the electron cloud and, hence, results in the ejection of a (valence-shell) electron.
- **Atomic clocks based on multiply and highly-charged ions:** For highly-charged ions, the hyperfine transitions are often in or near to the optical region, in contrast to the present microwave cesium standard. Very narrow optical lines can be found especially within the ground

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configurations or near to the ground levels of multiply and highly-charged ions, and if all (electric-) dipole or even quadrupole transitions are forbidden. Such ions can also be considered for optical frequency standards because they are often different in their (low-lying) level structure as well as sensitivity to the environmental perturbations.

- **Atomic clocks based on hyperfine-induced transitions in highly-charged ions:** Magnetic-dipole hyperfine-induced transitions in highly-charged ions may serve as reference transition because of their reduced *size* that is  $\sim (Z - N)^{-1}$  for  $N$ -electron ions with nuclear charge  $Z$ . Such a reduced size also leads to reduced blackbody radiation (BBR), quadratic Zeeman, frequency-dependent (ac) Stark and static electric-quadrupole shifts in these ions.
- **Atomic clocks with highly-charged ions:** Optical E1, M1 and E2 transitions among low-lying atomic levels also occur for highly-charged ions due to level crossings along selected isoelectronic sequences. In HCI, such clock transitions may have the advantage that systematic effects, such thermal shifts, can be reduced when compared with existing optical atomic clocks.

### Applications of atomic clocks:

- **Atomic clock:** Atomic clocks are the most accurate time and frequency standards; they are frequently applied as **primary standards for international time distribution services**, to control the wave frequency of television broadcasts as well as to operate the global navigation satellite systems such as GPS.
- **Application of atomic clocks:** Various applications of atomic clocks are now in reach or have already been realized owing to the improved precision and the high stability of these clocks. These applications include: (1) the study of many-body physics and quantum simulations; (2) relativistic geodesy; (3) very-long baseline interferometry; (4) searches for the variation of the fundamental constants; (5) searches for dark matter candidates; (6) tests of the Lorentz invariance and several others. Further improvement of clock precision is needed for several of these applications.
- **Application of atomic clocks:** Modern atomic clocks require precisely-known transition frequencies and, hence, can be utilized as well in order to probe the temporal and spatial variations of many fundamental physical constants. Such measurements at (atomic) low energies form a valuable alternative to experiments in high-energy physics but require a careful treatment and precise predictions from relativistic atomic structure theory.
- **Global positioning system (GPS):** Atomic clocks are essential for the global positioning system (GPS) where multiple such devices are onboard of each GPS satellite, and which must provide the time to within 100 billionths ( $10^{-7}$ ) of a second. Atomic clocks are applied also in radio astronomy, meteorology, telecommunications as well as for military services.

- **Atomic clocks for gravitational wave detection:** These and further ideas and applications, such as the use of atomic clocks for gravitational wave detection, will require even more precise clocks in the future.

### 7.4.c. Atomic partition functions

#### Motivation:

- The atomic partition function  $U(T)$  includes a **summation over all bound levels of the atom** and is defined as

$$U(T) = \sum_j g_j \exp\left(-\frac{E_j}{kT}\right).$$

### 7.4.d. Quantum similarity measures & similarity indices for pairs of atoms and ions

#### Quantum similarity measures:

- **Quantum similarity measures (QSM):** A number of such similarity measures has been worked out formally in the early 1980s by Carbo and coworkers (1980, 2004). These similarity measures and (so-called) similarity indices for pairs of atoms or molecules are mainly based on the (overlap of the) electron density distribution of two *distinguishable* quantum systems. When applied to isolated atoms, these measures can help analyze the chemical periodicity in the periodic table of elements.
- **Quantum similarity measure:** For two quantum systems with (spinless, electron) densities  $\rho^{(A)}(\mathbf{r})$ ,  $\rho^{(B)}(\mathbf{r})$  and a separation operator  $\Omega(\mathbf{r}_1, \mathbf{r}_2)$ , Carbo *et al.* (1980) define such a similarity measure by

$$Z^{(A,B)}(\Omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(A)}(\mathbf{r}_1) \Omega(\mathbf{r}_1, \mathbf{r}_2) \rho^{(B)}(\mathbf{r}_2).$$

Often, the separation operator  $\Omega(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$  is chosen which *reduces* the double integration to a ‘overlap’ integral of the two electron densities. For  $\Omega(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ , in contrast, a Coulomb-interaction integral is obtained.



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- **Quantum similarity index:** A *normalized* similarity measure, known as similarity index, is obtained by

$$I^{(A,B)}(\Omega) = \frac{Z^{(A,B)}(\Omega)}{\sqrt{Z^{(A,A)}(\Omega)} \sqrt{Z^{(B,B)}(\Omega)}}, \quad 0 \leq I^{(A,B)}(\Omega) \leq 1.$$

Both, the quantum similarity measure and similarity index can be evaluated quite easily by using proper densities of ions, atoms or molecules.

- **Application of QSM:** These measures can be used to provide compact information about (pairs of) molecules with regard to their shape and extent of the electron density. Moreover, these measures might be used as **atomic and molecular descriptors** in order to predict molecular structures and reactivities. Various modifications have been suggested for the quantum similarity measures from above by using different separation operators or reactivity-motivated densities.

### 7.4.e. Atom-atom and atom-ion interaction potentials

#### Theory of interatomic forces:

- **Interatomic forces and potentials:** Accurate interatomic potentials are of fundamental importance for understanding and modelling the static and dynamic properties of gases, liquids or even solids.
- **Interatomic forces:** While the theory of interatomic forces has been developed over the last four decades, fast and reasonably reliable predictions are often still not so easily available, especially if a whole range of intermolecular separations (distances) need to be considered.
- **Interatomic forces:** A good **knowledge of the interatomic forces in (closed-shell) molecules has been found a key especially for understanding the behavior of various systems**, such as the geometry and stability of molecular solids, the properties of liquids and their phase transitions as well as for collisions between molecules in gases or in molecular beams.
- **Interatomic forces:** The (attractive) interatomic interaction is **dominated by correlation or dispersion effects at large internuclear distances  $R$** , where perturbation theory gives rise to a series expansion  $R^{-2n}$ ,  $n \geq 3$ . However, this perturbation series is known to be asymptotically divergent and is best truncated to its smallest term, following the work of Dalgarno and Lewis.
- **Intermolecular interaction:** The (inter-molecular) interaction energies are often partitioned into the SCF parts of the individual atoms and the correlation energy of the molecule as a whole. For atoms, the SCF computation can be carried out quite easily, while the correlation energies need to be obtained semi-empirically by means of standard long range multipolar expansion (Douketis *et al.*, 1982).



- **Ion-atom interactions at cold temperatures:** At cold temperatures of just a few Kelvin or even lower, ion-atom interactions are often affected by (i) rapid energy variations in the potentials as induced by long-range polarization contributions; (ii) the generally large number of contributing partial waves; and (iii) a rather sensitive dependence of the interatomic interactions upon the details of the short-range potential. Further difficulties may arise from (iv) other weak interactions, such as hyperfine interactions and other.
- **Application of interatomic forces:** While the scattering of charged particles has already a rather long history, collisions of ions and neutral particles at ultracold temperatures has emerged only recently as an exciting (new) field in AMO physics.

### Interatomic potentials:

- **Different theoretical approaches:** Different regions of the molecular potential curves have been investigated by different theoretical methods. Perturbation theory has been applied, in particular, to describe the long-range attraction, and where the first- and second-order perturbation energies are often approximated by just the first few terms in a multipole-series expansion of the Coulomb interaction between the molecules.
- **Failure of perturbation theory:** A perturbative treatment of interatomic potentials fails to describe the potential at short and intermediate distances since it: (i) does not include exchange interactions between the electrons, (ii) diverges for strong interatomic interactions, and (iii) because a multipole expansion generally fails when the electron distributions overlap each other.
- **Intermediate distance:** At intermediate distances, i.e. in the region of the minimum of the intermolecular potential, only SCF computations typically predict the potentials reasonably well if the molecule does not form strong chemical bonds.
- **Experimental interatomic potential:** Because of the difficulties in obtaining good interatomic potentials, many accurate such potentials have been determined experimentally by combining data from beam scattering experiments, virial and transport coefficient measurements as well as liquid and solid state properties. In practise, however, the interatomic potentials are still best probed in the intermediate regions.
- **Analytic interaction potentials:** Analytic interatomic potentials have been widely applied in organic chemistry for estimating the minimum energy structures of (energy) surfaces, grain boundaries and others. These analytic potentials are known also as bond-order, semi-empirical or even classical potentials. All analytic potentials are defined by some functional form of the interatomic interactions, and whose parameters are fitted to data from selected databases (Andrienko *et al.*, 2016).
- **Properties of analytic interaction potentials:** Following Brenner (2010), an analytic potential needs to be:
  - **Flexible:** ... to account for a relatively wide range of structures from the fitting database;
  - **Accurate:** ... able to accurately reproduce quantities such as energies, bond lengths, elastic constant, and related properties entering a fitting database.
  - **Transferable:** ... able to reproduce related properties that are not yet included in the fitting database.

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- **Computationally efficient:** ... so that it is tractable for a desired calculation, given the available computing resources.

➤ **Interaction between two spherical-symmetric atoms at large distance  $R$ :** For two spherical-symmetric atoms, the dominant interaction at large distance  $R$  is usually given in terms of **dispersion coefficients**. If atom A is at the origin with an electron at  $\mathbf{r}$  (relative to the nucleus of A) and atom B at the position  $(0, 0, R)$  on the  $z$ -axis with an electron at  $\mathbf{r}'$  (relative to the nucleus of B), the perturbing interaction can be written as

$$V^{(\text{perturbation})} = \frac{1}{R} - \frac{1}{|\mathbf{R} - \mathbf{r}|} - \frac{1}{|\mathbf{R} + \mathbf{r}'|} + \frac{1}{|\mathbf{R} - \mathbf{r} + \mathbf{r}'|}$$

If there are more than one electron at some atom, the corresponding term(s) must be formally added for all pairs of electron coordinates. In the perturbation above, the last term is crucial as it requires a more advanced multipole expansion, cf. 2.4.b

➤ **Modified Buckingham potential:** Already 1941, Heller suggested a modified Buckingham potential by including a  $R^{-10}$  dispersion term

$$V^{(\text{mod. Buckingham})} = A e^{-bR} - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}}.$$

➤ **Molecules with ionic bonds:** For ionic bonds, **the summation over the ionic neighbours can then be carried out using the standard techniques**; hereby, the total interaction energy is often called the **crystal energy** and can be expressed in terms of the nearest-neighbor distance  $R$  as

$$V(R) = -\frac{\alpha^{(\text{Madelung})}}{R} + n_s V_s(R),$$

where  $n_s$  is the number of nearest neighbours and  $V_s(R)$  a short-range potential as worked out by Gordon and Kim (1974). From  $V(R)$ , one can obtain the **equilibrium internuclear distances**, the dissociation energies to the free ions, the nearest-neighbor separations  $R$ , the cohesive energies  $D$ , or the bulk moduli for these crystals.

### Gordon-Kim (1972) theory for atom-atom interactions:

➤ **Gordon-Kim model:** Gordon and Kim (1972) developed a model in order to calculate the interaction between closed-shell atoms, ions and molecules. In this model, the **electron density of the system is taken as the sum of the two separate densities**, and the non-Coulombic part of the interaction potential is calculated from this density by using energy expressions from the free-electron gas.

- **Assumptions of the Gordon-Kim theory:** Three basic assumptions were made by Gordon and Kim (1972):
  - i) No rearrangement or distortion of the separate atomic densities occurs when the two atoms are brought together and, hence, **the total electron density is just the sum of the two (spherically symmetric) atomic densities**. This assumption neglects of course the rearrangement of the electron density and therefore restricts the theory to systems with a strong chemical bond, including covalent chemical bonds and to interatomic distances that are smaller than about half of the equilibrium separation.
  - ii) The interatomic interaction can be evaluated from the combined atomic density, including the Coulomb interactions between all charges.
  - iii) Gordon and Kim applied originally Hartree-Fock wave-functions in order to obtain the electron densities of the separate atoms, although other, and perhaps more accurate, wave functions should work as well.
- **Total interaction of the two (atomic) charge distributions:** The total energy includes the **contributions from the kinetic, exchange and correlation energies as well as the (direct) Coulomb interactions energy**. Below, we briefly summarize how these contributions can be calculated by just using atomic wave functions.
- **Total interaction of the two (atomic) charge distributions:** Apart from the Coulomb interaction of the two (atomic) charge distributions, the **kinetic, exchange and correlation energy contributions to the total interaction energy are obtained from the electron density and the free-electron gas approximation**.
- **Uniform electron gas model:** The regions around the nuclei (in which the density varies rather rapidly) do overall not contribute much to the interaction energy, even if they strongly affect the total energy. These contributions to the total energy cancel out if the atomic energies are subtracted. **Only the outer regions of the atoms, in which the atomic densities overlap, contribute significantly to the interaction energy**. For these reasons, the uniform electron gas model should be reasonably accurate (Gordon and Kim, 1972).
- **Application of the Gordon-Kim potential:** The rather simple Gordon-Kim potential have been used, for example, in the treatment of ionic compounds such as alkali-halide and alkaline-earth-dihalide molecules in order to predict (surprisingly) accurate molecular properties (Kim and Gordon, 1974). In this work, Gordon and Kim made the following two basic assumptions in addition to those assumptions already made for their pair potentials: (a) the systems are made of free ions; (b) the interactions of ions are pairwise additive, i.e. the total interaction is the sum of all the pair interactions, neglecting the many-body interactions.
- **Coulomb interaction of the two (atomic) charge distributions:** For two separated atoms with nuclear charges  $Z_a$  and  $Z_b$  and with (total)

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atomic density  $\rho = \rho_a + \rho_b$ , the total Coulombic interaction energy but without the energies of the infinitely separated atoms is

$$\begin{aligned}
 V^{(\text{Coulomb})} &= \frac{Z_a Z_b}{R} + \int d^3 r_1 d^3 r_2 \frac{\rho_a(\mathbf{r}_1) \rho_b(\mathbf{r}_2)}{r_{12}} - Z_b \int d^3 r_1 \frac{\rho_a(\mathbf{r}_1)}{r_{1b}} - Z_a \int d^3 r_2 \frac{\rho_b(\mathbf{r}_2)}{r_{2a}} \\
 &= \int_0^\infty dr_1 r_1^2 \rho_a(r_1) \int_0^\infty dr_2 r_2^2 \rho_b(r_2) \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_2 \int_0^\pi d\vartheta_1 \sin \vartheta_1 \int_0^\pi d\vartheta_2 \sin \vartheta_2 \left( \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right) \\
 &= \int_0^\infty dr_1 r_1^2 \rho_a(r_1) \int_0^\infty dr_2 r_2^2 \rho_b(r_2) \times (4\pi)^2 I(R, r_1, r_2),
 \end{aligned}$$

where (in the upper line) the first term on the right-hand side represents the repulsion between nuclei, the second term the electron-electron repulsion, and where the third and fourth terms include attractions between the electrons of the atom with the *other* nuclei.

- **Coulomb interaction of the two (atomic) charge distributions:** In the final expression, moreover, the atomic densities are to be assumed spherically symmetric (which is the case for closed-shell atoms), so that  $\rho_a$  and  $\rho_b$  just depend on the radial distances from their own atomic nucleus.
- **Coulomb interaction of the two (atomic) charge distributions:** The integral  $I(R, r_1, r_2)$  depend on the charges of the two atoms and can be expressed as

$$I(R, r_1, r_2) = \begin{cases} \frac{1}{R} + F(R, r_1, r_2) - \frac{4}{R + r_1 + |R - r_1|} & \text{for homo - nuclear pairs of atoms} \\ \frac{1}{R} + F(R, r_1, r_2) - \frac{2}{R + r_1 + |R - r_1|} - \frac{2}{R + r_2 + |R - r_2|} & \text{for hetero - nuclear pairs of atoms} \\ \frac{Z_a Z_b + 1}{(Z_a - 1)(Z_b + 1)R} + F(R, r_1, r_2) - \frac{2Z_b}{(Z_b + 1)(R + r_1 + |R - r_1|)} - \frac{2Z_a}{(Z_a - 1)(R + r_2 + |R - r_2|)} & \text{for ion pairs,} \end{cases}$$

if we utilize for the electron densities of the ion pair in the last line  $\int d^3 \mathbf{r} \rho_a(\mathbf{r}) = Z_a - 1$ ,  $\int d^3 \mathbf{r} \rho_b(\mathbf{r}) = Z_b + 1$ .

- **Charge-density expectation values:** The expression above contains the  $\langle r_{12}^{-1}; R \rangle$  expectation value of which the two charge densities depends (parametrically) upon the internuclear separation  $R$ , and which can be evaluated analytically for two spherical-symmetric charge

distributions:

$$F(R, r_1, r_2) = \langle r_{12}^{-1} \rangle = \begin{cases} \frac{2}{R + r_1 + |R - r_1|} & \text{for } r_2 < |R - r_1| \\ \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) - \frac{R}{4r_1 r_2} - \frac{(r_1 - r_2)^2}{4R r_1 r_2} & \text{for } |R - r_1| < r_2 < R + r_1 \\ \frac{1}{r_2} & \text{for } r_2 > R + r_1. \end{cases}$$

- **Total Coulomb interaction:** With these three expressions, the total Coulomb interaction can be obtained from the just two-dimensional integral over the radial coordinates  $r_1$  and  $r_2$ . This integral from above can be carried out numerically by using a Gauss-Laguerre quadrature. Despite the piecewise form of the integrand, it appears continuous and well behaved. Gordon and Kim (1972) note that the numerical quadrature for the Coulomb interaction converges easily and that  $24 \times 24$  points generally gives rise to a four-figure accuracy.
- **Kinetic and exchange energy:** The contributions to the total interaction energy due to the (kinetic) motion of the electrons and their exchange interaction is derived from expressions for the free-electron gas. To this end, one integrates the electron density contribution from the electron gas over the molecular volume and subtracts the atomic contributions.
- **Total energy density from electron gas:** Gordon and Kim (1972) define the total energy density functional for the electron gas as

$$E^{(\text{total})}(\rho) = E^{(\text{HF})}(\rho) + E^{(\text{correlation})}(\rho), \quad E^{(\text{HF})}(\rho) = \frac{3}{10} (3\pi^2)^{2/3} \rho^{2/3} - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{1/3},$$

and where additional corrections can be made for the correlation energy  $E^{(\text{correlation})}$ .

- **Total electron gas contribution:** The electron-gas contribution to the interatomic interaction is

$$V^{(\text{total})} = \int d^3\mathbf{r} \{ [\rho_a(\mathbf{r}_a) + \rho_b(\mathbf{r}_b)] E^{(\text{total})}(\rho_a + \rho_b) - \rho_a(\mathbf{r}_a) E^{(\text{total})}(\rho_a) - \rho_b(\mathbf{r}_b) E^{(\text{total})}(\rho_b) \}$$

Obviously, the total interatomic potential is the sum of the Coulomb terms above and these electron gas terms.

#### 7.4.f. Dispersive interactions in liquids and solids

##### Dispersive interactions in molecular-dynamics and Monte-Carlo simulations:

- **Dispersive interactions:** Dispersive forces and interactions in media often refer to contributions due to intermolecular interactions, and which that arise from the polarization of one (of the) atoms in the fluctuating but instantaneous multipole field of other atoms. Therefore, dispersive interactions exist between each pair, triple, etc. of atoms or ions.
- **Dispersive interactions:** For dense-phase and solid-state systems, full quantum mechanical calculations of the interaction energy are generally not feasible and, hence, require to describe the interactions by means of interatomic or intermolecular potentials; cf. section 7.4.e.
- **Dispersive interactions:** In principle, the dispersive interactions in media can be captured also by first-principles simulations, for instance, based on density functional theories (DFT). Although such simulations are quite promising, reliable results are obtained only for systems with covalent bonding, while difficulties arise when dealing with dispersion interactions.
- **Dispersion coefficients:** Expressions for the dispersion coefficients can be derived from perturbation theory; however, the theory of intermolecular interaction also shows clearly that the dispersive interactions in media are generally not pair-additive. Apart from the two-particle interactions, the three-body terms are known to play a significant role in the thermodynamics of condensed phases.
- **Application of dispersive interactions:** Apart from inert-gas or crystallized solids of various organic molecules, the dispersive interactions are typically small, though not negligible. Reasonable estimates of the magnitude of the dispersion interaction are therefore necessary for many solid-state studies, such as the cohesion of matter, the behaviour of ionic crystals, for molecular liquids, the adsorption on surfaces or in porous media (Pellenq and Nicholson, 1998).
- **Application of dispersive interactions:** In Monte-Carlo and molecular-dynamics simulations, for example, a reasonable accurate potential energy function is required and need to be based on quantum-mechanical estimates, even if the dynamics of the particles is described classically.

##### Two-body dispersive interactions:

- **Long-range dispersive interactions:** If we consider two interacting neutral atoms, time-dependent perturbation theory gives rise to a long-range dispersive interaction due to charge fluctuations of the interacting species.
- **Multipole expansion:** For two spherically symmetric atoms or molecules  $A$  and  $B$ , that are separated by a distance  $R$ , a multipole expansion

is given by (Pellenq and Nicholson, 1998)

$$V^{(\text{dispersion, AB})}(R) = - \left[ \frac{C_6}{R_6} + \frac{C_8}{R_8} + \frac{C_{10}}{R_{10}} + \dots \right].$$

- In this expansion, the dispersion coefficient  $C_6$  describes the interaction between two instantaneous dipoles,  $C_8$  the interaction between a quadrupole and a dipole and  $C_{10}$  both, the interaction between an octopole and a dipole as well as between two quadrupoles.

### Three-body dispersive interactions:

- In the multipole expansion, the terms with three species  $A$ ,  $B$  and  $C$  are obtained from perturbation theory at in third and higher orders. For such a triplet, the total dispersion energy is however non-additive:

$$V^{(\text{dispersion})} = V^{(\text{dispersion, AB})} + V^{(\text{dispersion, BC})} + V^{(\text{dispersion, CA})} + V^{(\text{dispersion, ABC})} + \dots$$

where  $V^{(\text{dispersion, ABC})}$  represents a sum of several terms describing the three-body interaction.

## 7.4.g. Mean excitation energy of atomic ions & stopping powers

### Mean excitation energy of atomic ions:

- **Application of mean excitation energies of atoms and ions:** Such mean excitation energies  $E(Z; N)$  if ions might be helpful for simple models in the time evolution of plasmas, warm dense matter or complex biochemical structures. In all these systems, energy is often pumped in by the stopping power of fast ions. The characteristic energy transfer is given by the stopping power, i.e. the energy deposit by the projectile per unit length of the projectile trajectory. For ions with velocity  $v$  and the material density  $n(x)$ , the stopping power is

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related to the (so-called) **stopping cross section**  $S(v)$  by

$$-\frac{dE(v)}{dx} = n(x) S(v) = \frac{4\pi e^4 n(x) [Z^{(\text{projectile})}]^2 Z^{(\text{target})}}{m v^2} L(v)$$

$$L(v) = \sum_{j=0} [Z^{(\text{projectile})}]^j L_j \approx L_o^{(\text{Bethe})}(v) + Z^{(\text{projectile})} L_1^{(\text{Lindhard})}(v) + [Z^{(\text{projectile})}]^2 L_2^{(\text{Bloch})}(v)$$

$$L_o^{(\text{Bethe})}(v) = \ln \frac{2m v^2}{I_o} - \frac{C}{Z^{(\text{projectile})}}.$$

In these expressions,  $L(v)$  is the so-called **stopping number** which includes terms from different contributors. The Bethe term  $L_o^{(\text{Bethe})}(v)$  is usually the most relevant contribution to the stopping number. Moreover,  $I_o$  is the mean excitation energy of an element for a given charge state.

- **Mean excitation energy of an element for a given charge state:** The mean energy tells how easily an atomic or molecular target can absorb kinetic energy from the projectile; this mean energy depends on the target but not on the projectile. It can be expressed as the weighted sum (integral) of all relevant oscillator strength of the target in the given charge state

$$\ln I_o = \frac{\int dE \ln E \frac{df}{dE}}{\int dE \frac{df}{dE}}.$$

Because of the oscillator strength, it should be possible to re-express this mean energy in second-order perturbation theory by an approximate summation over the complete spectrum (Sauer *et al.*, 2015). This would be a useful application of JAC.

### 7.4.h. Transport coefficients for ion mobility and diffusion in gases

#### Transport coefficients in gases:

- **Ion-mobility spectrometry (IMS):** The IMS is an analytical technique that is used to separate and identify ionized molecules in the gas phase, based on their mobility within a carrier buffer gas.
- **Ion-mobility spectrometry (IMS):** IMS has been heavily employed for military or security purposes, such as detecting drugs and explosives, but also for the analysis of both, small and large biomolecules.



- **Ion mobility  $K$ :** The ion mobility is defined as the proportionality factor between the drift velocity  $v_d$  of the ions and the applied electric field  $\mathcal{E}$ :  $\mathbf{v}_d = K \mathcal{E}$ . These ion mobilities are usually reported as (standard) **reduced (ion) mobilities for a standard gas density  $n_0$** , i.e. for standard temperature  $T = 273$  K and pressure  $p_o = 1013$  hPa.
- **Ion mobility  $K$ :** Ion mobilities also help in analysis of collision broadening in ion cyclotron resonance, the study of ion-molecule reactions as a function of electric field strength in flow-drift tubes, and especially the use of mobility data to test or determine ion-neutral interaction potentials.
- **Ion mobility  $K$ :** While the reduced ion mobility just refers to the standard density, the ion mobility is still temperature dependent  $K_o = K \frac{n}{n_o} = K \frac{T_o}{T} \frac{p}{p_o}$ .
- **Kinetic theory of ion mobility in neutral gases:** Viehland and Mason (1978) present the first rigorous kinetic theory of ion mobility in neutral gases which is valid for electric fields of arbitrary strength and without restriction to the ion-neutral mass ratio or interaction potential. These results proved to be useful in a number of applications: the calculation of low-field ion mobilities in high-temperature gases, if measurements as function of electric field strength were made before in low-temperature gases.

### 7.4.i. Polarizability and optical absorbance of nanoparticles

#### Optical properties of nanoparticles:

- **Color of nanoparticles:** Noble-metal nanoparticles with a size, that is comparable to the wavelength of the incident light, show characteristic colors owing to the strong absorption and scattering of light in the visible region.
- **Localized surface plasmon resonance (LSPR).** The LSPR are often explained as collective oscillation of free electrons in the nanoparticle that are induced by the electro-magnetic waves. Therefore, the **color of the absorbed light can be tuned by the size, shape, materials as well as the surrounding environment of the nanoparticles**, and with applications in chemistry, physics and biomedical fields.
- **Surface-to-volume ratio:** Nanoparticles with a size below 10 nm have extremely high surface-to-volume ratios and, thus, substantially different optical properties, when compared to large nanoparticles or to the bulk material. These optical properties also depend on the atomistic structure of the nanoparticles.
- **Discrete dipole approximation (DDA):** This classical discrete dipole approximation and various variants of this method has been applied extensively for studying plasmonic nanoparticles. However, since the DDA makes usually use of the bulk dielectric constant, it cannot so easily be applied to quantum-sized nanoparticles.

### Methods for calculating the polarizability of nanoparticles:

- **Polarizability of a discretized medium:** The polarizability of a discretized medium is in general proportional to its volume.
- **Polarizability of the i-th atom  $\alpha_i$ :** In a given nanoparticle, the polarizability of the i-th atom  $\alpha_i$  can be approximated by multiplying the polarizability of the free atom  $\alpha^{(\text{free})}$  with the relative volume (ratio), i.e. by dividing the effective volume  $V^{(\text{eff})}$  by the volume of the free atom  $V^{(\text{free})}$ ,

$$\alpha_i = \frac{V^{(\text{eff})}}{V^{(\text{free})}} \alpha^{(\text{free})} = \frac{V^{(\text{eff})}}{V^{(\text{free})}} \frac{e^2}{m} \sum_{\nu} \frac{f_{\nu o}}{\omega_{\nu o}^2 - \omega^2 - i \omega \delta}$$

where  $\omega_{\nu o}$  is the n-th absorption frequency (with regard to the ground level),  $f_{\nu o}$  its oscillator strength and where the frequency shift  $\delta$  depends on the coordination factor within the nanoparticle.

- **Optical absorbance of nanoparticles:** The optical absorbance of the nanoparticle is obtained from the total polarizability of all atoms  $i = 1 \dots N$  by

$$\sigma^{(\text{absorption})} = \frac{4\pi\omega}{c} \Im \{ \alpha^{(\text{total})}(\omega) \} = \frac{4\pi\omega}{c} \Im \left\{ \sum_i^N \alpha_i^{(\text{ac E1})}(\omega) \right\}.$$

### 7.4.j. Plasma diagnostics

#### Remarks and classification:

- **Physical parameters of plasma:** However, in order to determine the relevant physical parameters that describe both, the astrophysical and laboratory plasmas, i.e. its electron temperature, density distribution, ion and element abundances, etc., we need to compare the observed data to a theoretical model spectra.
- **Energy exchange:** In a plasma, in general, any collision between particles cause energy exchange and changes in the state distribution changes.

- **Laboratory *versus* astrophysical plasma:** Laboratory plasmas can differ from astrophysical sources in various ways:
  - Laboratory plasmas can be (very) short-lived so that they do not reach any statistical equilibrium.
  - Although much larger densities occur in laboratory plasma, when compared to typical astrophysical sources, by far not all lines are optically thick in such a plasma and, in particular, the **re-bound and free-free transitions (continuum radiation) remain usually optically thin**.
  - In laboratory plasma, most atomic levels are often collisionally rather than radiatively dominated.
  - The (large) density of laboratory plasma can dramatically affect the line profiles, and this should/need to be taken into account in the radiative-transfer calculations.
- **Non-local thermodynamic equilibrium (NLTE):** NLTE exists in a wide variety of astrophysical and laboratory-created plasmas. Examples of NLTE astronomical plasmas are the stellar corona, interstellar nebulae and some other low-density ionized plasmas. In the laboratory, NLTE exists in laser-produced plasmas, tokamaks and Z-pinch based experiments.
- **Stratification of the plasma:** In order to calculate synthetic spectra from laboratory plasma or expanding stars, one first needs to determine the stratification of the plasma temperature, density and velocity. This **stratification of the plasma** can be either obtained from some hydrodynamic code or from some simplified self-similar analytic model.
- **Role of helium-like ions for plasma physics:** The intensity ratio of spectral lines from helium-like ions are important for plasma diagnostics and, especially, in order to derive the electron densities and temperatures in plasma. This diagnostics is frequently applied both, in astrophysics and fusion research. Unfortunately, however, there are quite different spectroscopic notations in use in the literature for helium-like ions, which (may) hamper the quick comparison. Only rather recently, a more standard notation [cf. NIST data tables] has begun to become more popular in the field.

### Interpretation of line spectra:

- **Line spectra:** More often than not, any detailed interpretation of the line spectra from laboratory plasmas and astrophysical sources has been found a great challenge since it often requires to go often beyond a local thermodynamical equilibrium (LTE) approach. If no equilibrium is reached, the spatially-dependent photon emission and absorption then need to be taken into account in the solution of the rate equations throughout the emitting medium.
- **Line spectra:** X-ray satellites, such as CHANDRA and XMM-NEWTON have provided large amounts of high-resolution line spectra from astronomical objects, and with many of them in NLTE.

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- **Thermonuclear fusion devices:** Beryllium and boron are two key elements in the (edge) plasma of thermonuclear fusion devices. While boron is released by plasma-wall interaction processes from boronized graphites, beryllium is the suggested wall material for ITER. To **model the transport in such plasma, various elastic and inelastic cross sections are required** to understand the energy transport and particle loss in the plasma. Liu *et al.* (2010) studied the radiative charge-transfer process for electron energies between  $10^{-5} - 0.1$  eV/u by using an optical potential method and for  $0.1 - 100$  eV/u by means of a semiclassical method.

### Diagnostics of astrophysical plasma:

- **Plasma in different astrophysical objects:** Hot plasmas are present in the universe in a variety of astrophysical objects, from stellar coronae to the birth of stars and up to the intergalactic medium in clusters of galaxies. The high-quality data, that have been obtained during the last few decades from space observatories like EINSTEIN, ROSAT, ASCA and SAX, enabled one to study in great detail the physical condition of several astrophysical plasmas.
- **Solar corona plasma:** The solar corona plasma is low-density plasma and is believed to be dominated by the spontaneous decay and radiative recombination. For these two processes, the corresponding decay rates are much higher than the collisional decay and three-body recombination and, hence, the plasma is not in a local thermodynamic equilibrium and cannot be described by Saha or Boltzmann equations.
- **Static stellar atmospheres:** In the standard models of static stellar atmospheres, the atomic (or ionic) populations, the radiation field, the temperature and density are calculated **self-consistently by means of rate equations and radiative transfer equations but owing to certain constraints, such as statistical equilibrium, radiative equilibrium or a hydrostatic equilibrium.**

### Diagnostics of laboratory plasma:

- **Heat transfer:** For ITER, various concepts have been developed to reduce the peak heat at the plasma-facing components of the tokamak. Indeed, much of the current experimental and theoretical work in fusion research now focus on the question of how the heat from the plasma need to be transferred to the walls of the main and divertor chambers.
- **Heat transfer:** To analyse this heat transfer and to enroll the relative importance of the primary atomic processes, simple quasi-analytic models and refined rate coefficients and cross sections have been utilized. Important heat transfer processes refer to the radiation losses through bremsstrahlung, impurity radiation losses from the plasma edge, the charge exchange and radiation losses from hydrogen in outer layers as well as to radiation losses due to impurities in the divertor plasma.
- **Heat transfer:** In large fusion devices, such as ITER, most of the heating power strikes the divertor plate and results in a high peak-heat loads of all plasma-facing components.

- **Heat transfer:** The ITER divertor has been designed in order to enhance the charge exchange processes, hydrogen and impurity line radiation, ionization, or elastic collisions between the recycling gas and the plasma in the diverted plasma and, hence, to spread out the heat and momentum transfer over the device.
- **Simulation of emission spectra:** To simulate the emission spectra from laboratory plasma, special attention has been placed on the coupling between the ionic population and the transfer of line radiation through the plasma. Often, this coupling is taken into account iteratively by deriving the level population from the temperature, density as well as the velocity profile of a plasma. While the ion population in the plasma is computed from linearized rate equation, the **line transfer is calculated within the (so-called) core saturation approximation and with a complete frequency redistribution** (Peyrusse 1992).

### Diagnostics of tungsten plasma:

- **Tungsten@ITER:** Atomic physics has been crucial for understanding the plasma-energy balance and for diagnostic development. In particular, tungsten is nowadays very frequently used on present-day tokamaks in preparation for ITER.
- **Tungsten@ITER:** Tungsten has become of high importance since it will be a major constituent of ITER plasmas. Tungsten will be applied as plasma-facing component that is able to withstand high heat loads and with a lower tritium retention than other possible materials.
- **ITER Core Imaging X-ray Spectrometer (CIXS):** The CIXS has been designed to measure the ion temperature and the motion of ITERs plasma core, based especially on the x-ray emission of neon-like  $W^{64+}$  ions (Beiersdorfer *et al.*, 2015). The emission from tungsten will be measured by extreme ultraviolet (EUV) and optical spectrometers in order to determine its concentration in the plasma and to assess the power loss and the sputtering rate of tungsten.
- **Spectra of multiply-charged tungsten:** Extensive magnetic fusion plasma studies on the spectra of multiply-charged tungsten have been carried out at the Livermore electron beam ion trap, the Sustained Spheromak Physics Experiment (SSPX), the National Spherical Torus Experiment (NSTX) and the Alcator C-mod tokamak.
- **Ionization balance calculations:** There is currently a need for reliable ionization balance calculations since the CIXS will provide radial profiles of the ion abundance in ITER which can be used in order to extract the ion transport parameters. These parameters refer to the radial ion diffusion coefficient and the inward pinch velocities, when compared to accurate ionization balance calculations. Such ionization balance calculations are still highly non-trivial for tungsten.

## Diagnostics of lanthanide ions:

- Lanthanide ions have very **complex spectra owing to the presence of the open  $4f$  shell** that can be resolved only by high-resolution laboratory studies. Tchang-Brillet *et al.* (2018) have performed a systematic comparison and analysis of such high-resolution spectra for several lanthanide ions in the vacuum ultra-violet (VUV) region, including especially the fourth and fifth spectra and partially also the third spectra.
- The **radiative properties of the lanthanide ions** have numerous applications in solid-state laser materials, photonics and the lighting industry. Radiative transitions of lanthanide ions were observed in doped crystals and in solution with small shifts relative to those of the free ions.
- **Emission spectra from multiply-charged lanthanide ions:** First investigations of the spectral intensities within the ground-state  $4f^n$  configurations of the trivalent lanthanides in solution have been carried out by Carnall *et al.* in the early 1960s and were supported also by calculations of transition probabilities by Judd and Ofelt.
- **Emission spectra from multiply-charged lanthanide ions:** The bright emission spectra from highly-charged ions of lanthanide elements ( $Z = 57 - 71$ ) are known to appear in the extreme ultraviolet (EUV) or soft x-ray wavelength range due to  $n = 4 - 4$  transitions of lanthanide ions in the wavelength range of 5–12 nm. These emission spectra are typically strongly affected by relativistic effects and multi-electron correlations. Likely, these emission spectra will play an important role in application to the next generation light sources for EUV lithography.
- **Emission spectra from multiply-charged lanthanide ions:** Suzuki *et al.* (2018) have systematically observed extreme ultraviolet (EUV) spectra from the highly-charged ions of nine lanthanide elements with nuclear charge  $Z = 60 \dots 70$  in optically thin plasmas as produced in the Large Helical Device (LHD). The wavelengths of the main peaks in the quasi-continuum features were found to agree well previously measured singlet transitions of Pd-like ions as well as with the discrete spectral lines from Cu-like and Ag-like ions.
- **Emission spectra from multiply-charged lanthanide ions:** Charge-separated EUV spectra from Sm, Gd, Dy, Er and Yb have recently been observed also in electron beam ion trap (EBIT) facilities at higher electron beam energies (Suzuki *et al.*, 2018).
- **Hubble Space Telescope:** In astrophysics, observations with the Hubble Space Telescope of spectra of chemically peculiar stars have proven the presence of lanthanide ions up to doubly-charged ions. More recently, the shortly delayed observation of gravitational waves and the emission of electromagnetic waves during a neutron-star merger have renewed the interest for radiative properties of higher-charged lanthanide ions.

### 7.4.k. Radial distribution functions for plasma and liquid models

#### General remarks:

- **Distribution function for plasma:** The radial distribution function for a plasma is often required and need to be calculated. In these computations, quantum effects have to be taken into account for small inter-particle separations, either by using a modified path-integral technique or, equivalently, by a **summation over states, together with the assumption that the charged particles interact via a shielded Coulomb potential**.
- **Distribution function for plasma:** General expressions for the radial distribution function in an electron-ion plasma outside of thermal equilibrium have been obtained in the literature in first-order of the plasma parameters.
- **Distribution functions for fluids:** Radial distribution function and static structure factors have been computed at several places in the literature. The radial distribution function can be utilized to characterize a fluid, for instance in terms of the pronounced maxima at some inter-particle distance, and followed by successive minima and maxima with reduced amplitudes.
- **Ion-electron plasma:** A plasma or a liquid metal are two fundamental examples for a mixture of ions and electrons that mainly interact via the Coulomb force. The properties of such admixtures in thermal equilibrium just depend on the temperature  $T = 1/k_B \beta$  and density of nuclei  $n_o$  as well as the atomic number  $Z_a$  of these ions.
- **Ion-electron plasma:** In practice, it is difficult to describe the plasma dynamics since the ions and plasma just depend on each other: i) The internal structure of an ion need to be determined for the given plasma and ii) the plasma, i.e. the external distribution of the ions and electrons, requires to know the potential between them.

#### Quantal hypernetted-chain approximation:

- **Hypernetted-chain equation:** In statistical mechanics, the **hypernetted-chain equation** arises as a closure relation in order to solve the **Ornstein-Zernike equation, i.e. a relation between the direct and total correlation functions**. The hypernetted-chain equation is commonly applied in fluid theory in order to obtain, e.g. expressions for the **radial distribution function**.
- The hypernetted-chain approximation is an integral-equation method from statistical physics that arises from the theory of liquids.
- A quantal version of the hypernetted-chain equation (QHNC) was derived in the literature by using the density-functional method, and extended to treat a liquid metal and a plasma as an ion-electron mixture.
- Hou *et al.* (2015) combined the average-atom model with the **hypernetted chain approximation** (to a so-called AAHNC approximation) in order to describe the electronic and ionic structure in the WDM regime.

### 7.4.1. Average-atom model for warm-dense matter

#### Warm-dense matter:

- **Warm-dense matter (WDM):** This term generally refers to some state of matter under plasma conditions, and which can range from condensed matter to weakly-coupled plasmas with typical temperatures from a few to a few hundred eV as well as with densities from a few hundredths to about a hundred times of the solid density.
- **Model of WDM:** In modeling WDM, great challenges arise from the partial ionization of the plasma, the degeneracy of the electron states, the bound-state level shifts, the pressure ionization in plasma as well as the strong coupling of the ion-ion pairs that must all be taken into account self-consistently.
- **Equation of state:** A good understanding of the properties and behaviour of WDM, such as the equation of state, its radiative opacity or the transport properties, has been found important, for modeling for example astrophysical objects or inertial confinement fusion experiments (Hou *et al.*, 2015).
- **Electronic structure of impurities:** Studies on the electronic structure of impurities within an electron gas have been performed in the literature as function of their density and temperature. For these investigations, one needs to know the dependence of screening effects on the plasma parameters.
- **Friedel oscillations:** Especially at low temperatures and metallic densities, the electron density of a plasma often exhibits Friedel oscillations, similar as known also from solid-state physics.

#### Average-atom model for WDM simulations:

- **Average-atom (AA) model:** This model divides the plasma into separate neutral Wigner-Seitz cells with a nucleus of charge  $Z$  and  $Z$  free electrons. Various versions of the AA model have been implemented in plasma physics for describing warm- and hot-dense matter and plasma.
- **Average-atom (AA) model:** In the AA model, each ion or atom is described within a finite (ion) sphere and by using a central-field approximation for the bound electrons. For heavy atoms and ions, a (radial) Dirac equation can be applied but where the potential  $V(r)$  needs again to be calculated self-consistently.
- **Electron density in the AA model:** For an isolated atom or ion, the electron density is calculated in the AA model in order to include the level broadening of the energy levels within a plasma environment. This density is applied also for studying the temperature and density effects upon the electron distributions within a statistical way.



- **Radial potential in the AA model:** A radial potential in terms of the bound-electron radial density  $\rho_b(r)$  and uniform electron density  $\rho_{e,0} = \rho(r_b)$  has been given by (Hou *et al.*, 2015)

$$V(r) = -\frac{Z}{r} + \int d^3r' \frac{\rho_b(r')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[\rho_b(r) + \rho_{e,0}] - V_{xc}(\rho_{e,0}) - \frac{\rho_{e,0}}{\beta} \int d^3r' C_{ee}(|\mathbf{r} - \mathbf{r}'|) h_{ie}(r') - \frac{\rho_{i,0}}{\beta} \int d^3r' C_{ie}(|\mathbf{r} - \mathbf{r}'|) h_{ii}(r')$$

but need to be better analyzed in order to understand its validity and limitations. Here, the first four terms constitute the **contributions from a single ion: electron-nucleus interaction, the electro-static repulsion with the other bound electrons as well as the exchange and correlation potential**, which are often evaluated by using some local density approximation. The last two terms in this expression represent the **interaction of the ion with the surrounding free electrons and with the other ions**.

### Spectral emission from plasma in a non-local thermodynamic equilibrium (NLTE):

- **NLTE versus LTE:** In a non-local thermodynamic equilibrium (NLTE), in which the levels of each configuration are still considered to be in LTE, the population  $N_a$  of a given electron configuration follows as solution of a system of rate equations

$$\frac{\partial N_a}{\partial t} = -N_a \sum_b R_{ab} + \sum_b R_{ba} N_b,$$

and where  $R_{ab}$  is a global (averaged) transition rate that connects the configurations  $a$  and  $b$ .

- **NLTE versus LTE:** Many collisional-radiative models, that are applied for a realistic modelling of NLTE line emission, often account for several individual levels explicitly, that occur in the spectroscopic observations, while the levels of other configurations are simply lumped together. These **superlevels** have no spectroscopic meaning but are included to just describe the population kinetics.

## 7.4.m. Equation-of-state relations for astro physics and condensed matter

### Equation-of-state:

- **Equation-of-state relations:** More often than not, the equation-of-state just refers to some particular **pressure-density** or **pressure-temperature relation** for matter under (more or less) extreme conditions.

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- **Equation-of-state relations:** When the atomic density is rather low, we can deal with isolated atoms that are in equilibrium with the surrounding free electrons, while the statistical or Thomas-Fermi-Dirac model has been found useful at (very high density).

### Liberman's self-consistent model:

- **Liberman model:** Liberman (1979) describes a model for condensed matter in which the ions surrounding a particular atom are replaced by a **positive charge distribution that is constant outside of a sphere containing the atom and zero inside**. This model enables one to separate the quantities that pertain to the atom from those of the electron gas (in which the atom is imbedded) and, hence, to derive the desired equation-of-state data.
- **Liberman model:** The model assumes that there are locally sufficient electrons near to the atom in order to give overall electrical neutrality together with the (required) electrical neutrality inside the sphere.
- **Liberman model:** Instead of a – more natural – polyhedral cell, and which are surrounded by other identical cells, a **nearly equivalent spherical cell is assumed in Liberman's model, and surrounded by a uniform electron gas**. The density of this electron gas is the same as the mean density of ionic charges. Therefore, the electron gas outside will neither alter the charge distribution inside the cell (if its density is correctly chosen), nor will the atom affect the electron gas outside of the cell.

## 7.4.n. Radiation damage of DNA by electron impact

### Radiation damage of DNA:

- **Radiation damage:** This term often refers to the damage of biological material on rather short time scales, i.e. reactions and processes that occur within ns or even less following the interaction of high-energetic light or particles with a living cell. These initial events may ultimately lead to the collapse of such cells. In practice, they result in the death of the individual cells within hours or days but may affect the matter also on much longer time scales.
- **Low-energy electrons (LEE) that interact with the DNA:** The absorption of high-energetic photons by biological matter often leads to low-energy electrons (LEE) that interact with the DNA. These LEE can cause specific resonant processes and may lead eventually either to single- or double-strand breaks in DNA materials, to the damage of its molecular components and possibly even to biological apoptosis (Bacarelli *et al.*, 2011).
- **Energy deposition by LEE:** Several theoretical and computational approaches have been developed in order to explore the molecular processes that occur in the various steps of the energy deposition by LEE.

- **Radiative background on Earth:** In general, any exposure of living beings to high-energy radiation (photon or particles) may result into serious effects, although everybody is typically exposed to some constant dosage of high-energy radiation due to natural radio-activity as well as medical treatments. Indeed, a constant background of low-intensity but high-energy radiation is found all over the Earth and arises from cosmic radiation and radioactive  $^{222}\text{Rn}$  isotopes as  $\alpha$ -decay product of radioactive uranium isotopes on earth (Bacarelli *et al.*, 2011).

### Electron-molecule dynamics:

- **Computation of electron-impact processes:** To understand the electron-impact of bio-molecules, a quite sizeable computational machinery need to be developed. The multiple inelastic scattering of these electrons typically result in a re-distribution in the energy content and may then lead to a fragmentation as well as the excitation of various vibrational modes.

### **7.4.o. Binding energies and quantum defects of Rydberg atoms**

### Scaling of Rydberg atoms:

- **Scaling of Rydberg atoms:** (Lebedev and Beigman, 1998)

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Property	Scaling	Short explanation
Radius	$r_n \sim \frac{n^2}{Z} a_o$	Radius of a Rydberg atom as defined by its (Rydberg) electron.
Geometric area	$A_n \sim \pi \frac{n^4}{Z^2} a_o^2$	Geometric cross section of a Rydberg atom.
Period of electron	$T_n \sim \frac{n^3}{Z^2} 2\pi \frac{a_o}{v_o}$	Period of an electron in a semi-classical interpretation, and where $v_o = 2.188 \cdot 10^8 \text{ cm s}^{-1}$ is the mean velocity of a $1s$ electron in hydrogen.
Velocity	$v_n \sim \frac{Z}{n} v_o$	Velocity of the Rydberg electron that is much smaller than the velocity of the ionic core electrons.
Energy	$E_n = -\frac{Z^2}{2n^2} \text{ Hartree}$	From these level energies, the ionization potential $I_n$ as well as the transition frequency $\omega_{n,n\pm 1}$ and wavelength $\lambda_{n,n\pm 1}$ to neighbored levels can be easily derived.
Statistical weight	$g_n = 2 \sum_{\ell=0}^{n-1} g_\ell = 2n^2$	Number of (magnetic) substates of shell $n$ .
Density of states	$\rho(E_n) = \frac{n^5}{Z^2} \text{ Rydberg}^{-1} = \frac{2m^{3/2} Z^3 e^6}{\hbar^3 (2 E_n )^{5/2}}$	Density of states per unit energy interval
Transition frequency	$\omega_{n,n\pm 1} \approx \frac{Z^2}{\hbar n^3} \text{ Hartree}$	Characteristic transition energy between neighbored levels.
Transition frequency	$\omega_{n,J \rightarrow J'} \approx \frac{\alpha^2 Z^4}{2\hbar n^3 \ell(\ell+1)} \text{ Hartree}$	Characteristic transition energy between fine-structure levels of the same shell $n$ .
Fine structure	$E_{nJ} = -\frac{Z^2}{2n^2} \text{ Hartree} + E_{nJ}^{(1)}$ $E_{nJ}^{(1)} = -\frac{\alpha^2 Z^4}{2n^3} \left( \frac{1}{j+1/2} - \frac{3}{4n} \right)$	Characteristic fine-structure splitting of Rydberg electrons.
Radiative lifetime	$\tau_n \approx \frac{n^5}{3A_o Z^4 \ln(n/1.1)}$ $A_o = \frac{8\alpha^3 (v_o/a_o)}{3\pi\sqrt{3}}$	Radiative lifetime of a Rydberg electron in shell $n$ , averaged over all magnetic substates $ \ell m\rangle$ . This averaged lifetime is based on all $n\ell \rightarrow n', \ell' \pm 1$ transitions, and where $A_0 \approx 7.9 \cdot 10^9 \text{ s}^{-1}$ refer to the characteristic Einstein coefficients for $2p \rightarrow 1s$ transition in hydrogen.

- **Radiative lifetime of Rydberg electrons:** In Rydberg atoms, the most efficient  $n\ell \rightarrow n', \ell' \pm 1$  transitions occur for low  $n'$  because of the energy scaling of the transition rates  $\sim (\Delta E)^3$  and to neighbored levels with  $n' = n - 1$ . Therefore, the radiative lifetime of Rydberg electrons increases drastically with  $n$  and becomes larger than 10 sec for  $n \gtrsim 100$ .
- **Binding energies and quantum defects of Rydberg atoms:** For a Rydberg atom with  $N$  electrons in its ionic core, the binding energy of

the Rydberg electron is given by

$$E_{n\ell} = -\frac{(Z-N)^2}{2(n-\delta)^2}, \quad n \gg 1.$$

- **$N+1$ -electron Hamiltonian for Rydberg atoms:** For an ionic core with  $N$  electrons, the non-relativistic  $N+1$  electron Hamiltonian can be written as

$$H = H_o + V = H^{(\text{ionic core})} + \frac{p^2}{2} - \frac{(Z-N)^2}{r} + \sum_{j=1}^N \left( \frac{1}{|\mathbf{r} - \mathbf{r}_j|} - \frac{1}{r} \right)$$

$$\rho^{(\text{ionic core})}(r \gg 1) = A r^{2u} e^{-2ar}, \quad a = \sqrt{2E_s}, \quad u = \frac{Z-N+1}{a} - 1,$$

where  $E_s$  is the binding energy of the least-bound core electron and  $A$  the coefficient of the asymptotic density of the core ion.

- **Penetration energy for Rydberg atoms:** The (so-called) penetration energy refers to the first-order energy shift that arises from the perturbation  $V$  in the  $N+1$ -electron Hamiltonian above (Lebedev and Beigman, 1998)

$$\begin{aligned} E^{(\text{penetration})} &= \int d^3r d^3r' |\psi(\mathbf{r})|^2 \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{r} \right] \rho^{(\text{ionic core})}(r') = \int d^3r |\psi(\mathbf{r})|^2 V^{(\text{penetration})}(r) \\ &\approx - \left( \frac{2\pi A}{a^3} \right) \frac{2^{2\ell} (Z-N)^{2\ell+3} (n+\ell)! \Gamma(2\ell+2+2u)}{n^{2\ell+4} (n-\ell-1)! (2\ell+1)! \Gamma(2\ell+2)} \\ &\quad \times \left[ 2(2u+1) + 2a \frac{(2\ell+2+2u)}{2a + 2(Z-N)/(\ell+1)} \right] \left( 2a + \frac{2(Z-N)}{\ell+1} \right)^{-2\ell-2-2u} \\ &\approx - \left( \frac{\pi A}{a^3} \right) \left[ \frac{(n+\ell)! (\ell+1)^{2u} (Z-N)^{2\ell+3}}{n^{2\ell+4} (n-\ell-1)! (2\ell+1)!} \right] \left[ \ell + 2 + 3u - \frac{(Z-N)}{a} \right] \left( a + \frac{(Z-N)}{\ell+1} \right)^{-(2\ell+2+2u)} \quad \text{for large } \ell. \end{aligned}$$

Here,  $\psi(\mathbf{r})$  describes the hydrogenic wave function of the Rydberg electron for an ionic core of charge  $Z-N$  with a charge density  $\rho^{(\text{ionic core})}(r)$ .

### 7.4.p. Radiative transitions and form factors of Rydberg atoms

#### Oscillator strength and radial integrals of hydrogenic ions:

- **Relation between oscillator strength and radial integrals:** The **absorption oscillator strength** between two hydrogenic levels  $f(n\ell \rightarrow n'\ell')$  can be readily expressed in terms of the energies (in Hartree) and the radial integrals  $\langle n'\ell' | r | n\ell \rangle$  as

$$f(n\ell \rightarrow n'\ell') = \frac{2}{3} \frac{\max(\ell, \ell')}{2\ell + 1} \frac{E_{n'\ell'} - E_{n\ell}}{\text{Hartree}} |\langle n'\ell' | r | n\ell \rangle|^2, \quad \langle n'\ell' | r | n\ell \rangle = \int_0^\infty dr P_{n'\ell'}(r) r P_{n\ell}(r)$$

- **Radial transition integral with hydrogenic wave functions for bound-bound transitions:** For  $n' \neq n$ , one finds (Lebedev and Beigman, 1998)

$$\begin{aligned} \langle n'\ell' | r | n\ell \rangle &= \frac{a_0}{Z} \frac{(-1)^{n'-\ell} (4nn')^{\ell+1} (n-n')^{n+n'-2\ell-2}}{4(2\ell-1)!(n+n')^{n+n'}} \left[ \frac{(n+\ell)!(n'+\ell-1)!}{(n'-\ell)!(n-\ell-1)!} \right]^{1/2} \\ &\quad \times \left\{ F\left(-n+\ell+1; -n'+\ell; 2\ell; -\frac{4nn'}{(n-n')^2}\right) - \left(\frac{n-n'}{n+n'}\right)^2 F\left(-n+\ell-1; -n'+\ell; 2\ell; -\frac{4nn'}{(n-n')^2}\right) \right\} \\ \langle n, \ell-1 | r | n\ell \rangle &= \frac{a_0}{Z} \frac{3n\sqrt{n^2-\ell^2}}{2} \end{aligned}$$

$$\sum_{n'} |\langle n', \ell-1 | r | n\ell \rangle|^2 = \sum_{n'} |\langle n', \ell+1 | r | n\ell \rangle|^2 = \frac{a_0^2}{2Z^2} n^2 (5n^2 + 1 - 3\ell(\ell+1)).$$

- **Radial transition integral with hydrogenic wave functions for bound-free transitions:** With the generalized principal quantum number  $\nu = \sqrt{Z^2/\varepsilon}$  (from the non-relativistic theory:  $\varepsilon_n = -Z^2/n^2$  for bound electrons), these bound-free transition matrix elements can be

written as (Lebedev and Beigman, 1998) as

$$\begin{aligned} \langle \varepsilon \ell' | r | n \ell \rangle &= \frac{a_o}{2} \frac{\nu^2}{Z^2} c_o \frac{\exp(-2\nu \arctan(\frac{n}{\nu}))}{\sqrt{1 - e^{-2\pi\nu}}} \left[ \frac{4\nu n}{n^2 + \nu^2} \right]^{\ell_{>}+1} (1 - z)^{(\ell_{>}+1-\nu)/2} \\ &\quad \times \prod_{s=1}^{\ell'} \sqrt{s^2 + \nu^2} \left[ F(\ell_{>} + 1 - i\nu, -n + \ell + 1, 2\ell_{>}, z) - \frac{1}{1 - z} F(\ell - i\nu, -n + \ell_{>} + 1, 2\ell_{>}, z) \right] \\ \ell_{>} &= \max(\ell, \ell'), \quad \nu^2 = \frac{Z^2}{\epsilon}, \quad z = \frac{4i\nu}{(n + i\nu)^2}, \quad \ell' = \ell \pm 1 \\ c_o &= \frac{i^{\ell_{>}-\ell} (-1)^{n-\ell_{>}}}{4(2\ell_{>} + 1)!} \left[ \frac{(n + \ell)!}{(n - \ell - 1)!} \right]^{1/2}. \end{aligned}$$

- **Collisions of Rydberg atoms:** The collision of Rydberg atoms and ions with electrons at different velocity as well as with neutral atoms has attracted much interest in astrophysics and elsewhere (Lebedev and Beigman, 1998). Unfortunately, however, the language in this field is quite different from what is used in atomic-structure theory, and will first require a honest discussion to overcome the quite technical language presented that often occurs so far.

#### 7.4.q. Exotic atoms and ions

##### Muonic atoms and ions:

- **Muonic atoms:** When a muon is captured by the nucleus, it generally forms a hydrogen-like muonic ion, although it often remains still surrounded by other atomic electrons.
- **Muonic hydrogen:** In muonic hydrogen, the electron is replaced by a muon  $\mu$  with a 200 times larger mass. This large mass results in orbits that are 200 times closer to the nucleus, when compared to the electron in regular hydrogen.
- **Muonic hydrogen:** Because of the finite extent of the proton, muons in their  $s$ -state have therefore some enhanced probability to be inside the proton, and where it sees also a slightly reduced electric charge of the proton. Therefore, the muon is less bound as larger the proton is.

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- **Transition energies in muonic atoms:** Measurements of the transition energies in muonic atoms help determine nuclear parameters, such as charge radii, quadrupole moments and magnetic hyperfine constants. One of the most precise measurements of the nuclear root-mean-square radius by means of muonic atoms refer to the radius of  $^{208}\text{Pb}$  at the 0.2 % level.

### 7.4.r. Spectroscopy of (super-) heavy elements

#### Super-heavy nuclei:

- **Radioactive isotopes & island of stability:** All nuclei with  $Z > 98$  have typically rather short lifetimes from fractions of a second to, say, hundreds of days. For the super-heavy nuclei ( $Z > 104$ ), in contrast, an **island of stability has been hypothetically proposed several decades ago**, mainly based on quite limited nuclear structure computations at that time. In particular, the **double-magic flerium nucleus with  $Z = 114$  and  $N = 184$**  is expected to be more stable (than other super-heavy nuclei), because both protons and neutrons form closed shells for this isotope. Such a **weakly-stable island may include also the elements Ubn, Ubh as well as some other isotopes**. — In practice, however, no (nearly-) stable super-heavy nuclei are nowadays expected anymore.
- **Magic numbers:** For spherical, super-heavy nuclei, the **magic neutron number  $N = 184$**  is supposed quite generally, while several **magic proton numbers  $Z = 114, 120, 126$**  are still discussed in the literature. Further magic number from the literature are:  $Z = 122$  and  $N = 172, 178, 182, 194$ , respectively.
- **Neutron-poor isotopes:** Until the present, **all synthesized superheavy nuclei ( $Z > 104$ ) are neutron-poor**, i.e. with significantly less neutrons than expected for reasonably stable nuclei. For example, the heaviest synthesized flerium isotope,  $^{292}\text{Fl}$ , still miss 6 neutrons to the (expected) *magic neutron number*  $N = 184$ . In general, a larger neutron number help compensate the strong Coulomb repulsion among the protons.

#### Laser spectroscopy of (super-) heavy elements:

- **Laser spectroscopy for (super-) heavy elements:** While laser spectroscopy offers great precision  $\sim \mu\text{eV}$ , it usually requires prior knowledge about the level structure and allowed transitions of the elements that need to be synthesized by nuclear fusion reactions at large accelerator facilities.
- **Isotope shifts of superheavy elements ( $Z > 104$ ):** Until the present, isotope shifts have been measured for the (heavy) elements Pu, Am, Cm and No, while no experimental data are available near to flerium or other super-heavy isotopes.



- **Laser spectroscopy for (super-) heavy elements:** Chhetri *et al.* (2018) applied laser spectroscopy on an atom-at-a-time scale in order to probe the optical spectrum of **neutral nobelium near the ionization threshold**. These measurements pave the way for high-precision spectroscopy of the atomic properties of heavy elements and also provide a benchmark for state-of-the-art atomic computations, including many-body, relativistic and QED contributions at an equal footing.
- **Theoretical ionization potentials for (super-) heavy elements:** For neutral nobelium, in particular the **intermediate Hamiltonian Fock-space coupled-cluster (IHFSCC)** and **configuration interaction with linearized single-double coupled-cluster** computations were found to agree within  $\sim 2\%$  with the observed ionization potential, while larger deviations occur for the  $7s6d\ ^3D_3$  excitation energy.

### 7.4.s. Electronic structure and properties of quantum dots

#### Electronic-structure calculations:

- **Electronic structures of the quantum dots:** Quite similar to atoms, the structures of quantum dots is often described in terms of single-particle states as well as the Coulomb interaction between these states.
- **Electronic structures of quantum dots:** In addition to quantum dots of different size (and number of electrons), these dot structures have been studied especially with regard to external perturbations, such as electron-phonon interactions, a magnetic or electric field, or for their dependence on the temperature, impurity and pressure. Various models were developed in order to understand the **role of different confinement potentials, including disk-like (cylindrical), rectangular, spherical-harmonic, non-spherical oscillator, ring-shaped oscillator or ring-shaped non-spherical oscillator confinement potentials**.
- **Oscillator strength and radiative lifetimes of excitons:** The decay of excitons via photon emission competes with the recombination of (free-) electron-hole pairs. A typical photoluminescence decay is *non-exponential* with typical time constants from nanosecond (ns) to millisecond (ms). The **non-exponential decay of the photoluminescence signal** can be hereby discussed in terms of the size inhomogeneity of the Si nanostructures as well as the presence of nonradiative relaxation channels. In a non-uniform quantum wire, for example, an exciton near to some thinner part of the wire shows a faster luminescence decay but may also first relax back nonradiatively to some thicker part of wire, and where it may subsequently decay slower by luminescence.
- **Electronic structures of the quantum dots:** The DFT and other *ab-initio* methods, that have been found useful for large molecules, do often not describe well the multiply-excited states of quantum dots. In contrast to atoms and molecules, multiply-excited quantum dots can lose their energy not only through **radiative or nonradiative processes but also by phonon emissions to the surrounding (semiconductor)**

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**lattice.** Such phonon relaxation processes involves initial and final states with an equal number of electron-holes pairs (Lehtonen *et al.*, 2008).

- **Fock-Darwin energy levels:** For an conduction-band electron in an external magnetic field, whose motion is confined in a two-dimensional parabolic well with axis  $\mathbf{e}_z \parallel \mathbf{B}$ , the Hamiltonian is given in the effective-mass approximation by

$$\mathbb{H} = -\frac{1}{2m^{(\text{eff})}} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + \frac{m^{(\text{eff})} \omega_o^2 r^2}{2} = \frac{\mathbf{p}^2}{2m^{(\text{eff})}} + \frac{m^{(\text{eff})}}{2} \left( \omega_o^2 + \frac{\omega_c^2}{4} \right) r^2 - \frac{\omega_c l_z}{2},$$

and where  $\mathbf{r}$  is the position and  $\mathbf{p}$  the momentum of the confined electron, while  $l_z$  is the projection of its angular momentum upon the field direction. For a constant magnetic field  $\mathbf{B} = \text{rot } \mathbf{A}$ , one can assume  $\mathbf{A} = \mathbf{B}/2 (y, -x, 0)$  and the cyclotron frequency  $\omega_c = e\mathbf{B}/(m^{(\text{eff})}c)$ . The energies and eigenstates of this Hamiltonian were determined analytically by Fock and Darwin long before the use of nanostructures.

- **Fock-Darwin energies:** The Hamiltonian above can be expressed also as **sum of two independent harmonic oscillators with the characteristic frequencies** and with energies

$$\begin{aligned} \omega_{\pm} &= \sqrt{\omega_o^2 + \frac{\omega_c^2}{4}} \pm \frac{\omega_c}{2}, & \Omega^2 &= \omega_o^2 + \frac{\omega_c^2}{4} \\ \epsilon(n_+ n_-) &= \hbar \omega_+ \left( n_+ + \frac{1}{2} \right) + \hbar \omega_- \left( n_- + \frac{1}{2} \right) \\ \epsilon(n, m) &= \hbar \Omega (n + 1) - \frac{\hbar \omega_c m}{2}, & n &= n_- + n_+, & m &= n_- - n_+, \end{aligned}$$

Obviously, these energy levels are degenerate in the absence of a magnetic field  $\omega_+ = \omega_- = \omega_o$ , whereas a strong magnetic field ( $\omega \gg \omega_o$ ) leads to the formation of **Landau levels**, approximately separated by the cyclotron energy  $\hbar \omega_+ \approx \hbar \omega_c$ . Often, the energies are displayed as function of the magnetic field.

- **Quantum dots in external magnetic fields:** Maksym and Chakraborty (1990) studied the energies of interacting electrons if the quantum dot obeys an external magnetic field. Although the excitation energy are of course a function of the magnetic field, they crucially depend

also on the interelectronic interaction. For a quadratic confinement potential, for instance, the optical excitation energies of the many-body system are very much the same as those of a single electron.

### Charge transport in quantum dots:

- **Methods for charge transport in quantum dot computations:** To describe the charge transport in quantum dots in first-order perturbation theory, the Pauli (classical), first-order Redfield, first-order von Neumann master equations as well as some particular form of the Lindblad equation have been applied (Kirsanskas *et al.*, 2017). Other methods are the numerical-renormalization group, non-equilibrium Greens functions, and master equation based approaches. In practice, however, such charge transport computations are quite complex, and especially if phenomena like **Coulomb blockade** occur.

### Simulation of impurities and nanostructure:

- **Low-dimensional nano structures:** Modern technologies enable one to fabricate low-dimensional nanostructures, such as quantum wells, quantum wires and quantum dots, in which the charge carriers (electrons or holes) are confined either in one-, two- and even within three-dimensions. Quantum dots are hereby often referred to as **artificial atoms** because of their similar shell structure and discrete energy levels.
- **Quantum dots embedded into bulk materials:** If quantum dots are embedded into bulk material, they occur as defects and perturb the periodicity of the surrounding solid-state material. Two classes of methods are applied in order to describe the electronic structure of such *embedded* quantum dots (Lehtonen *et al.*, 2008): (1) Molecular-type electronic structure calculation as developed for free-standing quantum dots; (2) so-called **effective-mass approximations (EMA)**. Both of these classes have their pros and cons, and are complementary to each other. EMA calculations have difficulties to describe the properties of (quite) small quantum dots because their *atomic* character directly affects the optical properties; however, they are suitable to describe large quantum dots whose properties are mainly determined by the *confinement*. EMA methods can be applied also to model the transition from large quantum dots towards bulk material by using smoothly larger and shallower confinement potentials.
- **Hydrogenic impurity in spherical quantum dots:** In the effective mass approximation, the nonrelativistic Hamiltonian for a hydrogenic impurity at the center of a quantum dot is given by (Yakar *et al.*, 2013)

$$H_o = -\frac{\hbar^2 \nabla^2}{2m^*} - \frac{k e^2}{\epsilon r} + V^{(\text{confinement})}(r), \quad V^{(\text{confinement})}(r) = \begin{cases} 0 & r < R \\ \infty & r \geq R, \end{cases}$$

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and where  $k$ ,  $m^*$  and  $\epsilon$  are the electric constant, effective mass of electron and the dielectric constant of medium, respectively, and where  $V^{(\text{confinement})}(r)$  refers to a spherical confining potential well. The eigenvalues of this Hamiltonian are then further modified by adding the relativistic contributions due to the mass-velocity, Darwin as well as spin-orbit terms; all these relativistic terms have been calculated perturbatively since they small.

### Applications of quantum dots:

- **Low-dimensional nano structures:** These structures have attracted recent interest because of their properties and potential applications in physics, chemistry and engineering. They are promising structures for developing semiconductor microelectronic and optoelectronic devices, such as electro-optic modulators, inter-band lasers and inter-sub band long wavelength detectors. In particular, quantum dots have been explored extensively, both experimentally and theoretically.

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### 8.1. In JAC implemented processes

#### 8.1.a. Photoemission. Transition probabilities (PhotoEmission)

##### Process, notation & application:

- **Photoemission:** from an atom or ion  $A^* \longrightarrow A^{(*)} + \hbar\omega$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega$
- **JAC's standard multipole amplitudes for photon emission:** Although all (one- and many-electron) electron-photon interaction matrix elements are always evaluated in *absorption* within JAC, we wish and need to retain the intuitive description of matrix elements as typically applied in quantum mechanics:  $\langle \text{final} - \text{state} | \text{operator} | \text{initial} - \text{state} \rangle$ . In JAC, we therefore introduce an explicit and independent notation for a *standard (reduced) emission as well as absorption multipole matrix element*

$$\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{emission})} || \alpha_i \mathbb{J}_i \rangle = \left\langle \alpha_i \mathbb{J}_i \left\| \sum_{k=1}^N \boldsymbol{\alpha}_k a_{k,L}^p \right\| \alpha_f \mathbb{J}_f \right\rangle^* \equiv \langle \alpha_i \mathbb{J}_i || \mathbb{O}^{(\mathbb{M}, \text{absorption})} || \alpha_f \mathbb{J}_f \rangle^*$$

which retains the right order and can be obtained from `Jac.PhotoEmission.amplitude()`; cf. section 5.3.c. A multipole  $\mathbb{M} \equiv (L, p) = \text{E1, M1, E2, ...}$  hereby contains all information about its multipolarity (angular momentum)  $L$  and type *magnetic* ( $p = 0$ ) or *electric* ( $p = 1$ ).

- Using JAC: Perform an `Atomic.Computation(.., process=Jac.Radiative, processSettings=PhotoEmission.Settings(..), ..)` or call directly functions from the module `PhotoEmission`.

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- In JAC, the transition probabilities and radiative lifetimes are tabulated by default for all selected transitions  $i \rightarrow f$ .
- In JAC, the anisotropy (structure) parameters  $f_k(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f)$  are calculated and tabulated if the flag `calcAnisotropy = true` is set in `PhotoEmission.Settings`.

### Transition probabilities and oscillator strengths:

- With the notation of the (standard reduced) emission multipole matrix element from above, the transition probability and oscillator strengths are given by

$$W_{i \rightarrow f} = \frac{8\pi \alpha \omega}{2J_i + 1} \sum_{\mathbb{M}} |\langle \alpha_f \mathbb{J}_f \| \mathbb{O}^{(\mathbb{M}, \text{emission})} \| \alpha_i \mathbb{J}_i \rangle|^2, \quad f_{i \rightarrow f} = \frac{2\omega}{3(2J_i + 1)} \sum_{\mathbb{M}} |\langle \alpha_f \mathbb{J}_f \| \mathbb{O}^{(\mathbb{M}, \text{emission})} \| \alpha_i \mathbb{J}_i \rangle|^2,$$

and where the sum over  $\mathbb{M} = E1, M1, E2, \dots$  runs over all requested multipoles in a given computation.

### Angular distribution and anisotropy parameters of the fluorescence radiation:

- The fluorescence (radiation) from an excited atom is characterized not only by its frequency  $\hbar\omega$  but also by the **angular distribution and polarization of the emitted radiation**. Both of these properties of the emitted photons depend on the sublevel occupation of the excited atom or ion and, hence, on its reduced statistical tensors  $\mathcal{A}_{kq}(\alpha_i \mathbb{J}_i)$  which are **associated with the prior excitation process**.
- **Angular distribution for the photoexcitation of initially unpolarized but aligned atoms:** For initially unpolarized but aligned atoms, the angular distribution of the (characteristic) fluorescence radiation is given in perturbation theory by:

$$W(\vartheta) = \frac{W_o}{4\pi} \left( 1 + \sum_{k=2,4,\dots} f_k(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) \mathcal{A}_{k0}(\alpha_i \mathbb{J}_i) P_k(\cos\vartheta) \right),$$

where  $W_o$  is the total decay rate and  $\vartheta$  the angle of the photons with regard to the alignment axis (quantization axis).

- **Anisotropy (structure) parameters  $f_k(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f)$ :** In the angular distribution above, the **anisotropy (or structure) parameters  $f_k(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f)$**  are independent of the particular excitation process of the level  $(\alpha_i \mathbb{J}_i)$  and merely reflects the electronic structure of

the ion in the two levels involved in the fluorescence

$$f_k(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) = \left[ \sum_{\mathbb{M}} |\langle \alpha_i \mathbb{J}_i || \mathbb{O}^{(\mathbb{M}, \text{emission})} || \alpha_f \mathbb{J}_f \rangle|^2 \right]^{-1} \frac{\sqrt{2J_i + 1}}{2} \sum_{\mathbb{M} \mathbb{M}'} i^{L' + p' - L - p} (-1)^{J_f + J_i + 1 + k} [L, L']^{1/2} \langle L1, L' - 1 | k0 \rangle \\ \times \left( 1 + (-1)^{L + p + L' + p' - k} \right) \begin{Bmatrix} L & L' & k \\ J_i & J_i & J_f \end{Bmatrix} \langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{emission})} || \alpha_i \mathbb{J}_i \rangle \langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}', \text{emission})} || \alpha_i \mathbb{J}_i \rangle^*,$$

- Of course, there is usually one multipole term that dominates the radiative decay (fluorescence) for any given pair of initial and final-bound states.

### Semi-empirical calculations of transition probabilities:

- Semi-empirical calculations of transition probabilities are often performed by using Cowan's code and, especially, the components RCN/RCN2/RCG/RCE. In a first step, Hartree-Fock calculations of radial integrals are carried out, including relativistic corrections (HFR) to generate all required atomic orbitals and average energies of configurations. The diagonalization of the Hamiltonian matrix then leads to approximate energy values and eigenvectors of levels in intermediate coupling.
- When, in addition, also experimental energies are available, RCE is run to perform an iterative least-squares fit with the aim to minimize the differences between the calculated and experimental energies, and where the radial integrals are applied as fitting parameters. The mean error of such a fit is defined by  $\Delta E = \sqrt{\sum_i (E_i^{(\text{exp})} - E_i^{(\text{calc})})^2 / (N_i - N_p)}$  where  $N_i$  is the number of experimentally known energies and  $N_p$  the number of free parameters.

### Unresolved transition arrays (UTA):

- **Unresolved transition arrays:** The UTA approach has become the method of choice in order to calculate the radiative properties of high- $Z$  elements. Within this approach, a group of lines (i.e. a so-called array) which belongs to the same pair of electron configurations are treated globally by a Gaussian distributions whose width and position are given by analytical formulae.
- The UTA approach is computationally efficient and accurate for plasma conditions where the line broadening is such, that individual line profiles merge. This approach has been further extended to a group of arrays in the so-called super-transition array method (STA) where set of arrays are treated globally.

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- **Resolved transition arrays (RTA):** The RTA method was proposed to overcome the shortcoming of the UTA method that just a few transitions often dominate the spectral emission distribution of the array. This RTA method improves on the UTA approach by resolving the transition array into individual lines by using random lines but without performing an explicit atomic structure calculation.
- **UTA method:** For a group of lines with known transition energies  $E_i$  and corresponding the oscillator strengths  $g_i$ , the UTA is obtained by calculating the first two moments for the array of  $N$  transitions:

$$\mu^{(1)} = \frac{\sum_i^N g_i E_i}{\sum_i g_i}, \quad \mu^{(2)} = \frac{\sum_i^N g_i E_i^2}{\sum_i g_i},$$

- These two moments can be utilized together with the variance  $\sigma^2 = \mu^{(2)} - (\mu^{(1)})^2$  in order to define the **spectral distribution of the UTA**

$$f(\mathcal{E}) = \frac{1}{\sigma \sqrt{\pi}} \exp \left[ -\frac{(\mathcal{E} - \mu^{(1)})^2}{2\sigma^2} \right].$$

- By avoiding the explicit calculation of the properties of each line, that belongs to a given array, the UTA method enables one to account for a large number of transitions for a rather low computational cost.
- Overall, however, the use of such UTA appears quite tedious, and the application of the formulas derived by Bauche-Arnould and coworkers (1985, 1988) might lose its importance as more powerful computers become available.

### Two-electron one-photon transitions (TEOP):

- Two-electron one-photon transitions were postulated almost 100 years ago and are well-known from the optical region.
- In the early 1970s, Wölfl *et al.* reported results for nickel and iron, for which high-energetic satellites arose due to two-electron one-photon transition. In these experiments, two vacancies in the K-shell were simultaneously filled by two L-shell electrons under the emission of a single photon.
- Since the interaction with the electro-magnetic field is governed by an one-electron operator, the contribution of two-electron one-photon (TEOP) transitions can usually be ignored in comparison to other, E1 allowed one-electron transitions.



### Fractional occupation number (FON) approach:

- **Fractional occupation number (FON) approach:** The FON approach involves the prescription of a single, fictitious configuration with FONs for each  $(n, \kappa)$  subshell in order to represent an entire set of physical configurations within a given model. This fictitious configuration is used to first generate a single set of bound wave functions. Second, integer occupation numbers are then combined with the (averaged) wave functions in order to describe all the physical configurations that are enumerated in a particular model (Sampson *et al.*, 2009).

### 8.1.b. Photoexcitation or photoabsorption (PhotoExcitation)

#### Process, notation & application:

- **Photoexcitation** of an atom or ion:  $A + \hbar\omega \longrightarrow A^*$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbf{k}, \lambda) \longrightarrow |\alpha_f \mathbb{J}_f\rangle$
- Using JAC: Perform an `Atomic.Computation(.., process=Jac.PhotoExc, processSettings=PhotoExcitation.Settings(..), ..)` or call directly functions from the module `PhotoExcitation`.
- In JAC, the photoexcitation cross sections are calculated by default for resonant and completely linearly-polarized plane-wave radiation.
- In JAC, the photoexcitation cross sections are calculated also for plane-wave radiation with given Stokes parameters  $(P_1, P_2, P_3)$  if the flag `calcStokes = true` are set in `PhotoExcitation.Settings` and if the Stokes parameters are given explicitly by `PhotoExcitation.Settings.stokes`.
- In JAC, the statistical tensors  $\rho_{kq}(\alpha_f \mathbb{J}_f)$  and the alignment parameters  $\mathcal{A}_{kq}(\alpha_f \mathbb{J}_f)$  are calculated and tabulated for unpolarized atoms and plane-wave photons with given Stokes parameters, if the flag `calcTensors = true` is set in `PhotoExcitation.Settings` and if the Stokes parameters are given explicitly by `PhotoExcitation.Settings.stokes`.

### Photoexcitation cross sections:

- **Total photoabsorption cross section:** For **initially unpolarized atoms** and incident photons with given (photon) density matrix  $\langle \mathbf{k}\lambda | \rho_\gamma | \mathbf{k}\lambda' \rangle$ , the total photoabsorption cross section can be most easily defined in the **limit of a zero linewidth** as

$$\begin{aligned} \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; \omega) &= \frac{4\pi^2\alpha}{\omega(2J_i+1)} \sum_{M_i M_f, \lambda\lambda'} \langle \mathbf{k}\lambda | \rho_\gamma | \mathbf{k}\lambda' \rangle \langle \alpha_f \mathbb{J}_f M_f | \mathbb{T}^{(\text{absorption})}(\mathbf{k}, \lambda) | \alpha_i \mathbb{J}_i M_i \rangle \\ &\quad \times \langle \alpha_f \mathbb{J}_f M_f | \mathbb{T}^{(\text{absorption})}(\mathbf{k}, \lambda') | \alpha_i \mathbb{J}_i M_i \rangle^* \delta(\omega + E_i - E_f), \end{aligned}$$

and where  $\mathbb{T}^{(\text{absorption})}(\mathbf{k}, \lambda)$  formally describes the electron-photon interaction operator for absorbing a photon  $\hbar\omega(\mathbf{k}, \lambda)$ .

- In order to allow for a **finite natural width  $\Gamma_f$  of the excited level**, we need to replace the  $\delta(\omega + E_i - E_f)$  function in the above expression by a (Lorentzian) spectral distribution

$$\begin{aligned} \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; \omega) &= \frac{4\pi^2\alpha}{\omega(2J_i+1)} \sum_{M_i M_f, \lambda\lambda'} \langle \mathbf{k}\lambda | \rho_\gamma | \mathbf{k}\lambda' \rangle \langle \alpha_f \mathbb{J}_f M_f | \mathbb{T}^{(\text{absorption})}(\mathbf{k}, \lambda) | \alpha_i \mathbb{J}_i M_i \rangle \\ &\quad \times \langle \alpha_f \mathbb{J}_f M_f | \mathbb{T}^{(\text{absorption})}(\mathbf{k}, \lambda') | \alpha_i \mathbb{J}_i M_i \rangle^* \frac{1}{\pi} \frac{\Gamma_f/2}{(\omega + E_i - E_f)^2 + \Gamma_f^2/4}. \end{aligned}$$

- **Photoexcitation cross sections for initially unpolarized atoms:** For incident plane-wave photons with (photon) density matrix  $(c_{\lambda\lambda'}) = \frac{1}{2} \begin{pmatrix} 1 + P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1 - P_3 \end{pmatrix}$ , which are resonant to the given transition  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f\rangle$ , the total photoexcitation cross section is

$$\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; \omega) = \frac{2\pi^3\alpha}{\omega(2J_i+1)} \sum_{\mathbb{M}, \lambda} c_{\lambda\lambda} \left| \langle \alpha_f \mathbb{J}_f | \mathbb{O}^{(\mathbb{M}, \text{absorption})}(\lambda) | \alpha_i \mathbb{J}_i \rangle \right|^2 \times \begin{cases} \delta(E_i + \omega - E_f) \\ \frac{1}{\pi} \frac{\Gamma_f/2}{(E_i + \omega - E_f)^2 + \Gamma_f^2/4} \end{cases}.$$

- **Photoexcitation cross sections for initially unpolarized atoms and linear-polarized, circularly-polarized or unpolarized incident photons:** For resonant and unpolarized or completely linearly-polarized or circularly-polarized plane-wave photons, especially, the total photoexcita-

tion cross section is given by

$$\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f; \omega) = \frac{8\pi^3 \alpha}{\omega (2J_i + 1)} \sum_{\mathbb{M}} |\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}, \text{absorption})}(\lambda) || \alpha_i \mathbb{J}_i \rangle|^2 \times \begin{cases} \delta(E_i + \omega - E_f) \\ \frac{1}{\pi} \frac{\Gamma_f/2}{(E_i + \omega - E_f)^2 + \Gamma_f^2/4} \end{cases}$$

### Final-level statistical tensors and alignment parameters:

- **Statistical tensors:** Instead of the (final-level) density matrix, it is often more convenient to describe the population of the magnetic sublevels in terms of (so-called) statistical tensors of the atom or ion

$$\rho_{kq}(\alpha_f \mathbb{J}_f) = \sum_{M_f M'_f} (-1)^{J_f - M'_f} \langle J_f M_f, J_f (-M'_f) | kq \rangle \langle \alpha_f \mathbb{J}_f M_f | \rho | \alpha_f \mathbb{J}_f M'_f \rangle.$$

and which are **non-zero only for**  $0 \leq k \leq 2J_f$  and  $-k \leq q \leq k$ .

- **Reduced statistical tensors or alignment parameters:** The reduced statistical tensors of the excited levels or so-called **alignment parameters** are defined by

$$\mathcal{A}_{kq}(\alpha_f \mathbb{J}_f) = \frac{\rho_{kq}(\alpha_f \mathbb{J}_f)}{\rho_{00}(\alpha_f \mathbb{J}_f)}.$$

- **Statistical tensors for the photoexcitation of initially unpolarized atoms and incident plane-wave radiation:** For incident plane-wave photons with (photon) density matrix  $(c_{\lambda\lambda'}) = \frac{1}{2} \begin{pmatrix} 1 + P_3 & P_1 - iP_2 \\ P_1 + iP_2 & 1 - P_3 \end{pmatrix}$ , which are resonant to the given transition  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f\rangle$ , the reduced statistical tensors can be written as

$$\rho_{kq}(\alpha_f \mathbb{J}_f) = \dots$$

- **Statistical tensors for the photoexcitation of initially unpolarized atoms by incident plane-wave radiation with well-defined helicity  $\lambda$ :** For

incident plane-wave photons with helicity  $\lambda$ , the reduced statistical tensors can be written as (Surzhykov *et al.*, 2015)

$$\begin{aligned} \rho_{kq}(\alpha_f \mathbb{J}_f) &= \delta_{q0} C \sum_{\mathbb{M}\mathbb{M}'} i^{L+L'} [L, L]^{1/2} (i\lambda)^p (-i\lambda)^{p'} (-1)^{L'+J_f+J_i+k} \langle L\lambda, L' - \lambda | kq \rangle \begin{Bmatrix} L & L' & k \\ J_f & J_f & J_i \end{Bmatrix} \\ &\times \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}', \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle^* . \end{aligned}$$

### Photoabsorption and line-shape function:

- **Absorption coefficient  $\alpha(\omega)$ :** For a beam of light that propagates in  $x$ -direction, the absorption coefficient is phenomenologically defined in terms of changes of the spectral intensity  $I(\omega)$ , cf. Hilborn (2002)

$$\frac{1}{I(\omega)} \frac{dI(\omega)}{dx} = -\alpha(\omega) .$$

The spectral intensity  $I(\omega)$  is spectroscopically a time-averaged quantity over, at least, several optical cycles.

- **Line-shape function  $g(\omega)$ :** In most practical applications, the **frequency dependence of the absorption and emission processes (coefficient) is important but is often approximated simply by means of a normalized line-shape function  $g(\omega)$  with  $\int_{-\infty}^{\infty} d\omega g(\omega) = 1$** , and where negative frequencies have no special physical meaning. Here, the use of  $-\infty$  as the lower limit in the normalization integral greatly simplifies the normalization calculation. — For atoms in motion or in collision, the line-shape function  $g(\omega)$  describes the appropriate ensemble-averaged line shape. The line-shape function  $g(\omega)$  has the dimensions of 1/angular frequency and, hence, the explicit functional form of  $g(\omega)$  and  $\tilde{g}(\lambda)$  is not equivalent.
- **Absorption cross section  $\sigma^{(\text{absorption})}(\omega)$ :** If we assume  $\alpha(\omega)$  to be proportional to the number  $N_o$  of atoms per unit volume in the lower level  $(\beta_o \mathbb{J}_o)$ , which the beam intercepts, the absorption cross section is given by:

$$\alpha(\omega) = N_o \sigma^{(\text{absorption})}(\omega) .$$

➤ **Relation between absorption cross section and Einstein's A and B coefficients:** (Hilborn 2002)

$$\begin{aligned}\sigma^{(\text{absorption})}(\omega) &= \frac{g_f}{4 g_i} \lambda_{fi}^2 g(\omega) A_{fi}, & \sigma_o^{(\text{absorption})}(\omega) &= \frac{g_f}{4 g_i} \lambda_{fi}^2 A_{fi} \\ \sigma^{(\text{absorption})}(\omega) &= \frac{\hbar \omega}{c} B_{12}^\omega g(\omega), & \sigma_o^{(\text{absorption})} &= \frac{\hbar \omega_{21}}{c} B_{12}^\omega.\end{aligned}$$

➤ **Relation between line strength and Einstein A coefficient for a spontaneous  $i \rightarrow f$  emission:**

$$S_{if} = \frac{3 \epsilon_o \hbar c^3}{2 \omega_{if}^3} g_i A_{if}.$$

➤ **Weighted oscillator strength:** From the principle of detailed balance and in order to avoid confusion about the absorption or emission viewpoint, one often reports the weighted oscillator strength  $g f = g_1 f_{12}^{(\text{absorption})} \equiv -g_2 f_{21}^{(\text{emission})}$ .

➤ **Rabi frequency for on-resonance excitations:** At resonance  $\omega = \omega_{fi}$  of the incident (linearly-polarized) light field and for two non-degenerate levels  $(i, f)$ , the Rabi frequency can be expressed in terms of the electric field amplitude of the (and the transition dipole moment  $\mu_{fi}$  by

$$\Omega_R = \frac{\mu_{fi} E}{\hbar}, \quad \mu_{fi} = \langle \alpha_f \mathbb{J}_f M = 0 | \mathbb{O}^{(\mathbb{M}, \text{absorption})} | \alpha_i \mathbb{J}_i M = 0 \rangle$$

For degenerate upper and lower levels, there are generally several Rabi frequencies for each combination  $\langle \alpha_f \mathbb{J}_f M_f | \mathbb{O}^{(\mathbb{M}, \text{absorption})} | \alpha_i \mathbb{J}_i M_i \rangle$ , and this gives usually rise to a rather complicated dynamical behaviour (Hilborn 2002).

## Photoexcitation by plane-wave photons:

➤ **Vector potential for a plane-wave light field:** As usual, the electron-photon interaction operator  $R = \sum_q \boldsymbol{\alpha}_q \mathbf{A}^{(\text{plane-wave})}(\mathbf{r}_q)$  is given in terms of the Dirac matrices  $\boldsymbol{\alpha}_q$  of the  $q^{th}$  particle and the vector potential  $\mathbf{A}^{(\text{plane-wave})}(\mathbf{r}_q)$ . For an incident plane-wave radiation with wave vector  $\mathbf{k}$ , polarization vector  $\mathbf{e}_{\mathbf{k}\lambda}$  and with helicity  $\lambda = \pm 1$ , the vector potential can be written in Coulomb gauge as

$$\mathbf{A}^{(\text{plane-wave})}(\mathbf{r}) = \mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}}.$$

## 8. Atomic processes

- **Multipole operators of the electron-photon interaction:** For the analysis of atomic photo-excitation and ionization processes, it is generally convenient to expand the vector potential  $\mathbf{A}^{(\text{plane-wave})}(\mathbf{r})$  in terms of its electric and magnetic multipole fields. If the (plane-wave) field propagates along  $\mathbf{n}_k = \mathbf{k}/k = (\theta_k, \phi_k, 0) \nparallel \mathbf{e}_z$ , this expansion is given by:

$$\mathbf{e}_{k\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} = \sqrt{2\pi} \sum_{LM} \sum_{p=0,1} i^L [L]^{1/2} (i\lambda)^p D_{M\lambda}^L(\varphi_k, \theta_k, 0) \mathbf{a}_{LM}^{(p)}(\mathbf{r}).$$

Here,  $[L] = 2L + 1$ ,  $D_{M\lambda}^L$  is the Wigner rotation matrix, while  $\mathbf{a}_{LM}^{(p)}(\mathbf{r})$  refers to magnetic ( $p = 0$ ) and electric ( $p = 1$ ) multipole components of the vector potential; these components are constructed as irreducible tensors of rank  $L$  and, eventually, enable one to evaluate the transition amplitude  $M_{fi}^{(\text{plane-wave})}$  analytically.

- **Transition amplitudes of the multipole fields:** Using the expansion for the plane-wave vector potential from above and by making use of the Wigner-Eckart theorem, the transition amplitudes of the multipole fields can be written in terms of (many-electron) *reduced* matrix elements as

$$M_{fi}^{(\text{plane-wave})} = \sqrt{2\pi} \sum_{LM} \sum_{p=0,1} i^L \frac{[L]^{1/2}}{[J_f]^{1/2}} (i\lambda)^p D_{M\lambda}^L(\theta_k, \varphi_k, 0) \langle J_i M_i LM | J_f M_f \rangle \langle \alpha_f J_f || H_\gamma(pL) || \alpha_i J_i \rangle ,$$

$$\langle \alpha_f J_f || H_\gamma(pL) || \alpha_i J_i \rangle \equiv \left\langle \alpha_f \mathbb{J}_f \left\| \sum_q \boldsymbol{\alpha}_q \mathbf{a}_L^{(p)}(\mathbf{r}_q) \right\| \alpha_i \mathbb{J}_i \right\rangle .$$

These (reduced) matrix element does *neither* depend on the projections of the angular momenta of an atom and photon *nor* the particular choice of the quantization axis *nor* the propagation direction  $\mathbf{n}_k$ . They solely reflect the electronic structure of an atom and its coupling to a particular multipole component ( $pL$ ) of the radiation field.

### Photoexcitation by twisted light:

- **Photoexcitation by twisted light:**

$$\hbar\omega^{(\text{twist})} + A \longrightarrow A^*$$

- **Photoinduced processes with twisted light:** Since the helical phase structure of twisted beams causes a non-uniform intensity profile and a rather complex energy flow, many photo-induced atomic processes are modified in twisted light. This applies to both, the photo-excitation

and ionization as well as to Rayleigh, Raman and Compton scattering processes. For example, the use of twisted (vortex light) may help reduce the light shift of bound-state transitions and, hence, in the control of electric dipole-forbidden (atomic) clock transitions.

- **Photoexcitation by twisted light:** For the different multipole components of the radiation field, the ratio of partial photoexcitation cross sections is quite sensitive with regard to the topological charge  $\ell$  and the parameters of the incident light. In particular, this (photoexcitation) cross section ratio differs significantly from the excitation by a plane wave.
- **Photoexcitation of macroscopic targets:** For macroscopic targets, the sublevel-dependent photoexcitation cross sections  $\sigma_{m_f}^{(\text{twist})} = f(\vartheta_k)$  as well as the cross section ratio with regard to incoming plane-wave radiation  $\sigma^{(\text{twist})}/\sigma^{(\text{plane})}$  have been calculated.
- **Finite, localized targets:** For finite, localized targets, the sublevel-dependent photoexcitation cross sections as well as alignment and polarization parameters all depend on the impact parameter of the target with regard to the beam axis,

$$\sigma_{m_f}^{(\text{twist})} = f(\vartheta_k, \dots, \mathbf{b}, m), \quad \frac{\sigma^{(\text{twist})}}{\sigma^{(\text{plane})}} = f(\mathbf{b}, \text{target size}), \quad \mathcal{A}_2, P_1 = f(\mathbf{b}, \text{target size}).$$

- The photoexcitation of atoms by a Bessel beam of twisted light has been investigated for low- $Z$  hydrogen-like ions. Markgraf-Scholz *et al.* (2014) have calculated especially the *partial* (subshell) cross sections and the alignment of the excited states, if the beam interacts with macroscopic hydrogen target.
- **Vector potential for twisted Bessel beams:** For an incident Bessel beam, the vector potential  $\mathbf{A}^{(\text{Bessel})}(\mathbf{r})$  is given by (Schulz *et al.*, 2019)

$$\mathbf{A}^{(\text{Bessel})}(\mathbf{r}) = \mathbf{A}_{\varkappa m k_z \lambda}^{(\text{Bessel})}(\mathbf{r}) = \int \frac{d^2 \mathbf{k}_\perp}{(2\pi)^2} \mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} a_{\varkappa m}(\mathbf{k}_\perp) e^{-i\mathbf{k}_\perp \cdot \mathbf{b}}, \quad a_{\varkappa m}(\mathbf{k}_\perp) = e^{im\varphi_k} \frac{2\pi}{k_\perp} \delta(k_\perp - \varkappa).$$

This vector potential represents *Bessel* photons with well-defined helicity  $\lambda$ , the longitudinal component  $k_z$  of the wave vector and the projection  $m$  of the total angular momentum (TAM) upon the light propagation axis ( $z$ -axis). These Bessel photons also have a well-defined (absolute) value of the transverse momentum  $|\mathbf{k}_\perp| = \varkappa$  and are, hence, monochromatic with  $\omega = k/\alpha = \sqrt{k_z^2 + \varkappa^2}/\alpha$ .

- **Amplitude for twisted Bessel beams:** The expression above expands the vector potential of *Bessel* photons in terms of (a coherent superposition of) plane waves  $\mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}}$  whose wave vectors  $\mathbf{k}$  are uniformly distributed upon the surface of a cone with a polar opening angle  $\theta_k = \arctan(\varkappa/k_z)$ . Using the standard expansion of these plane waves in terms of multipoles and by inserting  $\mathbf{A}_{\varkappa m k_z \lambda}^{(\text{Bessel})}(\mathbf{r})$ , one finds after some algebra the amplitude for the  $|\alpha_i J_i M_i\rangle + \gamma \rightarrow |\alpha_f J_f M_f\rangle$  transition induced by Bessel light

$$M_{fi}^{(\text{Bessel})} = \sqrt{\frac{1}{[J_f]}} \sum_{LM} \sum_{p=0,1} i^{L+M} [L]^{1/2} (i\lambda)^p d_{M\lambda}^L(\theta_k) J_{m-M}(\varkappa b) e^{i(m-M)\varphi_b} \langle J_i M_i LM | J_f M_f \rangle \langle \alpha_f J_f || H_\gamma(pL) || \alpha_i J_i \rangle.$$

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Similar as for plane waves,  $M_{fi}^{(\text{Bessel})}$  is now written as a sum of reduced matrix elements  $\langle \alpha_f \mathbb{J}_f \| H_\gamma(pL) \| \alpha_i \mathbb{J}_i \rangle$  that are weighted by some additional geometric (angular) factors. For Bessel photons, these weight factors depend on the opening angle  $\theta_k$  and the TAM projection  $m$  of the beam as well as on the impact parameter of an atom  $b$ ; they enter the amplitude above in particular through the small Wigner function  $d_{M\lambda}^L(\theta_k)$  and the Bessel function  $J_{m-M}(b\kappa)$ .

- **Excitation rate for twisted Bessel beams:** The total rate for the excitation of atoms by Bessel light is obtained as usual by taking the average (summation) over the magnetic quantum numbers of the initial and final states,

$$W_{fi}^{(\text{Bessel})} = \frac{2\pi}{[J_i] \alpha^2} \sum_{M_i M_f} \left| M_{fi}^{(\text{Bessel})} \right|^2 = \sum_{pL} W_{fi}^{(\text{Bessel})}(pL) = \sum_{pL} \sum_M \left| d_{M\lambda}^L(\theta_k) J_{m-M}(b\kappa) \right|^2 W_{fi}^{(\text{plane-wave})}(pL).$$

- **Excitation rate for twisted Bessel beams:** Similar to  $W_{fi}^{(\text{plane-wave})}$ , the rate  $W_{fi}^{(\text{Bessel})}$  is still a sum of partial rates of allowed multipole transitions ( $pL$ ). Moreover, each partial rate  $W_{fi}^{(\text{Bessel})}(pL)$ , is a product of its plane-wave counterpart *times* a geometrical term that describes the properties of the Bessel beam and the position of the target atom. This decomposition ensures that the relative contributions of the multipole channels ( $pL$ ) to the total rate of the  $|\alpha_i \mathbb{J}_i\rangle + \gamma \rightarrow |\alpha_f \mathbb{J}_f\rangle$  transition can be modified by changing the parameters of twisted light, such as  $\theta_k$ ,  $\kappa$ , ....
- **Excitation rate for twisted Bessel beams & Gaussian target:** Making use of the Gaussian target distribution above, the photoexcitation rate can be written as:

$$W_{fi}^{(\text{Bessel})}(\mathbf{b}_0, \sigma) = \sum_{pL} \sum_M \left| d_{M\lambda}^L(\theta_k) \right|^2 \mathcal{J}_{m-M}(b_0) W_{fi}^{(\text{pl})}(pL)$$

$$\mathcal{J}_{m-M}(b_0) = \int \frac{d\mathbf{b}}{(2\pi)^2} f(\mathbf{b}; \mathbf{b}_0) |J_{m-M}(\kappa b)|^2 = \frac{1}{(2\pi)^2 \sigma^2} \int_0^\infty db b I_0\left(\frac{b b_0}{\sigma^2}\right) |J_{m-M}(\kappa b)|^2 e^{-\frac{b^2 + b_0^2}{2\sigma^2}}$$

and where  $I_0$  is the modified Bessel function of the first kind. Similar as before, the partial multipole rates in this rate expression are given by the product of the plane-wave counterparts  $W_{fi}^{(\text{plane-wave})}(pL)$  *times* a weight function that depends on the properties of twisted beam as well as the geometry and the distribution of the target but does not depend on the electronic structure of the atoms.

- **Excitation rate for plane-wave *versus* twisted beams:** While, for plane-wave radiation, the partial multipole rates are entirely determined by the electronic structure of the target atom, these partial multipole rates  $W_{fi}^{(\text{Bessel})}(pL)$  also depend on the (geometrical) properties of the radiation as well as the position of the atom with regard to the beam axis for twisted light. For instance, we can consider how the



(relative) strength of multipoles is affected by properties of the twisted light by taking the probability ratio (Schulz *et al.*, 2019)

$$\frac{W_{fi}^{(\text{Bessel})}(p_1 L_1)}{W_{fi}^{(\text{Bessel})}(p_2 L_2)} = \mathcal{R}_{L_1 L_2}(\kappa b) \frac{W_{fi}^{(\text{plane-wave})}(p_1 L_1)}{W_{fi}^{(\text{plane-wave})}(p_2 L_2)}, \quad \mathcal{R}_{L_1 L_2}(\kappa b) = \frac{\sum_M |d_{M\lambda}^{L_1}(\theta_k) J_{m-M}(b\kappa)|^2}{\sum_M |d_{M\lambda}^{L_2}(\theta_k) J_{m-M}(b\kappa)|^2}.$$

In this factorization, the first term just describes the geometry of the electron-photon interaction which depends on the TAM projection  $m$  and the opening angle  $\theta_k$  of the Bessel beam as well as on the position of the target atom.

- **Excitation rate for Bessel beams & Gaussian target:** For a Gaussian distributed target, located at the impact parameter  $b$ , the geometrical factor  $\mathcal{R}_{L_1 L_2}(\kappa b)$  has for a located atom to be modified by just the *averaged* geometrical factor

$$\langle \mathcal{R}_{L_1 L_2}(\kappa b_0) \rangle = \frac{\sum_M |d_{M\lambda}^{L_1}(\theta_k)|^2 \mathcal{J}_{m-M}(b_0 \kappa)}{\sum_M |d_{M\lambda}^{L_2}(\theta_k)|^2 \mathcal{J}_{m-M}(b_0 \kappa)},$$

With this *averaged* geometrical factor, we can analyze the role of different multipole transitions in atomic trap experiments.

- **Geometrical contribution to multipole excitations:** For plane-waves, the geometrical factor is  $\mathcal{R}^{(\text{plane-wave})} = 1$  for all ratios of the partial multipole rates. For the interaction of atoms with a Bessel beam, in contrast, the geometrical factor  $\mathcal{R}_{L_1=2, L_2=1}(\kappa b)$  can be much larger, and especially for  $m > 1$  and small impact parameters  $kb \rightarrow 0$ . This enhancement is observed for all (non-zero) opening angles  $\theta_k$  and can be explained based on the *selection rules* for a transition  $|\alpha_i \mathbb{J}_i M_i\rangle + \gamma \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  induced by twisted light. Generally, these modified selection rules strongly depend on the position of the target atom in the Bessel wave front. For the particular case of  $b \rightarrow 0$ , i.e. when atom is located at the beam axis, the magnetic quantum numbers  $M_i$  and  $M_f$  of the initial and final state are related to the TAM projection  $m$  of the Bessel beam by

$$M_f = m + M_i.$$

From this simple relation and the transition amplitudes for Bessel radiation it immediately follows that only multipoles with  $L \geq |m|$  can contribute to the excitation. For  $m = 2$  and small impact parameters, therefore, dipole transitions are strongly suppressed, and this then results in a drastic enhancement of  $\mathcal{R}_{L_1=2, L_2=1}(\kappa b)$ .

- **Selection rules for twisted light:** These rules tell which atomic transitions are possible for the given multipole decomposition of the radiation field. For different light fields, of course, different atomic fine-structure transitions can be excited, while the atom appears *transparent* with regard to all other multipole components. In optical (low-frequency) fields, moreover, the electric-dipole component is far dominant so that all other allowed multipole transitions are usually negligible. However, the relative importance of the different multipoles change with the

photon frequency and if more subtle properties about the (subsequent) photon or electron emission is considered. In general, the strength of excitation hereby also depends on a **geometrical component** due to the coupling as well as the real weight of a given multipole field in the decomposition. Here, let us start explicitly from the QN of the light beams. .... Note: **Twisted light does not change the selection rules but their multipole decomposition of the radiation field is different.**

- **Quadrupole excitation of trapped  $\text{Ca}^+$  ions:** Schmiegelow *et al.* (2016) observed a (dominant)  $4s\ ^2S_{1/2} - 3d\ ^2D_{5/2}$  electric-quadrupole excitation at ... nm if  $\text{Ca}^+$  ion were trapped and localized within a thermal spatial spread of about 60 nm around the origin, i.e. near to the dark center of a vortex beam. This observation has often been *interpreted* as the twisted light would modify the selection rules and would efficiently induce higher-order multipole transitions, a quite misleading interpretation. Moreover, this experiment showed that the use of twisted light may reduced the ac Stark shift considerably. Such excitations may enable one to drive atoms on dipole-forbidden transitions with a reduced light shift, and which might appear useful for high precision measurements (optical atomic clocks).
- Duan *et al.* (2019) analyzed the vector potential of twisted light and their decomposition in multipole components. In twisted beams, the multipole decomposition locally depends on both, the radial (and angular) position in the wavefront. For well-localized atomic targets, this dependence then becomes visible also in its excitation and subsequent decay dynamics of the atom or ion. To make the decomposition explicit, Duan *et al.* (2019) introduced (the term of) *position-dependent selection rules*, which are however misleading since only the light field but not the selection rules depend of the relative position of the target with regard to the beam (axis). The selection rules are also independent of the particular atom, even if their interaction with the twisted beam will lead to different observations. For their analysis, Duan *et al.* (2019) expand a Bessel beam into its multipole components, from which the total transition amplitude is obtained as weighted sum of multipole amplitudes.
- **Multipole expansions of light fields:** Any incident (and practically relevant) light field can be readily expanded in terms of its multipole fields

$$\mathbf{A}(\mathbf{r}; \text{geometry \& polarization}) = \sum_{\mathbb{M}, M} w(\mathbf{r}, \mathbb{M}, M; \text{geometry \& polarization}) a_M^{(\mathbb{M})}(\mathbf{r}) = \sum_{p, LM} w(\mathbf{r}, p, L, M; \text{geometry \& polarization}) a_{LM}^{(p)}(\mathbf{r})$$

where the first line is the notation in JAC, and the second the frequently applied notation in the literature, cf Rose (1964) and Johnson (2007). For transverse fields, the multipole components refer explicitly to either magnetic ( $p = 0$ ) or electric fields ( $p = 1$ ). These multipole fields are chosen to form a basis of well-defined (total) angular momentum:  $\mathbf{j}^2 a_{LM}^{(p)} = L(L+1) a_{LM}^{(p)}$ ,  $j_z a_{LM}^{(p)} = M a_{LM}^{(p)}$ . For the light field, we can therefore write

$$j_z \mathbf{A}(\mathbf{r}; \text{geometry \& polarization}) = \sum_{\mathbb{M}, M} w(\mathbf{r}, \mathbb{M}, M; \text{geometry \& polarization}) a_M^{(\mathbb{M})}(\mathbf{r}).$$

Therefore, the light field will be an eigenfunctions if the summation over  $M$  just selects on particular value  $M'$  :  $w(\mathbf{r}, \mathbb{M}, M) = w(\mathbf{r}, \mathbb{M}, M) \delta_{MM'}$ , a value which can vary also locally within the field.

### 8.1.c. Atomic photoionization (PhotoIonization)

#### Process, notation & application:

- **Photoionization** of an atom or ion:  $A + \hbar\omega \longrightarrow A^{+*} + e_p^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + e_p^-(\mathbf{p}, m_s)$  or  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{e_p^-(\varepsilon \kappa)\}$ .
- Using JAC: Perform an `Atomic.Computation(.., process=Jac.Photo, processSettings=PhotoIonization.Settings(..), ..)` or call directly functions from the module `PhotoIonization`.
- In JAC, the total photoionization cross sections are calculated and tabulated by default, while the partial cross sections into the final magnetic substates  $|\alpha_f \mathbb{J}_f M_f\rangle$  with well-defined projection  $M_f$  are printed only if the flag `calcPartialCs = true` is set in `PhotoIonization.Settings`.
- In JAC, the statistical tensors of the photoion are calculated and tabulated for the photoionization of initially unpolarized atoms by plane-wave photons with given Stokes parameters, if the flag `calcTensors` is set in `PhotoIonization.Settings` and if the Stokes parameters are provided explicitly by `Ionization.Settings.stokes`.
- Using JAC: Perform an `Atomic.Computation(.., process=Jac.PhotoInPlasma, processSettings = PlasmaShift.PhotoSettings(..), ..)` or call directly functions from the modules `PhotoIonization` and `PlasmaShift`. Until the present, however, only a Debye-Hückel plasma model is supported in JAC, and where the Debye-Hückel screening of the electron-nucleus and electron-photon interaction is incorporated only in first-order perturbation theory into the CI matrix.
- In JAC, the reduced photoionization amplitudes (matrix elements) above are the main *building blocks* in order to represent and discuss most photo-ionization properties as they arise from the interaction of atoms and ions with the radiation field.
- **Quantization axis:** While the magnetic quantum numbers of the ion and photo electron refer to the adopted *usually, the quantization axis* of the overall system ( $z$ -axis), the **helicity  $\lambda$  of the photon is *always* defined with regard to the wave vector  $\mathbf{k}$  of the photon**, i.e. with regard to the direction of the incident photons.

## 8. Atomic processes

- **Quantization axis:** In practice, a proper quantization axis has to be chosen for the computation of all photoionization processes; here, one often needs to take into account **the geometry of the experiment**. To describe, for instance, the alignment of the photoion for its (photo-) ionization by *unpolarized* light, it is most convenient to adopt the quantization axis along the incoming photon momentum:  $\mathbf{k} \parallel z$ .
- **Fano's propensity rule for photoionization:** According to this (propensity) rule, the dipole transition to the partial wave with larger orbital angular momentum  $\ell_c = \ell_i + 1$  is usually dominant and the photoemission group delay is then approximately given by  $\tau^{(\text{Wigner})} = \frac{d\sigma_{\ell_c}}{dE}$ .
- **Electron-electron correlations:** **Interesting correlation effects with regard to the exchange interaction, interchannel coupling, relaxation and polarization of the incident photons and/or photoelectrons** occurs often in the vicinity of the photoionization threshold.
- **Dichroism:** A dichroism in the photoelectron emission is conventionally related to a change in the polarization of the incident light, while the initial polarization state of the target is kept fixed in most of these measurements.
- **Giant resonances:** The  $4d$  ionization of xenon and barium are both characterized by a rather broad and delayed absorption peak with a widths of approximately 50 eV above of the  $4d$  ionization threshold, a so-called **giant resonance**. Photoelectron spectroscopy measurements in this region have shown that a significant fraction of this strong absorption arises for xenon and barium due to the formation of – valence-shell excited – autoionizing resonances.
- **Solid-state experiments:** Since inner-shell photoionization from solids can be considered in good approximation as an atomic photoionization process, owing to the local character of inner-shell electrons, atomic-like photoionization calculations can also be applied in order to design solid-state experiments.

### Photoionization amplitude:

- **Emission of an electron with well-defined asymptotic momentum  $\mathbf{p}$  and spin projection  $m_s$ :** If the atom undergoes the transition  $|\alpha_i \mathbb{J}_i M_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  during the photoionization process, the transition amplitude for the absorption of a photon with wave vector  $\mathbf{k}$  and helicity  $\lambda = \pm 1$  is given by:

$$\mathcal{M}(M_f, m_s, \lambda, M_i) = \left( \frac{4\pi^2 \alpha}{\omega} \right)^{1/2} \left\langle \alpha_f \mathbb{J}_f M_f, \mathbf{p} m_s \left| \sum_{j=1}^N \boldsymbol{\alpha}_j \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}_j} \right| \alpha_i \mathbb{J}_i M_i \right\rangle.$$

- The population of the magnetic sublevels  $|\alpha_f \mathbb{J}_f M_f\rangle$  of the photoion depends (of course) on the spin projection  $\lambda$  of the incident photons as well as the magnetic quantum numbers  $M_f$  of the final state of the photoion, while one need to average over the initial sublevels as well as the spin projections of the emitted electron.

- **(Reduced many-electron) photoionization amplitude:** For both, a partial-wave decomposition of the outgoing photoelectron *and* with a multipole expansion of the electron-photon interaction, the reduced photoionization amplitude describes the contribution of individual multipole components of the radiation field to the formation of a scattering state  $|(\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t\rangle$  with well-defined total symmetry and asymptotic energy  $\varepsilon$  of the outgoing photoelectron; this reduced amplitude is related to the photoabsorption amplitude by:

$$\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{O}^{(\mathbb{M}, \text{photoionization})} | \alpha_i \mathbb{J}_i \rangle = i^{-\ell} \exp(i \Delta_\kappa) \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{O}^{(\mathbb{M}, \text{absorption})} | \alpha_i \mathbb{J}_i \rangle .$$

Here, the photoionization amplitude also accounts for the proper phase (or the asymptotic boundary condition) of the outgoing electron.

- In JAC, the reduced photoionization amplitudes (matrix elements) above are the main *building blocks* in order to represent and discuss most photoionization properties as they arise from the interaction of atoms and ions with the radiation field.

### Partial and total cross sections:

- **Partial photoionization cross sections for the photoionization of an initially unpolarized atom:** For the photoionization of an initially unpolarized atom from level  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  by unpolarized plane-wave photons with wave vector  $\mathbf{k} \parallel \mathbf{e}_z$  (quantization axis), the partial cross sections can be expressed as:

$$\begin{aligned} \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f M_f) &= \frac{1}{2(2J_i + 1)} \sum_{M_i \lambda m_s} \int d\Omega_p |\mathcal{M}(M_f, m_s, \lambda, M_i)|^2 \\ &= \frac{4\pi^2 \alpha}{2\omega(2J_i + 1)} \sum_{M_i \lambda} \sum_{\kappa m} \sum_{JJ'M} \langle J_f M_f j m | JM \rangle \langle J_f M_f j m | J'M \rangle \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J} M \left| \sum_{i=1}^N \alpha_i \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}_i} \right| \alpha_i \mathbb{J}_i M_i \right\rangle \\ &\quad \times \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}' M \left| \sum_{i=1}^N \alpha_i \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}_i} \right| \alpha_i \mathbb{J}_i M_i \right\rangle^* . \end{aligned}$$

Here, the integration over all emission angles  $\Omega_p = (\vartheta_p, \varphi_p)$  of the photoelectron results into a *incoherent* summation over the partial waves of the many-electron scattering states with different  $\kappa$ -symmetries of the photoelectron.

- **Partial photoionization cross sections for initially unpolarized atoms by unpolarized plane-wave photons:** For unpolarized atoms and

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unpolarized incident plane-wave photons, the partial cross sections from above can be simplified and expressed as:

$$\begin{aligned} \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f J_f M_f) &= \frac{8\pi^3 \alpha}{2\omega (2J_i + 1)} \sum_{t\lambda} \sum_{\kappa} \sum_{JJ'} \sum_{\mathbb{M}\mathbb{M}'} i^{L-L'} (i\lambda)^p (-i\lambda)^{p'} (-1)^{L+L'} \sqrt{(2L+1)(2L'+1)(2J+1)(2J'+1)} \\ &\quad \times \langle L'\lambda J_f M_f | t, \lambda + M_f \rangle \langle L\lambda J_f M_f | t, \lambda + M_f \rangle \begin{Bmatrix} j & J' & J_f \\ J & J_i & L \\ J_f & L' & t \end{Bmatrix} \\ &\quad \times \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J} \left\| \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \right\| \alpha_i \mathbb{J}_i \right\rangle \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}' \left\| \mathbb{O}^{(\mathbb{M}', \text{photoionization})} \right\| \alpha_i \mathbb{J}_i \right\rangle^* . \end{aligned}$$

- **Total photoionization cross sections for initially unpolarized atoms by unpolarized plane-wave photons:** For the photoionization of an initially unpolarized atom from level  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f\rangle$  by unpolarized plane-wave photons with wave vector  $\mathbf{k} \parallel \mathbf{e}_z$ , the total cross sections can be expressed as:

$$\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \sum_{M_f} \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f M_f) = \frac{4\pi^2 \alpha \omega}{2(2J_i + 1)} \sum_{\kappa \mathbb{J}} \sum_{\mathbb{M}} \left| \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J} \left\| \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \right\| \alpha_i \mathbb{J}_i \right\rangle \right|^2 .$$

In JAC, the summation over  $\kappa \mathbb{J}$  refers to the summation over all photoionization channels of a given photoionization line between fine-structure levels:  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$ .

### Final-state density matrix 'photo-ion + photo-electron':

- The final-state density matrix of the overall system 'photo-ion + photo-electron' is not so useful in general and is needed only for entanglement studies and related topics. Here, we just summarize some formulas but further work is needed to find the proper expression for incident light with different polarization properties.
- **Final-state density matrix of the 'photo-ion + photo-electron':** After the absorption of the photon, we have a free electron with asymptotic linear momentum  $\mathbf{p}$  and with spin projection  $m_s$ , while the photoion is left in a (magnetic) fine-structure state  $|\alpha_f \mathbb{J}_f M_f\rangle$ . Using a basis with well-defined (angular) momenta  $J_i$  and  $J_f$  of the initial and the residual ion as well as the asymptotic linear momentum  $\mathbf{p}$  and spin

projection  $m_s$  of the ejected electron, the final-state density matrix can be written as

$$\begin{aligned} & \langle \alpha_f J_f M_f, \mathbf{p} m_s | \rho_f | \alpha_f J_f M'_f, \mathbf{p} m'_s \rangle \\ &= \sum_{M_i M'_i \lambda \lambda'} c_{\lambda \lambda'} \left\langle \alpha_f J_f M_f, \mathbf{p} m_s \left| \hat{\mathcal{R}} \right| \alpha_i J_i M_i, \mathbf{k} \lambda \right\rangle \langle \alpha_i J_i M_i, \mathbf{k} \lambda | \rho_i | \alpha_i J_i M'_i, \mathbf{k} \lambda' \rangle \left\langle \alpha_i J_i M'_i, \mathbf{k} \lambda' \left| \hat{\mathcal{R}}^\dagger \right| \alpha_f J_f M'_f, \mathbf{p} m'_s \right\rangle \end{aligned}$$

where  $R = \sum_j \boldsymbol{\alpha}_j \cdot \mathbf{u}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}_j}$  represents the electron-photon interaction.

### Angular distribution of photoelectrons:

- **Measurement operator for angular distributions:** If the detector is neither sensitive to the spin state of the photoelectron nor to those of the residual photoion, a proper measurement (projection) operator is obtained if we sum over the electron spin projections  $m_s$  as well as the magnetic quantum numbers  $M_f$  of the ion. In the density matrix formalism, this projection operator for measuring the angular distribution of the emitted photoelectrons therefore is:

$$P = \sum_{M_f m_s} |\alpha_f J_f M_f, \mathbf{p} m_s\rangle \langle \alpha_f J_f M_f, \mathbf{p} m_s|,$$

- With this measurement operator, the well-known angular distribution of the photoelectrons is just the normal trace of the final-state density matrix:

$$W(\vartheta) = \text{Tr}(P \rho_f) = \sum_{M_f m_s} \langle \alpha_f J_f M_f, \mathbf{p} m_s | \rho_f | \alpha_f J_f M_f, \mathbf{p} m_s \rangle.$$

- **Photoionization of closed-shell atoms:** Derevianko *et al.* (1999) provide a detailed study of the photoionization cross sections and angular distributions of all rare-gas atoms up to xenon and by going beyond the typical dipole approximation. In particular, these authors include all corrections  $\mathcal{O}(ka)$  and  $\mathcal{O}(k^2 a^2)$  where  $k$  is the modulus of the wave vector and  $a$  the radius of the ionized subshell. While, within the electric-dipole approximation, the photoelectron angular distribution for the photoionization by linearly or unpolarized light is characterized by a single (anisotropy) parameter  $\beta$ , the  $\mathcal{O}(ka)$  corrections are characterized by two parameters  $\gamma$  and  $\delta$ , and the  $\mathcal{O}(k^2 a^2)$  corrections by even three parameters  $\lambda, \mu, \nu$  with the constraint  $\lambda + \mu + \nu = 0$  as well as a correction  $\Delta\beta$  to the dipole parameter.

- **Angle-differential photoionization cross section for closed-shell atoms:** For the photoionization of an electron from an initially closed subshell by linearly-polarized light, the angle-differential photoionization cross section is given by (Derevianko *et al.*, 1999)

$$\frac{d\sigma}{d\Omega}(\vartheta, \varphi) = \frac{\sigma_o}{4\pi} \{1 + (\beta + \Delta\beta) P_2(\cos \vartheta) + (\delta + \gamma \cos^2 \vartheta) \sin \vartheta \cos \varphi + \lambda P_2(\cos \vartheta) \cos 2\varphi + \mu \cos 2\varphi + \nu (1 + \cos 2\varphi) P_4(\cos \vartheta)\}$$

with  $\lambda + \mu + \nu = 0$ , and where  $(\vartheta, \varphi)$  are the polar angles of the outgoing photoelectrons. This expansion applies, if the quantization axis is chosen along the polarization,  $\mathbf{u} \parallel \mathbf{e}_z$ , and  $\mathbf{e}_x \parallel \mathbf{k}$  along the photon propagation. This expression also includes the standard angular distribution of photoelectron,  $1 + \beta P_2(\cos \vartheta)$  in the electric-dipole approximation, where  $\beta$  results from the interference of (electric-dipole) amplitudes for different partial waves of the outgoing electron. Derevianko *et al.* (1999) discuss also briefly which interferences due to the various multipole components of the radiation field give rise to all other anisotropy parameters, while expressions are given only in one-electron notation as appropriate for hydrogenic and closed-shell systems. No attempt has been made to derive expressions for open-shell atoms. Derevianko *et al.* (1999) found the non-dipole angular parameters rather insensitive with regard to details of the chosen potential  $V(r)$ .

- **Formulas of the (non-) dipole anisotropy parameters for closed-shell atoms:** All dipole and non-dipole anisotropy parameters can be readily expressed in terms of the (reduced) multipole transition amplitudes. Derevianko *et al.* (1999) provide tables and graphs of the seven angular distribution parameters, calculated within the relativistic independent-particle approximation (IPA). Results are shown for electron energies between 20-5000 eV for all subshells of the rare gas atoms He, Ne, Ar, Kr and Xe. For Ar and Kr, moreover, comparison is made for selected parameters with results from the random-phase approximation in order to illustrate the influence of electron correlations.

### Reduced statistical tensors of the photoion for plane-wave incident radiation:

- **Statistical tensors of the photoion in level  $(\alpha_f \mathbb{J}_f)$  after the photoionization of unpolarized atoms by unpolarized plane-wave photons:** If the incident light propagates along the  $x$ -axis (here used as quantization axis because of its frequent use in experimental discussions) and if the photoelectron remains unobserved, the statistical tensors are given by Kämpfer *et al.* (2016)

$$\begin{aligned} \rho_{kq}(\alpha_f \mathbb{J}_f) &= \frac{\pi}{2J_i + 1} \delta_{q0} \sum_{\mathbb{M} \mathbb{M}'} \sum_{\kappa J J'} \sum_{\lambda=\pm 1} i^{L+p-L'-p'} \lambda^{p+p'} [L, L', J, J']^{1/2} (-1)^{J+J'+J_f+J_i+j+1} \langle L\lambda, L' - \lambda | kq \rangle \begin{Bmatrix} J_f & j & J' \\ J & k & J_f \end{Bmatrix} \begin{Bmatrix} J' & J_i & L' \\ L & k & J \end{Bmatrix} \\ &\times \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J} \parallel \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \parallel \alpha_i \mathbb{J}_i \rangle \left\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}' \parallel \mathbb{O}^{(\mathbb{M}', \text{photoionization})} \parallel \alpha_i \mathbb{J}_i \right\rangle^* . \end{aligned}$$



- **Statistical tensors of the photoion in level  $(\alpha_f \mathbb{J}_f)$  after the photoionization of unpolarized atoms by plane-wave photons with given density matrix  $(c_{\lambda\lambda'})$ :** If, more generally, the incident plane-wave light propagates along the  $z$ -axis and refers to photons with well-defined (photon) density matrix  $(c_{\lambda\lambda'})$ , i.e. with given Stokes parameters  $(P_1, P_2, P_3)$ , the statistical tensors are given by (Sharma *et al.*, 2010)

$$\begin{aligned} \rho_{kq}(\alpha_f \mathbb{J}_f) &= \frac{\pi}{2J_i + 1} \sum_{\mathbb{M}\mathbb{M}'} \sum_{\kappa JJ'} \sum_{\lambda\lambda'} [\delta_{\lambda\lambda'}(1 + \lambda P_3) + (1 - \delta_{\lambda\lambda'})(P_1 - i\lambda P_2)] i^{L-L'+p-p'} \lambda^p (\lambda')^{p'} [L, L', J, J']^{1/2} \\ &\quad \times (-1)^{(J+J'+J_f+J_i+j+1)} \langle L\lambda L' - \lambda' | kq \rangle \begin{Bmatrix} J_f & j & J' \\ J & k & J_f \end{Bmatrix} \begin{Bmatrix} J' & J_i & L' \\ L & k & J \end{Bmatrix} \\ &\quad \times \langle (\alpha_f J_f, \varepsilon\kappa) J \parallel \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \parallel \alpha_i J_i \rangle \langle (\alpha_f J_f, \varepsilon\kappa) J' \parallel \mathbb{O}^{(\mathbb{M}', \text{photoionization})} \parallel \alpha_i J_i \rangle^* . \end{aligned}$$

- In JAC, the statistical tensors of the photoion are calculated and tabulated for the photoionization of unpolarized atoms by plane-wave photons with given Stokes parameters, if the proper information is provided by the `PhotoIonization.Settings`.

## Time-resolved photoionization:

- **Time-resolved photoionization experiments:** During the last two decades, experiments with subfemto-second resolution enabled one to study the electron dynamics of atoms. Examples refer to the observation of time-resolved autoionizing resonances, the decay of core vacancies or the (relative) delay time of emitted photoelectrons. All these relaxation processes usually occur within tens of attoseconds in dependence of the excitation energy and the electronic structure of the atomic targets. Following Heisenberg's uncertainty principle, of course, a **natural trade-off exist between the temporal and spectral resolution**, though resolution can be tune to either the time or frequency domain. In the time domain, such spectroscopic studies have largely benefitted from high-resolution frequency combs based on phase-stable femtosecond pulse trains.
- **Time-resolved photoionization experiments:** Isinger *et al.* (2017) used the high-order harmonic spectrum in order to analyze the interplay between high-resolution photoelectron spectroscopy and attosecond dynamics. This analysis enabled them to disentangle the direct  $2s$  ionization of neon from ionization-excitation processes of two  $2p$  electrons (shake-up processes) by utilizing a phase-stable interferences between attosecond pulses in the pulse train. The  $2s - 2p$  time delay derived from this detailed analysis agrees well with theoretical predictions based on the Wigner time. Here, the observation of the shake processes also provided an explanation to the discrepancy with earlier observations by Schultze *et al.* (2010).

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- **Wigner (time) delay:** The photoionization time delay or Wigner delay refers to the delay of the group velocity of the electronic wave packet as created by the absorption of xuv radiation. This Wigner delay can be obtained quite readily by taking the derivative of the scattering phase of the outgoing electron wave. — An additional time delay arises from the interaction of the laser probe field with the Coulomb potential, and this can be calculated accurately at high kinetic energies from either the asymptotic form of the wave function or by classical trajectories (Isinger *et al.*, 2017).
- **Time-resolved photoionization:** The measured time delays in (time-resolved) photoionization experiments general consists of different parts which need to be considered separately, and often also within different theoretical frameworks. Apart from the **quantum-mechanical Eisenbud-Wigner-Smith (EWS) delay**, which arises from group delay of the photoelectron wave packet, the interaction of the electrons with the additional laser field, e.g. the ir streaking field, has to be taken into account as well. The EWS delay practically refers to changes in the phase of the outgoing wave packets and require a careful treatment of the inter-electronic correlations in the photoionization process. Both contributions are assumed to be strictly additive with (sub-)9 attosecond precision and can therefore be determined independently of each other.
- **Time-resolved photoionization:** In attosecond-streaking experiments, the photoionization of a bound electron arises from the interaction of atoms with two light fields, an isolated attosecond pulse in the extreme ultraviolet (xuv) range of the spectrum and a streaking ir field

$$\mathcal{E}(t) = \mathcal{E}^{(\text{xuv})}(t) + \mathcal{E}^{(\text{ir})}(t).$$

The time-resolved information about the photoionization of single electrons are obtained by varying the temporal overlap between the xuv and ir fields. Theoretically, the xuv is usually weak and treated perturbatively, while the ir streaking field is moderately strong, although not strong enough to modify the ionization. However, the ir field strongly affects the motion of the quasi-free electron, once it is released from the atom (Feist *et al.*, 2014).

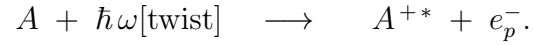
- **Eisenbud-Wigner-Smith (EWS) delay:** The EWS time for the photoionization of atom from the initial level  $\alpha_i \mathbb{J}_i$  to the final level  $\alpha_f \mathbb{J}_f$  of the residual photoion is given by the energy derivative of the (single-electron) photoionization amplitude

$$t^{(\text{EWS})} = \frac{\partial}{\partial \varepsilon} \langle \alpha_f \mathbb{J}_f, \mathbf{p} m_s | \mathbb{O}^{(\text{E1, photoionization})} | \alpha_i \mathbb{J}_i \rangle,$$

and where  $\mathbf{p} = \mathbf{p}(\varepsilon, \vartheta_p, \varphi_p)$  is the asymptotic momentum of the emitted electron. In this notation,  $(\vartheta_p, \varphi_p)$  just refers to the direction of the outgoing electron wave and E1 to the electric-dipole approximation. Details of this (single-electron) photoionization amplitude depend on the polarization of the incident xuv photons and how the inter-electronic correlations are taken into account.

## Photoionization by twisted light:

- Photoionization by twisted light:



### 8.1.d. Radiative recombination (PhotoRecombination)

#### Process, notation & application:

- Radiative recombination or photorecombination of an atom or ion:  $A^{q+} + e^- \longrightarrow A^{(q-1)+} + \hbar\omega$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon\kappa\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{\hbar\omega(\mathbb{M})\}$  or  $|\alpha_i \mathbb{J}_i\rangle + |\mathbf{p} m_s\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{\hbar\omega(\mathbb{M})\}$ .
- Using JAC: Perform an `Atomic.Computation(.., process=Jac.Rec, processSettings=PhotoRecombination.Settings(..), ..)` or call directly functions from the module `PhotoRecombination`.
- In JAC, the total radiative recombination cross sections are calculated and tabulated by default for all selected recombination lines.
- In JAC, the (reduced) photorecombination amplitudes are the building blocks in order to obtain most of the properties below.
- In JAC, the anisotropy parameters  $\beta_\nu^{(\text{REC})}$ ,  $\nu = 1, \dots, 4$  are calculated and tabulated for all selected photorecombination lines if the flag `calcAnisotropy = true` is set in `PhotoRecombination.Settings`.
- In JAC, the statistical tensors for the recombination of unpolarized ions and unpolarized plane-wave electrons are calculated and tabulated if the flag `calcTensors = true` is set in `PhotoRecombination.Settings`.
- The photorecombination of ions is known also as radiative recombination (RR) or radiative electron capture (REC) in the literature.
- The radiative recombination (RR) can be viewed as the time-reversed photoionization process and occurs very frequently in stellar and laboratory plasmas as well as in ion-trap and storage-ring experiments.

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- If a highly-charged ion circulates in a storage ring, it may capture electrons from rest-gas atoms in the ring and will then be misbent by subsequent steering magnets. Therefore, the **radiative recombination or electron capture typically results in a loss of the ion from the ring**, and where the lifetime is typically proportional to the inverse product of the capture cross section and target pressure.
- **Magnetic sublevel population  $|\alpha_f \mathbb{J}_f M_f\rangle$  of the recombined ion:** The radiative recombination amplitude from below can be utilized also to describe the (magnetic) sublevel population of the recombined ion. In the framework of density matrix theory, this sublevel population of the ionic (or atomic) states is described most conviniently in terms of the *statistical tensors*  $\rho_{kq}(\alpha_f \mathbb{J}_f)$  of the recombined ion in its final level  $(\alpha_f \mathbb{J}_f)$ .
- **Quantization axis:** Similar as in the photoionization process, the particular expressions for the statistical tensors depend on the choice of the quantization axis of the overall system ( $z$ -axis) as well as the geometry of the experiments.
- **Radiative recombination of bare ions:** This recombination process has attracted much interest from the very beginning of quantum mechanics, and has been treated semi-classically even before. Already in 1923, Kramers used semi-classical arguments in order to provide the cross section for the RR of hydrogenic ions into high- $n$  subshells. Several other authors also obtained approximate expressions for the RR cross sections of initially bare ions; for instance, the Bethe-Salpeter analytical formula provides an approximate cross section even for the recombination into the ground and low-excited levels. Katkov and Strakhovenko (1978) derived for initially bare ions another approximate expression for the RR cross section  $\sigma^{(\text{RR})}(\varepsilon; \text{bare} \rightarrow n)$  into shell  $n$ . Approximate expressions are known in the literature also for the total RR cross section  $\sigma^{(\text{RR})}(\varepsilon; \text{bare} \rightarrow \sum_n n)$ .

### Photorecombination amplitude:

- **Photorecombination amplitude:** In first-order perturbation theory, most radiative recombination properties can be traced back to the evaluation of the (reduced photon emission) matrix element

$$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J}_t \rangle = \langle (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \parallel \alpha_f \mathbb{J}_f \rangle^*,$$

and which describes the capture of a free electron with (asymptotic) energy  $\varepsilon$  and angular momentum  $\kappa$  under the – simultaneous – emission of a photon with multipolarity  $\mathbb{M} = (L, p)$ .

### Total recombination cross sections and rate coefficients:

- **Total recombination cross section:** If the density of states and the principle of detailed balance between the capture and the (photo-) ionization of an electron is taken into account, the total cross section reads as

$$\sigma(\epsilon; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \frac{8\alpha^3 \pi^3 \omega}{(2J_i + 1) \beta^2 \gamma^2} \left[ \sum_{\mathbb{M} \mathbb{J}_\kappa} \left| \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \epsilon \kappa) \mathbb{J} \rangle \right|^2 \right],$$

where  $\beta = v/c$  and  $\gamma = \sqrt{1 - \beta^2}$  arise from the Lorentz transformation in going from the projectile into the laboratory frame.

- **Radiative recombination rate coefficient  $\alpha^{(\text{recombination})}$ :** The calculations of radiative-recombination rates coefficients have an analogue form as for electron-impact excitation rate coefficients. This rate coefficient [in ] cm<sup>3</sup>/sec] is given for a Maxwell-distributed electron cloud with temperature  $T_e$  by

$$\alpha^{(\text{recombination})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \sqrt{\frac{8}{\pi m T_e^3}} \int_{\Delta\epsilon}^{\infty} d\epsilon \epsilon \sigma^{(\text{recombination})}(\epsilon; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \exp\left(-\frac{\epsilon}{T_e}\right).$$

### Angular distribution of emitted photons:

- **Angular distribution of emitted photons:** For initially unpolarized ions and unpolarized incident plane-wave electrons, the angular distribution of the emitted recombination photons can be readily obtained from the final-state density matrix by taking the trace  $\text{Tr}(P_{\mathbf{k}} \rho_f)$  with regard to the measurement (projection operator) of plane-wave photons:

$$W(\theta; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \frac{\sigma}{4\pi} \left( 1 + \sum_{\nu=1} P_{\nu}(\cos \vartheta) \beta_{\nu}^{(\text{REC})}(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) \right).$$

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➤ Anisotropy parameters of the emitted photons:

$$\begin{aligned}
& \beta_{\nu}^{(\text{REC})}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \\
&= -\frac{1}{2} \sum_{\mathbb{J} \mathbb{J}' \kappa \kappa'} \sum_{\mathbb{M} \mathbb{M}'} i^{L+p-L'-p'} (-1)^{J_i-1/2-J_f} [L, L', \ell, \ell', j, j', J, J']^{1/2} \langle \ell 0, \ell' 0 | \nu 0 \rangle \langle L 1, L' - 1 | \nu 0 \rangle \left( 1 + (-1)^{L+p+L'+p'-\nu} \right) \\
&\quad \times \left\{ \begin{matrix} J & J' & \nu \\ L' & L & J_f \end{matrix} \right\} \left\{ \begin{matrix} J & J' & \nu \\ j' & j & J_i \end{matrix} \right\} \left\{ \begin{matrix} j & j' & \nu \\ \ell' & \ell & 1/2 \end{matrix} \right\} \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J} \rangle^* \\
&\quad \times \left\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}', \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa') \mathbb{J}' \right\rangle \left[ \sum_{\mathbb{J} \kappa \mathbb{M}} \left| \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J} \rangle \right|^2 \right]^{-1}.
\end{aligned}$$

## Final-state density matrix ‘recombined ion + photon’:

➤ Final-state density matrix ‘recombined ion + photon’: For an unpolarized ion with nuclear spin  $I = 0$  and for unpolarized plane-wave electrons, the final-state density matrix can be expressed as:

$$\begin{aligned}
& \langle \alpha_f \mathbb{J}_f M_f, \mathbf{k} \lambda \mid \rho_f \mid \alpha_f \mathbb{J}_f M'_f, \mathbf{k} \lambda' \rangle \\
&= \frac{8\pi}{2(2J_i + 1)} \sum_{\mathbb{M} \mathbb{M}'} \sum_{J J'} \sum_{\kappa \kappa'} \sum_{\nu \mu_1 \mu_2 s s'} D_{\mu_1 \mu_2}^{\nu}(\mathbf{k} \rightarrow \mathbf{e}_z) i^{L'-L} (i\lambda')^{\pi'} (-i\lambda)^{\pi} (-1)^{1/2+J_i+J'+L+s+s'-M'_{J,f}} [\ell, \ell', L, L', j, j', J, J', s]^{1/2} \\
&\quad \times [s'] \left\{ \begin{matrix} j' & 1/2 & \ell' \\ \ell & s & j \end{matrix} \right\} \left\{ \begin{matrix} j' & J_i & J' \\ J & s & j \end{matrix} \right\} \left\{ \begin{matrix} J & L & J_f \\ \nu & s' & L' \end{matrix} \right\} \left\{ \begin{matrix} J & J' & s \\ J_f & s & L' \end{matrix} \right\} \langle \ell' 0 \ell 0 \mid s 0 \rangle \langle J_f M_f s' - M'_f \mid \nu \mu_1 \rangle \\
&\quad \times \langle s 0 s' M'_f \mid J_f M'_f \rangle \langle L' \lambda' L - \lambda \mid \nu \mu_2 \rangle \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J} \rangle \left\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}', \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa') \mathbb{J}' \right\rangle^*.
\end{aligned}$$

- In JAC, no attempt has been made so far to implement the density matrix of the overall system ‘recombined ion + photon’ because of its little relevance for practical computations. However, this density matrix could be implemented quite easily by using the photorecombination amplitudes from above.

### (Reduced) Statistical tensors of the recombined ion in the level $(\alpha_f \mathbb{J}_f)$ :

- **Statistical tensors  $\rho_{k0}(\alpha_f \mathbb{J}_f)$  of the final ion following the recombination of unpolarized ions with unpolarized plane-wave electrons:** If the quantization axis is adopted along the incoming electron momentum  $\mathbf{p} \parallel \mathbf{e}_z$ , the statistical tensors of the recombined ion in level  $(\alpha_f \mathbb{J}_f)$  are given by

$$\rho_{k0}(\alpha_f \mathbb{J}_f) = \frac{32 \pi^3}{2J_i + 1} \sum_{\mathbb{M}} \sum_{\mathbb{J} \mathbb{J}' \kappa \kappa'} [\ell, \ell', j, j', J, J']^{1/2} (-1)^{J_i + L - J_f + J - J' - 1/2} \langle \ell 0, \ell' 0 | k 0 \rangle \left\{ \begin{matrix} j & j' & k \\ \ell' & \ell & 1/2 \end{matrix} \right\} \left\{ \begin{matrix} j & j' & k \\ J' & J & J_i \end{matrix} \right\} \left\{ \begin{matrix} J & J' & k \\ J_f & J_f & L \end{matrix} \right\}$$

$$\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J} \rangle^* \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{recombination})} \parallel (\alpha_i \mathbb{J}_i, \varepsilon \kappa') \mathbb{J}' \rangle .$$

Here, the summation over  $\mathbb{M}$  refers to the multipoles of the radiation field and  $(\mathbb{J} \kappa)$ ,  $(\mathbb{J} \kappa)$  to summations over all photorecombination channels, i.e. all the many-electron continua  $|(\alpha_i \mathbb{J}_i, \varepsilon \kappa) \mathbb{J}\rangle$  of the initial ion.

- **Reduced statistical tensors:** Instead of using the statistical tensors  $\rho_{k0}(\alpha_f \mathbb{J}_f)$  of the recombined ion, it is often more convenient to describe the sublevel population of the residual ions in terms of the (so-called) *reduced* tensors:

$$\mathcal{A}_{k0}(\alpha_f \mathbb{J}_f) = \frac{\rho_{k0}(\alpha_f \mathbb{J}_f)}{\rho_{00}(\alpha_f \mathbb{J}_f)},$$

which are directly related to the population cross sections  $\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f M_f)$  for the electron capture into an ionic sublevel  $| \alpha_f \mathbb{J}_f M_f \rangle$ .

### Photorecombination plasma rate coefficient:

- **Plasma rate coefficient for radiative recombination:** The radiative recombination (plasma) rate coefficient is obtained from the convolution of the radiative recombination cross section for an ion  $\sigma^{(\text{RR})}(E)$  into the initially level  $(\alpha_i \mathbb{J}_i)$  for the isotropic Maxwellian distribution

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function of the electrons in the plasma

$$\alpha^{(RR)}(T_e; \alpha_i \mathbb{J}_i) = \frac{4}{\sqrt{2\pi m T_e}^{3/2}} \int_0^\infty dE E \left[ \sum_{\alpha_f \mathbb{J}_f} \sigma^{\text{plasma}}(E; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \right] \left( -\frac{E}{T_e} \right).$$

### Photorecombination of bare ions:

➤ **Radiative recombination of bare ions:** Four entities are often used to characterize the RR of bare ions (Kotelnikov and Milstein, 2019):

$$\sigma^{(RR)}(\varepsilon; \text{bare} \rightarrow \sum_n n) = \sum_n \sigma^{(RR)}(\text{bare} \rightarrow n) \quad \text{total cross section}$$

$$\kappa^{(RR)}(\varepsilon; \text{bare} \rightarrow \sum_n n) = \sum_n \hbar \omega_n \sigma^{(RR)}(\text{bare} \rightarrow n) \quad \text{total effective radiation}$$

$$\alpha^{(RR)}(\text{bare}) = \int d\varepsilon \sigma^{(RR)}(\varepsilon; \text{bare} \rightarrow \sum_n n) f_e(\varepsilon) \quad \text{RR plasma recombination coefficient}$$

$$q^{(RR)}(\text{bare}) = \int d\varepsilon \kappa^{(RR)}(\varepsilon; \text{bare} \rightarrow n) f_e(\varepsilon) \quad \text{RR plasma emission coefficient}$$

where  $\omega_n = \varepsilon + Z^2/(2n^2)$  [in a.u.] is the photon frequency (energy),  $Z$  the nuclear charge and  $f_e(\varepsilon)$  the electron energy distribution in the plasma.

➤ **Radiative recombination *versus* photoionization:** These processes are *time-reversed* to each other and, hence, closely related. For the radiative recombination of an ions with an electron with energy  $\varepsilon$ , the cross sections obey the **principle of detailed balance**

$$\sigma^{(RR)}(\varepsilon; \text{bare} \rightarrow n) = \frac{\omega_n^2}{c^2} \sigma^{(\text{photoionization})}(\varepsilon; n \rightarrow \text{bare}), \quad \omega_n = \varepsilon + Z^2/(2n^2) \quad [a.u.]$$

➤ **Photoionization cross section for hydrogen-like ions in the ground level:** The photoionization cross section of hydrogen-like ions in the 1s ground level can be expressed quite readily for photon energies near to the **threshold**  $\omega \approx Z^2/n^2$  and for large energies  $\omega \gg Z^2/n^2$  as



(Kotelnikov and Milstein, 2019; here,  $e$  is the Euler constant)

$$\sigma^{(\text{PI})}(\omega \approx Z^2/n^2; 1s \rightarrow \varepsilon) = \frac{2^9 \pi^2 \alpha a_o^2}{3 e^4 Z^2}, \quad \sigma^{(\text{PI})}(\omega \gg Z^2/n^2; 1s \rightarrow \varepsilon) = \frac{2^8 \pi \alpha}{3 Z^2 a_o^2} \left( \frac{Z^2}{2\omega} \right)^{7/2}$$

$$\sigma^{(\text{RR})}(\varepsilon \approx 0 \ll Z^2/2; \text{bare} \rightarrow 1s) = \frac{2^8 \pi^2 \alpha^3 a_o^2}{3 e^4} \frac{Z^2}{2\varepsilon}, \quad \sigma^{(\text{RR})}(\varepsilon \gg Z^2/2; \text{bare} \rightarrow 1s) \quad [a_o^2]$$

- **Stobbe formula for the radiative recombination cross section:** For the radiative capture of an electron with the scaled (hydrogenic) energy  $\varepsilon_o = \frac{2\varepsilon}{Z^2}$ , the (non-relativistic) recombination cross section for the capture into the subshell ( $n\ell$ ) can be expressed in terms of the this energy  $\varepsilon_o$  and the (absorption,  $Z = 1$ ) oscillator strengths  $f(n\ell \rightarrow \varepsilon_o)$  of neutral hydrogen:

$$\begin{aligned} \sigma^{(\text{RR, Stobbe})}(\varepsilon_o; n\ell) &= 2\pi^2 \alpha^3 a_o^2 (2\ell + 1) \frac{1}{\varepsilon_o} \left( \varepsilon_o + \frac{1}{n^2} \right)^2 f(n\ell \rightarrow \varepsilon_o) \\ &= 9.165 \cdot 10^{-21} \text{ cm}^2 \frac{1}{\varepsilon_o (\varepsilon_o + 1)^2} \frac{\exp(-\frac{4 \arctan \sqrt{\varepsilon_o}}{\sqrt{\varepsilon_o}})}{1 - e^{-2\pi/\sqrt{\varepsilon_o}}}, \end{aligned} \quad \text{for RR into the 1s shell}$$

$$f(n\ell \rightarrow \varepsilon_o) = \frac{1}{3(2\ell + 1)} \left( \varepsilon_o + \frac{1}{n^2} \right) \left[ (2\ell + 1) |\langle \varepsilon_o, \ell + 1 | r | n\ell \rangle|^2 + \ell |\langle \varepsilon_o, \ell - 1 | r | n\ell \rangle|^2 \right].$$

The scaled (hydrogenic) energy  $\varepsilon_o$  can be seen also as generalization of the (inverse of the) principal quantum number for the free electron in the continuum.

- **RR cross section for the electron capture into the ground-level of initially bare ions:** The (non-relativistic) exact cross section for the capture into the 1s ground level of initially bare ions was derived by Stobbe in terms of the (so-called) **Sommerfeld parameter**  $\eta = Z/v = \sqrt{Z^2/(2\varepsilon)}$  with the (1s) velocity in [a.u.]

$$\sigma^{(\text{RR})}(\eta; \text{bare} \rightarrow 1s) = \frac{2^8 \pi^2 \alpha^3 a_o^2}{3} \frac{\eta^6 e^{-4\eta \arctan(1/\eta)}}{(1 - e^{-2\pi\eta}) (\eta^2 + 1)^2}.$$

- **RR cross section for the electron capture into the shell  $n$  of initially bare ions:** For the radiative recombination of initially bare ions into

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any level of the shell  $n$ , both a semi-classical as well as exact formula is known (cf. Kotelnikov and Milstein, 2019)

$$\begin{aligned}\sigma^{(\text{RR, Kramers})}(\eta; \text{bare} \rightarrow n) &= \frac{32 \pi \alpha^3 a_o^2}{3 \sqrt{3}} \frac{\eta^4}{n (\eta^2 + n^2)} \\ \sigma^{(\text{RR, Katkov \& Strakhovenko})}(\eta; \text{bare} \rightarrow n) &= \frac{2^8 \pi^2 \alpha^3 a_o^2}{3} \frac{\eta^6 e^{-4 \eta \arctan(1/\eta)}}{(1 - e^{-2\pi \eta}) (\eta^2 + n^2)^2} S_n(\eta) \\ S_1 &= 1, \quad S_2 = 2 + \frac{3}{x_2} + \frac{1}{x_2^2}, \quad S_3 = 3 + \frac{14}{x_3} + \frac{19}{x_3^2} + \frac{8}{x_3^3} + \frac{1}{x_3^4}, \\ S_4 &= 4 + \frac{38}{x_4} + \frac{346}{3 x_4^2} + \frac{409}{3 x_4^3} + \frac{622}{9 x_4^4} + \frac{43}{9 x_4^5} + \frac{1}{x_4^6}, \quad x_n = \frac{n^2 + \eta^2}{4 \eta^2}.\end{aligned}$$

From this expression, the two (approximate) formulas above from Stobbe and Kramers can be derived.

- **Total RR cross section for the electron capture into any shell  $n$  of initially bare ions:** The approximate expressions for the RR into a given shell  $n$  of initially bare ions give rise also to different total RR cross section for the electron capture into any shell  $n$

$$\begin{aligned}\sigma^{(\text{RR, Kramers})}(\eta; \text{bare} \rightarrow \sum_n n) &= \frac{32 \pi \alpha^3 a_o^2}{3 \sqrt{3}} \sum_{n=1}^{\infty} \frac{\eta^4}{n (n^2 + \eta^2)} \approx \frac{16 \pi \alpha^3 a_o^2}{3 \sqrt{3}} \eta^2 \ln(1 + \eta^2), \quad \eta \gg 1 \\ \sigma^{(\text{RR, Bell \& Bell})}(\eta; \text{bare} \rightarrow \sum_n n) &= \frac{32 \pi \alpha^3 a_o^2}{3 \sqrt{3}} [\ln(\eta) + 0.1402 + 0.5250 \eta^{-2/3}], \quad \eta \gg 1.\end{aligned}$$

The latter fit formula by Bell and Bell (1981) is said to be accurate within 3.3 % for  $\eta \geq 10$  and even better than 1 % for  $\eta \geq 50$ .

- **Partial and total RR cross section for relativistic electrons:** For relativistic electrons, the partial and total RR cross section decreases very rapidly with the electron energy. The main contribution to the total cross section is then given by capture into the ground level.
- **Bound-bound and bound-free matrix elements:** For  $Z = 1$ , the matrix elements  $\langle n' \ell' | r | n \ell \rangle$  and  $\langle \varepsilon_o \ell' | r | n \ell \rangle$  for atomic hydrogen can

be generated recursively in terms of the quantum numbers and scaled hydrogenic energy by (Schipper 2020):

$$A(n\ell) = \frac{\sqrt{(n+\ell)(n-\ell)}}{n\ell}, \quad B(k\ell) = \frac{\sqrt{k^2 + \ell^2}}{k\ell}, \quad \nu = \frac{1}{\sqrt{\varepsilon_o}} = Z \frac{\text{Hartree}}{2\varepsilon}$$

$$\langle n'\ell - 1 | r | n\ell \rangle = \frac{(4n'n)^{n'+2}}{4} \frac{(n-n')^{n-n'-2}}{(n+n')^{n+n'-2}} \left[ \frac{(n+n')!}{(n-n'-1)!(2n'-1)!} \right]^{1/2}$$

$$2\ell A(n', \ell) \langle n'\ell - 1 | r | n\ell \rangle = (2\ell + 1) A(n, \ell + 1) \langle n'\ell | r | n\ell + 1 \rangle + A(n', \ell + 1) \langle n'\ell + 1 | r | n\ell \rangle$$

$$2\ell A(n, \ell) \langle n'\ell | r | n\ell \rangle = A(n, \ell + 1) \langle n'\ell | r | n\ell + 1 \rangle + (2\ell + 1) A(n', \ell + 1) \langle n'\ell + 1 | r | n\ell \rangle$$

$$\langle \varepsilon_o \ell | r | n\ell - 1 \rangle = \frac{\nu^2}{4\sqrt{2}} \left( \frac{4n\nu}{\nu^2 + n^2} \right)^{n+2} \left[ \frac{\prod_{s=1}^n (s^2 + \nu^2)}{(2n-1)!} \right]^{1/2} \frac{\exp(-2\nu \arctan(n/\nu))}{\sqrt{1 - e^{-2\pi\nu}}}$$

$$2\ell A(n, \ell) \langle \varepsilon_o \ell | r | n\ell - 1 \rangle = (2\ell + 1) B(\nu, \ell + 1) \langle \varepsilon_o \ell | r | n\ell \rangle + A(n, \ell + 1) \langle \varepsilon_o \ell | r | n\ell + 1 \rangle$$

$$2\ell B(k, \ell) \langle \varepsilon_o, \ell - 1 | r | n\ell \rangle = B(\nu, \ell + 1) \langle \varepsilon_o, \ell + 1 | r | n\ell \rangle + (2\ell + 1) A(n, \ell + 1) \langle \varepsilon_o \ell | r | n\ell + 1 \rangle .$$

- **Application of radiative recombination of bare and highly-charged ions:** Particle accelerators, plasma physics, astrophysics and antimatter production. In storage rings, the electron cooling of protons and highly-charged ions also lead to the recombination of ions and to their loss from the beam. In general, however, the radiative recombination competes with other free-free and free-bound (transition) processes, such as bremsstrahlung, dielectronic recombination, electron-impact excitation and ionization processes, and others.

### Photorecombination of ions with twisted electrons:

- **Angular distribution and the linear polarization of photons:** Expressions have been derived for the angular distribution and the linear polarization of the emitted photons following the capture of twisted electrons into the ground state of (bare) ions. These expressions showed that the angular and polarization distributions are sensitive to both, the transverse momentum and the topological charge of the incident electron beam.

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- **Photorecombination with twisted electrons:** For twisted electrons with well-defined values of the linear momentum  $p_z$  and with topological charge  $m = 0, \pm 1, \pm 2$ , i.e. with well-defined projection of the OAM upon the propagation direction, the initial-state wave function is given by:

$$\psi^{(\text{tw})}(\mathbf{r}; i) \equiv \psi_{\mathcal{Z}m p_z}^{(\text{tw})}(\mathbf{r}) = \int \frac{d^2 \mathbf{p}_\perp}{(2\pi)^2} a_{\mathcal{Z}m}(\mathbf{p}_\perp) e^{i(\mathbf{p}_\perp \cdot \mathbf{r}_\perp + p_z z)},$$

where  $a_{\mathcal{Z}m}(\mathbf{p}_\perp)$  refer to the Fourier coefficients that include also the transverse momentum profile of the beam.

- Final bound-state wave functions:

$$\psi_f(\mathbf{r} - \mathbf{b}_\perp; f) = e^{-i\mathbf{p} \cdot \mathbf{b}_\perp} \psi(\mathbf{r}; f).$$

### 8.1.e. Auger and autoionization processes (AutoIonization)

#### Process, notation & application:

- **Auger emission (autoionization)** of an atom or ion:  $A^{q+*} \longrightarrow A^{(q+1)+(*)} + e_a^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{|\varepsilon \kappa\rangle\}$ .
- Using JAC: Perform an `Atomic.Computation(..., process=Jac.Auger, processSettings=AutoIonization.Settings(...), ...)` or call directly functions from the module `Auger`.
- In JAC, the particular kind of the Auger operator  $\mathbb{V}^{(\text{Auger})}$  can be specified by selecting `AutoIonization.Settings.operator = ("Coulomb", "Breit", "Coulomb+Breit", ...)`.
- In JAC, the Auger rates and (Auger) lifetimes are tabulated by default for all selected (Auger) transitions.
- In JAC, the intrinsic anisotropy parameters are calculated and tabulated if the flag `calcAnisotropy = true` is set in `AutoIonization.Settings`.

- Using JAC: Perform an `Atomic.Computation(.., process=Jac.AutoIonizationInPlasma, processSettings=PlasmaShift.AutoIonizationSettings(..), ..)` or call directly functions from the modules `AutoIonization` and `PlasmaShift`. Until the present, however, only a Debye-Hückel plasma model is supported and where the Debye-Hückel screening of the electron-nucleus and electron-electron interaction is incorporated only in first-order perturbation theory within the CI matrix.
- In JAC, we generally support the computation of nonradiative (Auger) rates, relative Auger intensities and intrinsic angular anisotropy parameters. To this end, first the (reduced) Auger amplitudes are calculated for all selected pairs of initial and final levels and, later, these amplitudes are combined into Auger rates, intrinsic anisotropy or spin-polarization parameters.
- **Control features for autoionization computations:** Since the number of possible Auger transitions often increases very rapidly, especially if several inner-shell holes and/or valence electrons occur, JAC provides several additional control features for reducing the complexity: Apart from (1) the selection of individual Auger lines, these features include (2) the definition of an **energy threshold (i.e. a minimum energy of the free electron)** as well as (3) a **maximum angular momentum** (negative  $\kappa$ -symmetry quantum number) for the partial waves of the outgoing electron. A proper use of (3) mainly affects the number of the scattering states, that are taken into account, and can be chosen independently of the formally allowed scattering states of the residual ion.
- **Control features for autoionization computations:** The features (2) and (3) are in line with the **common experience that partial waves with high angular momenta do either not contribute at all** (i.e. have *zero* Auger amplitudes in most computational models) **or are simply negligible**. In addition, JAC supports the use of an **overall energy shift of all Auger transition energies** which can be specified interactively.
- **Energetic condition:** An autoionization of an (inner-shell) excited bound state can occur (only) if the **initial level is energetically embedded into the continuum of the next higher charge state**.
- **Inner-atomic interactions:** Formally, an electron emission from such an *embedded* resonance (level) arise due to its coupling to one or several scattering states of the residual ion; all these states are degenerate with the initial state but include one (or more) *free* electrons. Often, the number of the possible scattering states  $|(\alpha_f \mathbb{J}_f, \varepsilon \kappa) \alpha_t \mathbb{J}_t\rangle$  of a system increases rapidly since the free electrons may couple in quite different ways to the bound-state electrons from the final (Auger) ions.
- **Coulomb versus Breit interaction:** While the Coulomb repulsion in the Auger amplitude below is typically sufficient in order to describe the autoionization of light and medium elements, the Breit interaction has been found important for electron emission and capture processes of highly-charged ions.
- **Simplification of the transition operator  $\mathbb{H} - E$ :** The **restriction to the electron-electron interaction in the computation (evaluation) of the Auger amplitudes is quite standard in all presently available Auger codes**, even if the orbital functions of the resonant scattering level  $(\alpha_t \mathbb{J}_t)$  and the final-ionic state  $(\alpha_f \mathbb{J}_f)$  are not quite orthogonal to each other.

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- **Interchannel interaction:** Apart from a very few case studies on the  $K - LL$  and  $K - LM$  spectra of noble gases (Tulkki *et al.*, 1989; Fritzsche *et al.*, 1992), more often than not, **both the interchannel interactions as well as the nonorthogonality were neglected in the evaluation of the many-electron Auger amplitudes.**
- **Reaction plane of the Auger emission:** For a prior photo-absorption or particle impact, this reaction plane is usually defined by the directions of the incident photon (particle) beam and the emitted Auger electron.

### Autoionization amplitudes:

- **Autoionization amplitude:** Following Åberg and Howat (1982), the **Auger transition amplitude for the autoionization of an excited bound state**  $|\alpha_i \mathbb{J}_i M_i\rangle$  into the final scattering state  $|\alpha_t \mathbb{J}_t M_t\rangle$ , built from an ion in the final level  $(\alpha_f \mathbb{J}_f)$ , can be expressed most generally as

$$\begin{aligned} \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t M_t | \mathbb{V}^{(\text{Auger})} | \alpha_i \mathbb{J}_i M_i \rangle &= \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{V}^{(\text{Auger})} | \alpha_i \mathbb{J}_i \rangle \delta_{J_i, J_t} \delta_{M_i, M_t} \delta_{P_i, P_t} \\ &= \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{H} - E | \alpha_i \mathbb{J}_i \rangle \delta_{J_i, J_t} \delta_{M_i, M_t} \delta_{P_i, P_t}. \end{aligned}$$

**This amplitude is independent of the projection  $M_i$  of the initial state** owing to the rotational symmetry of free atoms and the scalar character of the Hamiltonian and/or interelectronic interactions.

- **Final scattering states**  $|\alpha_t \mathbb{J}_t M_t\rangle \equiv |(\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t M_t\rangle$ : In an autoionization process, these final scattering states arise from the coupling of the final state  $|\alpha_f \mathbb{J}_f M_f\rangle$  of the ion with well-defined symmetry with the partial-wave  $|\varepsilon \kappa m_j\rangle$  of the outgoing electron with energy  $\varepsilon$  and (one-electron) angular momentum  $\kappa = \kappa(j, l)$  as well as magnetic projection  $m_j$ .
- **Simplification of the transition operator  $\mathbb{H} - E$ :** In JAC, as in most other tools for computing autoionization processes, a **common set of orthonormal orbitals is often supposed** for the representation of the initial  $(\alpha_i \mathbb{J}_i)$  and final (ionic) bound levels  $(\alpha_f \mathbb{J}_f)$  **in the evaluation of the autoionization amplitudes.** In this case, the Auger transition operator  $\mathbb{V}^{(\text{Auger})} \equiv \mathbb{H} - E \approx \mathbb{V}^{(\text{e-e})}$  simplifies to the electron-electron interaction operator, while the (reduced) Auger amplitude becomes

$$\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{V}^{(\text{Auger})} | \alpha_i \mathbb{J}_i \rangle \simeq i^\ell \exp(-i \Delta_\kappa) \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t | \mathbb{V}^{(\text{e-e})} | \alpha_i \mathbb{J}_i \rangle \delta_{J_i, J_t} \delta_{M_i, M_t} \delta_{P_i, P_t}.$$

Here, the autoionization amplitudes also accounts for the proper phase (or asymptotic boundary condition) for the *incoming* free electron, if the autoionization is considered as scattering process.

- Within the framework of the Dirac-Coulomb-Breit Hamiltonian, the **interelectronic interaction is the sum of the Coulomb repulsion and Breit interaction**,  $\mathbb{V}^{(e-e)} = \mathbb{V}^{(\text{Coulomb})} + \mathbb{V}^{(\text{Breit})} \simeq \mathbb{V}^{(\text{Coulomb})}$ , although it is often approximated by just the Coulomb part.
- **Phase of the autoionization amplitudes:** In the scattering approach to the Auger emission (Åberg and Howat, 1982), the free electron appears as an incoming wave whose phase directly contributes to the overall phase of the Auger amplitude:  $e^{i\ell\ldots} \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle$ .
- **Evaluation of the autoionization amplitudes:** Until the present, the standard Racah algebra techniques (Grant, 1988) are always applied in order to evaluate the many-electron Auger amplitudes, independent of how the radial orbitals of the initial and final bound states were generated before.

### Auger rates:

- **Auger rates:** If the (continuum) interaction between the different autoionization channels is neglected, the Auger rates are simply given by

$$A(i \rightarrow f) = 2\pi \sum_{\kappa} \left| \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_i \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle \right|^2,$$

where the summation runs over all partial waves  $|\varepsilon \kappa\rangle$  that fulfill the triangular rule  $\delta(J_f, j, J_i)$  and where the transition operator  $\mathbb{V}^{(\text{Auger})}$  still need to be specified due to the (computational) framework and additional approximations that are made in practice.

- In JAC, the Auger rates and (Auger) lifetimes are tabulated by default for all selected (Auger) transitions.

### Angular distribution of Auger electrons:

- **Angular distribution of emitted electrons:** If the (inner-shell) excited ion in level  $(\alpha_i \mathbb{J}_i)$  is fully characterized by the reduced statistical tensors  $\mathcal{A}_{kq}(\alpha_i \mathbb{J}_i)$  and if only Auger electrons are detected, the angular distribution of the emitted electrons from the Auger transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  can be expressed in the general form (Balashov *et al.* 2000, equation 3.10)

$$W(\vartheta, \varphi; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \frac{A(i \rightarrow f)}{4\pi} \left[ 1 + \sum_{k=2,4,\dots}^{k_{\max}} \sqrt{\frac{4\pi}{2k+1}} \alpha_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \sum_{q=-k}^k \mathcal{A}_{kq}(\alpha_i \mathbb{J}_i) Y_{kq}(\vartheta, \varphi) \right],$$

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and where  $\alpha_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)$  designates the (so-called) **intrinsic anisotropy parameters** of the electron emission

$$\begin{aligned} \alpha_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = & \left[ \sum_{\kappa} \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_i \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle \right]^{-1} (-1)^{J_i + J_f + k - 1/2} \sqrt{2J_i + 1} \sum_{\kappa \kappa'} [\ell, \ell', j, j']^{1/2} \langle \ell 0, \ell' 0 \mid k 0 \rangle \\ & \times \left\{ \begin{matrix} J_i & j & J_f \\ j' & J_i & k \end{matrix} \right\} \left\{ \begin{matrix} \ell & j & 1/2 \\ j' & \ell' & k \end{matrix} \right\} \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_i \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa') \mathbb{J}_i \parallel \mathbb{V}^{(\text{Auger})} \parallel \alpha_i \mathbb{J}_i \rangle^* . \end{aligned}$$

- **Anisotropy parameters  $\alpha_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)$ :** Here, the factor  $A(i \rightarrow f)$  is the total probability of the Auger transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$ , integrated over all ejection angles. The **anisotropy parameters  $\alpha_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)$**  contain all information about the dynamics of the **decay**, while the tensors  $\mathcal{A}_{kq}(\alpha_i \mathbb{J}_i)$  just describe the polarization properties of the atom in its initial level.
- **Angular distribution of emitted Auger electrons averaged over several final levels:** If the final levels cannot be resolved by the detector, the total angular distribution of the Auger electrons is obtained by the incoherent sum of the angular distributions for all the unresolved final levels:

$$W(\vartheta, \varphi; \alpha_i \mathbb{J}_i \rightarrow \{\alpha_f \mathbb{J}_f\}) = \sum_{\alpha_f \mathbb{J}_f} W(\vartheta, \varphi; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) .$$

In this case, the angular distribution can be expressed also by means of an **average anisotropy parameter** within the electric-dipole approximation. Here, the electric-dipole approximation ensures the factorization of the anisotropy parameters  $\beta_2$ ,

$$\bar{\beta}_2 = \frac{\sum_{\alpha_f \mathbb{J}_f} \beta_2(i \rightarrow f) A(i \rightarrow f)}{\sum_{\alpha_f \mathbb{J}_f} A(i \rightarrow f)}, \quad \beta_2(i \rightarrow f) = \alpha_2(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) A_{20}(\alpha_i \mathbb{J}_i).$$

### Spin polarization of Auger electrons:

- **Polarization vector  $\mathbf{P}$  of Auger electrons:** The spin polarization of Auger electrons is usually described by an polarization vector  $\mathbf{P}$  whose three components can be expressed in terms of the statistical tensors  $\rho_{kq}(\alpha_i \mathbb{J}_i)$  of the initial level as well as the intrinsic anisotropy parameters of the considered Auger transition.



- **Coordinates used for characterizing the spin polarization:** Two coordinate systems,  $S(XYZ)$  and  $S'(X'Y'Z')$  are often employed in order to characterize the spin polarization of Auger electrons; cf. the figure below and Kabachnik *et al.* (2007).

### Two-electron single Auger emission (TESA):

- **Observation of TESA lines:** Non-resonant three-electron Auger transitions have been suggested several decades ago, although clear evidence for such TESA transition were found in Ar only with very low intensity relative to the normal Auger lines.
- The observed TESA transitions usually start with the creation of a double vacancy, i.e. with two vacancies in an inner shell, and which are filled simultaneously by two outer-shell electrons, while the released energy is passed to a third emitted electron.
- Such inner-shell double vacancies are normally at energies above the minimum fourfold ionization energy and can easily be filled also by two separate successive (two-electron) Auger transitions involving four electrons in total.

### 8.1.f. Dielectronic recombination (Dielectronic)

#### Process, notation & application:

- **Dielectronic recombination (DR)** of an atom or ion:  $A^{q+} + e^- \longrightarrow A^{(q-1)+*} \longrightarrow A^{(q-1)+(*)} + \hbar\omega$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon \kappa\rangle \longrightarrow |\alpha_d \mathbb{J}_d\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{\hbar\omega(\mathbb{M})\}$  or  $|\alpha_i \mathbb{J}_i\rangle + |\mathbf{p}_i m_i\rangle \longrightarrow |\alpha_d \mathbb{J}_d\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \{\hbar\omega(\mathbb{M})\}$ .
- Using JAC: Perform an `Atomic.Computation(.., process=JAC.Dierec, processSettings=Dielectronic.Settings(..), ..)` or call directly functions from the module `Dielectronic`.
- In JAC, both the individual  $S(i \rightarrow d \rightarrow f)$  and total resonance strengths  $S(i \rightarrow d)$  are calculated and tabulated by default for all selected pathways.
- In JAC, the capture (Auger) and radiative amplitudes and rates are always computed by the corresponding modules `Auger` and `PhotoEmission`.
- **Resonance strength:** As seen from the (total) below, the **experimentally observed strength of the dielectronic recombination for a given resonance level** ( $\alpha_d \mathbb{J}_d$ ) **is proportional to the capture rate**  $A_a(i \rightarrow d)$  **as well as the (total) radiative rate.**
- **Two-step process:** In most computations, the **dielectronic recombination of a  $N$ -electron target ion in the (initial) level** ( $\alpha_i \mathbb{J}_i$ ) **is typically handled as a two-step process**, in which first an electron is captured resonantly from the continuum into a  $[(N+1)\text{-electron}]$  resonance level ( $\alpha_d \mathbb{J}_d$ ), embedded into the continuum of the initial ion and with often two or more excited electrons. In a second step, this excited level ( $\alpha_d \mathbb{J}_d$ ) then either decays radiatively by the emission of photons to some (final) level ( $\alpha_f \mathbb{J}_f$ ) below of the ionization threshold of the ion. Most likely, however, the excited ion returns by autoionization back into the initial charge stage before the capture.
- **Two-step process:** If, in particular, the intermediate level ( $\alpha_d \mathbb{J}_d$ ) can autoionize only back to the ground state of the target ion, as for example for the  $3s$  valence excitation of a sodium-like target ion, the total Auger rate is then — up to statistical factors — equal to the capture rate.
- **Demands of DR computations:** Apart from the computation of accurate Auger rates, **helpful calculations of DR spectra critically depends on the simple control (and handling) of all the — radiative and non-radiative — decay branches of the resonantly excited ion.** In JAC, these branches are treated equally within the `Dielectronic` module.
- **Scattering states**  $|(\alpha_i \mathbb{J}_i, \varepsilon \kappa), \mathbb{J}_d M_d\rangle$ : In practice, the number of the possible scattering states  $|(\alpha_i \mathbb{J}_i, \varepsilon \kappa), \mathbb{J}_d M_d\rangle$  of the recombined ion often increases very rapidly since the free electrons may couple in many different ways to the bound-state electrons of the initial ion. This increase is analogue and follows from the autoionization (capture) process that is part of the dielectronic recombination.

- **Enhanced DR cross sections in external electric fields:** The DR cross sections for the capture into intermediate, high-energy Rydberg resonances are often enhanced owing to the  $\ell$ -mixing of the associated Rydberg levels. This behaviour has been verified both, experimentally and theoretically. However, a reduced influence of this mixing is expected for (rather) high- $Z$  ions because of the strong scaling of the radiative rates with  $Z$  and because less  $\ell$ -states are (then) take part in the recombination.
- **DR cross section for an isolated resonance:** For a narrow (non-overlapping) DR resonances, the DR cross section due to the electron capture into the intermediate resonance level  $d$  with energy  $E_d$  at the (center-of-mass) electron-ion energy  $E$  can be factorized in terms of the resonance strength  $S(i \rightarrow d)$  and a Lorentzian line-shape function  $L(E; d)$  with  $\int dE L(E; d) = 1$  and as

$$\begin{aligned}\sigma^{(\text{DR})}(E \simeq E_d; d) &= S(E_d; i \rightarrow d) L(E; d) \\ &= 4.95 \times 10^{-30} [\text{cm}^2 \text{ eV}^2 \text{ s}] \frac{g_d}{2 g_i E_d} \frac{A^{(\text{a})}(d \rightarrow i) \sum_f A^{(\text{r})}(d \rightarrow f)}{\sum_{i'} A^{(\text{a})}(d \rightarrow i') + \sum_{f'} A^{(\text{r})}(d \rightarrow f')} \cdot L(E; d).\end{aligned}$$

Here the summations over  $f'$  refer to all final states of the recombined ion,  $f$  to all final states below the first ionization limit and  $i'$  to all states of the initial ion, into which the intermediate ion can (re-) autoionize.

- **Excitation into high-lying (Rydberg) orbitals:** The need for an *efficient* handling of all (excited) ionic levels arises especially in all those DR studies, in which (single-electron) excitations with quite large principal quantum numbers occur below of the DR resonance. For such highly-excited resonance levels ( $\alpha_d \mathbb{J}_d$ ), the radiative transition probabilities need to be computed to all the lower-lying levels.
- **Stark mixing of Rydberg states in DR experiments:** In weak external electric fields, a Stark mixing occurs mainly *within* the  $(n\ell m)$  Rydberg manifold (and where  $m$  even remains a good quantum number). While the zero-field autoionization rates decrease very rapidly with the angular momentum  $\ell$  of the Rydberg electrons, such a mixing typically results in *effectively* lower autoionization rates for low- $\ell$ , and in higher autoionization rates for high- $\ell$  states, and compared to the field-free situation. The net effect is an increase of the number of states that contribute to the DR and, hence, an increase of the DR cross section (Böhm *et al.*, 2001).
- **Unified treatment:** Since the **radiative recombination often strongly increases close to the threshold**, the isolated-resonance approach is formally no longer valid in this case and should be better replaced by some unified treatment of the radiative and non-radiative decay pathes for the capture of low-energy electrons.
- **Electron-velocity corrected DR cross sections:** While the Lorentzian shape of the DR resonances apply for a uniformly distributed center-of-mass energy (electron) energy, a small correction occurs if the electron velocities follow some anisotropic (Maxwellian) distribution. At storage rings, such an anisotropic distribution often leads to cross section corrections in the order of ...

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- **Dielectronic recombination of  $W^{20+}$  ions:** For the DR of  $W^{20+}$  ions, Schippers *et al.* (2011) found many (strong) resonances near to the threshold ( $\varepsilon < 1$  eV) which also affect the DR plasma rate coefficient at much higher temperatures. For plasma temperatures  $100 \leq T_e \leq 300$  eV, these rate coefficients were found larger by a factor of 4 than those used (until then) in the modeling of magnetic fusion plasmas.
- **Dielectronic recombination (DR)** is the dominant electron-ion recombination process in many astrophysical and laboratory plasmas. This process also determines the level populations and the ionization balance of most plasma, both in high- and low-temperature plasmas. Since DR can often take place via many intermediate (doubly-excited) resonances, it may affect the plasma dynamics and spectral analysis over a wide range of electron densities. Burgess (1964) was one of the first who recognized the importance of dielectronic recombination for many plasmas and who derived first approximate formulas for the DR plasma rate coefficient.

### Strength of dielectronic recombination (DR) resonances:

- **Partial resonance strength:** If the interference between the radiative and dielectronic (nonradiative) capture of the electron is negligible in the field of the target, the dielectronic recombination of an ion from an initial, via the isolated resonance state and into the final (ground) state of the (recombined) atom,  $i \rightarrow d = f$  can be characterized by a (so-called) **resonance strength**. This strength can be solely expressed in terms of the Auger and radiative rates of the resonant state  $d$  as well as its (half-) widths  $\Gamma_d$  by

$$S(i \rightarrow d \rightarrow f) \equiv \int_{-\infty}^{\infty} dE \sigma^{(DR)}(E) = \frac{2\pi^2 \hbar}{k_i^2} \frac{A_a(i \rightarrow d) A_r(d \rightarrow f)}{\Gamma_d}.$$

In this expression,  $k_i$  is wave number of the incident electron,  $A_a(i \rightarrow d)$  the rate for the electron capture (inverse Auger) from the initial into the excited resonance state, and  $A_r(d \rightarrow f)$  the rate for the radiative stabilization into the state  $f$ . **The resonance strength refers to the area under the energy-dependent differential DR cross sections and is typically given in units of:  $[S] = \text{cm}^2 \text{eV}$ .**

- **Partial resonance strength:** In the resonance strength above,  $A_a(i \rightarrow d)$  is the rate for the inverse Auger capture from the initial into the (doubly-excited) resonance level ( $\alpha_d \mathbb{J}_d$ ), while  $A_r(d \rightarrow f)$  refers to the rate for the radiative stabilization into the final level ( $\alpha_f \mathbb{J}_f$ ) of the  $N+1$ -electron ion.
- **Total width of the resonance level ( $\alpha_d \mathbb{J}_d$ ):** The total width  $\Gamma_d$  is determined by all possible decay channels of the resonance level ( $\alpha_d \mathbb{J}_d$ ) and is given in first-order perturbation theory by

$$\Gamma_d = \hbar \left( \sum_j A_a(d \rightarrow j) + \sum_{f'} A_r(d \rightarrow f') \right),$$

i.e. by taking the sum over all the individual Auger and radiative rates (widths) of the intermediate level  $(\alpha_d \mathbb{J}_d)$ .

- **Principle of kinetic balance:** The Auger and inverse capture rates  $A_a(i \rightarrow d) = g_i/g_d A_a(d \rightarrow i)$  are proportional to each other owing to the principle of kinetic balance, and where the  $g$ 's refer to the statistical factors of the initial and intermediate resonance levels.
- **Partial resonance strength:** The use of the partial resonance strength  $S(i \rightarrow d \rightarrow f)$  is appropriate, especially if the energy-dependent DR cross section has a Lorentzian profile

$$\sigma^{(\text{DR})}(E) = \frac{S}{\pi} \frac{\Gamma/2}{(E_r - E)^2 + \Gamma^2/4}$$

around the resonance energy  $E_r = E_d - E_i$  as well as a natural width less or comparable to the energy spread of the electron beam. In general, this condition is well fulfilled for most  $\Delta n \geq 1$  resonances (with an excitation of a bound electron from the shell  $n_i \rightarrow n_f$ , for which the total widths are small in most cases), but this condition can usually be utilized also for the  $\Delta n = 0$  lines if the shape of the resonances is not to be analyzed in detail.

- **Threshold behaviour:** Owing to the energy of the incident electron [cf. the factor  $1/k_i^2$  above], the resonance strength increases rapidly towards the threshold of the dielectronic recombination and makes the process rather sensitive to low kinetic energies of the incoming electrons.
- **Total resonance strength:** At storage rings, the radiative stabilization of the ions into some final level  $(\alpha_f \mathbb{J}_f)$  via the (intermediate) resonance level  $(\alpha_d \mathbb{J}_d)$  is often not observed explicitly and, hence, the radiative rate for the individual transition  $d \rightarrow f$  in the resonance strength above has to be replaced by the total radiative rate of the (doubly-excited) resonance level  $(\alpha_d \mathbb{J}_d)$ :

$$A_r(d \rightarrow f) \longrightarrow \sum_{f'} A_r(d \rightarrow f') \implies S(i \rightarrow d \rightarrow f) \longrightarrow S(i \rightarrow d) = \sum_{f'} S(i \rightarrow d \rightarrow f')$$

In JAC, both the partial  $S(i \rightarrow d \rightarrow f)$  and total resonance strengthes  $S(i \rightarrow d)$  are calculated and tabulated by default for all selected pathways.

### Branching fractions for dielectronic recombination ...:

- **Radiative branching fraction for dielectronic recombination:** For the dielectronic recombination of an ion via well-defined resonance states,  $\alpha_i \mathbb{J}_i \rightarrow \{\alpha_d \mathbb{J}_d\}$ , the radiative branching fraction of the resonance level  $\alpha_d \mathbb{J}_d$  is

$$b(\alpha_d \mathbb{J}_d) = \frac{\sum_{f < 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_f \mathbb{J}_f) + \sum_{a > 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_a \mathbb{J}_a) b(\alpha_a \mathbb{J}_a)}{\sum_{i' < d} A^a(\alpha_d \mathbb{J}_d \rightarrow \alpha_{i'} \mathbb{J}_{i'}) + \sum_{f < 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_f \mathbb{J}_f) + \sum_{a > 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_a \mathbb{J}_a)},$$

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where  $A^r$  and  $A^a$  refer to radiative and Auger rates, and where  $f < 0$  refers to all final  $N + 1$ -electron levels of the recombined ion (below of its autoionization threshold),  $a > 0$  to all  $N + 1$ -electron above the autoionization threshold, and  $i'$  to  $N$ -electron levels that are allowed for (re-) autoionization. Moreover, since the radiative rates are usually much smaller than the autoionization rates, these radiative branching fractions can be approximated by

$$b(\alpha_d \mathbb{J}_d) = \frac{\sum_{f < 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_f \mathbb{J}_f)}{\sum_{i' < d} A^a(\alpha_d \mathbb{J}_d \rightarrow \alpha_{i'} \mathbb{J}_{i'}) + \sum_{f < 0} A^r(\alpha_d \mathbb{J}_d \rightarrow \alpha_f \mathbb{J}_f)}.$$

This approximation has been found useful even if the decay to low-lying autoionizing levels is not negligible. Moreover, since the radiative rates scale with the third power of the transition energies,  $A^r \propto (E_d - E_f)^3$ , it is often enough to include only a subset of low-lying final levels ( $\alpha_f \mathbb{J}_f$ ) in order to estimate a reasonable DR strength.

- **Dielectronic rate coefficient:** Instead of individual DR strengths, the DR rate coefficient describes the averaged rate of dielectronic recombination processes in plasma. For a Maxwellian distribution of the electrons in the plasma, the DR rate coefficient is given by (Gu 2008)

$$\alpha^{(\text{DR})}(T; \alpha_i \mathbb{J}_i) = \frac{h^3}{(2\pi m k_B T)^{3/2}} \sum_{df} \frac{g_d}{2 g_f} A^a(\alpha_d \mathbb{J}_d \rightarrow \alpha_i \mathbb{J}_i) b(\alpha_d \mathbb{J}_d) \exp\left(-\frac{E_d - E_i}{k_B T}\right).$$

Here, the units are made explicit since the DR rate coefficient is not (only) an atomic property but also depend on the distribution of the free electrons and, hence, the temperature of the plasma.

### DR plasma rate coefficients:

- **Dielectronic plasma rate coefficient:** The DR plasma rate coefficient is temperature-dependent and describes, for a single resonant capture of an ion (per unit volume) in the initial state  $i$ , the rate to recombine due to dielectronic recombination

$$\alpha^{(\text{DR})}(T_e; i) = \frac{4}{T_e^{3/2} \sqrt{2\pi m}} \int_0^\infty dE E \sigma^{(\text{DR})}(E) \exp\left(-\frac{E}{T_e}\right) \left[\frac{\text{cm}^3}{\text{s}}\right].$$

- **Dielectronic plasma rate coefficient in isolated resonance approximation:** For a single resonance, the dielectronic recombination cross section is  $\sigma^{(\text{DR})}(E; i \rightarrow d) = S(i \rightarrow d) \delta(E - E_d)$ , and the plasma rate coefficient then becomes

$$\alpha^{(\text{DR})}(T_e; i \rightarrow d) = \frac{4}{T_e^{3/2} \sqrt{2\pi m}} E_d S(i \rightarrow d) \exp\left(-\frac{E_d}{T_e}\right).$$

- **DR plasma rate coefficients in isolated resonance approximation:** In this approximation, the DR plasma rate coefficient can be expressed as (cf. Chen, 1986)

$$\alpha^{(\text{DR})}(T_e; \alpha_i \mathbb{J}_i) = \frac{\pi}{(2J_i + 1)} \frac{1}{T_e^{3/2}} \sum_{d, f, \kappa} \frac{(2J_d + 1) A_a(\alpha_i \mathbb{J}_i, \varepsilon \kappa \rightarrow d) A_r(d \rightarrow f)}{\Gamma_r(d) + \Gamma_a(d)} \exp\left(\frac{\varepsilon}{T_e}\right).$$

Here, the free electrons were assumed to have a Maxwellian distribution.

- **Plasma DR rate coefficient:** Following Burgess formula for the temperature-dependent plasma DR rate coefficient of an ion in the initial level  $(\alpha_i \mathbb{J}_i)$ , a convenient formula is given by:

$$\alpha^{(\text{DR})}(T; \alpha_i \mathbb{J}_i) = \frac{1}{T^{3/2}} \sum_d c_d \exp\left(-\frac{E_d}{k_B T}\right),$$

where the coefficients  $c_d$  and  $E_d$  are directly related to the oscillator strengths and excitation energies of all DR resonances  $d$  that can be excited by the given electron cloud.

- **Partial DR rate coefficient for the capture into a single resonance level  $(\alpha_d \mathbb{J}_d)$  with energy  $E_d$ :** For a  $\delta$ -like DR resonance, the cross section and (partial) DR rate coefficient can be expressed as

$$\sigma^{(\text{DR})}(E; \alpha_i \mathbb{J}_i \rightarrow \alpha_d \mathbb{J}_d) = S(i \rightarrow d) \delta(E - E_d); \quad \alpha^{(\text{partial DR})}(T_e; \alpha_i \mathbb{J}_i \rightarrow \alpha_d \mathbb{J}_d) = \frac{4 S(i \rightarrow d) c E_d}{\sqrt{2\pi m} c T_e^{3/2}} \exp\left(-\frac{E_d}{T_e}\right).$$

Similarly, for an isolated DR resonance level  $(\alpha_d \mathbb{J}_d)$  with energy  $E_d$  and finite width  $\Gamma_d$ , the cross section and (partial) DR plasma rate coefficient can be expressed as

$$\sigma^{(\text{DR})}(E; \alpha_i \mathbb{J}_i \rightarrow \alpha_d \mathbb{J}_d) = \frac{S(i \rightarrow d) E_d}{E} \frac{\Gamma_d/2}{(E - E_d)^2 + \Gamma_d^2/4} \delta(E - E_d)$$

$$\alpha^{(\text{partial DR})}(T_e; \alpha_i \mathbb{J}_i \rightarrow \alpha_d \mathbb{J}_d) = \frac{4 S(i \rightarrow d)}{\sqrt{2\pi^3 m} T_e^{3/2}} \left[ y \int_{-x}^{\infty} dt \frac{e^{-t}}{t^2 + y^2} + \frac{y}{x} \int_{-x}^{\infty} dt \frac{t e^{-t}}{t^2 + y^2} \right], \quad x = \frac{E_d}{T_e}; \quad y = \frac{\Gamma_d}{2T}.$$

- **Burgess-Merts (BM) approximation:** While most studies on DR plasma rate coefficients refer to this BM approximation, it is hardly shown and used explicitly. The DR plasma rate coefficients in BM approximation remains therefore rather unspecific in the literature.

- **DR plasma rate coefficient for plasma modelling:** Several approximations and hierarchies have been used over the decades to account for the DR in plasma, from simple estimates to more sophisticated computations of these rate coefficients. However, the complexity of these computations may become enormous already for ions with still reasonable simple (ground-state) shell structures. Nowadays, it becomes for instance necessary to deal with the ions of medium and heavy elements. For these elements, the competition between autoionizing and radiative transitions can no longer be derived from just (a partitioning of) term-resolved dielectronic recombination data over the individual fine-structure levels.
- **Modern requirements on plasma rate coefficients:** (i) Recombination data are needed not only for ground-state levels but also for (initially) metastable levels of ions; (ii) Such recombination data are required also for groups of final states of the recombined ion since not all of these ions will decay successively to their ground level; (iii) the final states of the recombined ion must be treated individually, and sometime handled just for certain intermediate resonance levels; (iv) recombination data into metastable and still autoionizing levels of the recombined ion might be of interest as well (although not many such levels will exist in practice; Badnell *et al.*, 2003).
- **Dependencies of DR plasma rate coefficients:** Quite different dependencies can be drawn in order to display and analyze the DR plasma rate coefficients. For instance, (1) the contribution to  $\alpha^{(\text{DR})}(T_e; \alpha_i \mathbb{J}_i; n)$  can be drawn for an ion and *one* series of doubly-excited configurations  $2p^5 3snl$  as function of the valence shell  $n$ . Here, one can either keep the temperature  $T_e$  fixed and display curves for different  $\kappa$ , or one sums over  $\kappa$  and displays curves for different temperatures. (2) Curves for different temperatures can be displayed also for a group of selected intermediate levels/configurations to distinguish the contribution for the capture into different shells  $n$ . (3) Comparison of the total DR plasma rate coefficients for selected temperatures with each other and with the literature.
- **DR plasma rate coefficients & plasma density:** The rate coefficients are derived by using perturbation theory for the non-radiative capture of an electron and, hence, are suitable for the low-density plasmas. If multiplied with a given plasma density, these coefficients directly give the overall rate of individual ions to recombine due to DR. These coefficients are expected to change, if micro-fields of the plasma, external electric fields or some collisional mixing of the ionic levels occur. For high-density plasmas of low- $Z$  ions, moreover, further density effect need to be included into the calculation of the DR rate coefficient.
- **Dielectronic rates and ionization equilibrium:** Mazotta *et al.* (1998) performed calculations on the ionization equilibrium at different electron temperatures  $T_e$  for all elements from hydrogen to nickel. In particular, these authors provide data for the 435 atoms and ions, from H ( $Z = 1$ ) to Ni ( $Z = 28$ ), and for plasma temperatures in the range  $0.001 \leq T_e \leq 100$  keV. They also provide the ion fractions  $X_i$  of the different charge states. In these computations, Mazotta *et al.* (1998) applied parametrizations of the RR and DR plasma rate coefficients from the literature, together with a number of fit formulas. In particular, the DR plasma rate coefficients were fitted by a single formula and the fit parameters tabulated. However, since low-density, high-temperature astrophysical and laboratory plasmas are generally not in a local thermodynamic equilibrium, the individual collisional, photoionization and recombination processes need to be treated in a



*collisional-radiative* model in order to obtain the population of different ion charges.

### 8.1.g. Photoexcitation & fluorescence (PhotoExcitationFluores)

#### Process, notation & application:

- Photoexcitation of an atom or ion with subsequent fluorescence emission:  $A + \hbar\omega_i \longrightarrow A^* \longrightarrow A^{(*)} + \hbar\omega_f$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbf{k} \parallel \mathbf{e}_z, \lambda; \{\mathbb{M}\}) \longrightarrow |\alpha_e \mathbb{J}_e\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega_f(\Omega; \mathbf{P})$
- Using JAC: Perform an `Atomic.Computation(..., process=PhotoExcFluor, processSettings=PhotoExcitationFluores.Settings(...), ...)` or call directly functions from the module `PhotoExcitationFluores`.
- In JAC, the reduced density matrix of a fluorescence photon can be calculated at a selected solid angle  $\{\Omega = \vartheta, \varphi\}$  by calling the function `PhotoExcitationFluores.computePhotonDM`, and if the solid angle is specified explicitly.
- The photoexcitation and (subsequent) fluorescence emission from atoms and ions has been investigated in good detail in the literature for both, incident plane-wave radiation as well as for twisted Bessel and Laguerre-Gaussian beams.
- Since the **properties of the photo-excited atoms** can be calculated by the module `PhotoExcitation` and the **properties of the radiative emission** by the module `Radiative`, here we shall focus only upon properties that are specific to the **overall photoexcitation & fluorescence process, such as the angular distribution or density matrix of the fluorescence photons**.
- In JAC, the alignment parameters of the (intermediate) excited level  $\mathcal{A}_{kq}(\alpha_e \mathbb{J}_e)$  can be calculated and tabulated by the module `PhotoExcitation`, while the structure functions  $f_k(\alpha_e \mathbb{J}_e, \alpha_f \mathbb{J}_f)$  can be obtained by using the module `PhotoEmission`.
- In JAC, the statistical tensors  $\rho_{kq}(\alpha_e \mathbb{J}_e)$  of the intermediate excited level can be calculated and tabulated by the module `PhotoExcitation`. These tensors are also required for describing the photoexcitation & fluorescence process.

### Density matrix of the fluorescence photon $\hbar\omega_f(\Omega)$ :

- (Reduced) density matrix of the fluorescence photons for the photoemission from an aligned or oriented atom: For photons emitted under the angle  $\Omega = (\vartheta, \varphi)$  with regard to the propagation direction of the incident plane-wave radiation  $\mathbf{k} \parallel \mathbf{e}_z$ , the (reduced) density matrix can be readily expressed in terms of the statistical tensors of the excited level  $\rho_{kq}(\alpha_e \mathbb{J}_e)$  as

$$\begin{aligned} \langle \mathbf{k}_0 \lambda \mid \rho_{\omega_f} \mid \mathbf{k}_0 \lambda' \rangle &= 2\pi \sum_{k, qq'} \sum_{\mathbb{M} \mathbb{M}'} D_{-qq'}^k(\varphi, \vartheta, 0) \rho_{kq}(\alpha_e \mathbb{J}_e) i^{L'+p'-L-p} \lambda^p (\lambda')^{p'} \sqrt{2L+1} \sqrt{2L'+1} (-1)^{J_f+J_e+k+q+1} \\ &\times \langle L\lambda, L'(-\lambda') \mid k-q' \rangle \begin{Bmatrix} L & L' & k \\ J_e & J_e & J_f \end{Bmatrix} \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}, \text{emission})}(\omega_f) \parallel \alpha_e \mathbb{J}_e \rangle \langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}', \text{emission})}(\omega_f) \parallel \alpha_e \mathbb{J}_e \rangle^* \end{aligned}$$

- In JAC, the reduced density matrix of a fluorescence photon can be calculated at a selected solid angles  $\{\Omega = (\vartheta, \varphi)\}$ , see above.

### Angular distribution and Stokes parameters of the fluorescence photon $\hbar\omega_f(\Omega; \mathbf{P})$ :

- Angular distribution of the fluorescence light for the photoemission from a aligned or oriented atom: Most generally, the angular distribution can be obtained from the photon density matrix above by a summation over the two polarization states:

$$W(\vartheta, \varphi) = \sum_{\lambda} \langle \mathbf{k}_0 \lambda \mid \rho_{\omega_f} \mid \mathbf{k}_0 \lambda \rangle .$$

- Using the expressions from above, this angular distribution can be readily calculated for a set of angles  $\{\Omega_1 = (\vartheta_1, \varphi_1), \Omega_2, \dots\}$ , see above.
- Angular distribution of the fluorescence light: For initially unpolarized atoms and unpolarized photons in the photo-excitation process, in particular, the angular distribution is given by the same formulas as for the photoemission (alone), i.e. in terms of the alignment parameters  $\mathcal{A}_{k0}(\alpha_e \mathbb{J}_e)$  and the structure function of the (intermediate) excited level  $(\alpha_e \mathbb{J}_e)$  :

$$W(\vartheta) = \frac{W_o}{4\pi} \left( 1 + \sum_{k=2,4,\dots} f_k(\alpha_e \mathbb{J}_e, \alpha_f \mathbb{J}_f) \mathcal{A}_{k0}(\alpha_e \mathbb{J}_e) P_k(\cos\vartheta) \right) .$$

### 8.1.h. Photoexcitation & autoionization (PhotoExcitationAutoion)

#### Process, notation & application:

- Photoexcitation & autoionization of an atom or ion:  $A + \hbar\omega \longrightarrow A^* \longrightarrow A^{(*)} + e_a^-$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbf{k} || \mathbf{e}_z, \lambda; \{\mathbb{M}\}) \longrightarrow |\alpha_r \mathbb{J}_r\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon\kappa\rangle$
- Using JAC: Perform an `Atomic.Computation(..., process=PhotoExcAuto, processSettings=PhotoExcitationAutoion.Settings(...), ...)` or call directly functions from the module `PhotoExcitationAutoion`.
- In JAC, the partial photoexcitation & autoionization cross sections  $\sigma(i \rightarrow r \rightarrow f)$  are calculated and tabulated by assuming that the direct photoionization cross sections  $\sigma^{(\text{photoionization})}(i \rightarrow f)$  is negligible.
- The photoexcitation and (subsequent) autoionization of atoms and ions has been explored in good detail, either as the dominant (photo-) ionization process within the vicinity of certain (photoionization) resonances or simply as competitive process to atomic photoionization.
- Often, the photoexcitation & autoionization can be considered independently from the *direct* photoionization and then leads to **partial and total photoexcitation & autoionization cross sections**.
- If the direct photoionization is negligible, the photoexcitation & autoionization is the time-reversed process to the dielectronic recombination.

### Fano profiles in photo-ionization cross sections:

- **Fano's parametrization:** For an isolated resonance  $(\alpha_r \mathbb{J}_r)$ , the **total photoionization cross section** can be (formally) parametrized in the **vicinity of this resonance** by the energy-dependent cross section

$$\sigma(\mathcal{E}) = \sigma^{(\text{EA})} \frac{(q + \mathcal{E})^2}{1 + \mathcal{E}^2} + \sigma^{(\text{D})}$$

where  $\sigma^{(\text{D})}$  is the direct photoionization cross section and  $\sigma^{(\text{EA})}$  the cross section due to the photoexcitation & autoionization of the **resonance**. Moreover,  $\mathcal{E} = (E_\omega - E_r)/(\Gamma/2)$  indicates the detuning of the incident photon energy  $E_\omega$  from the resonance energy  $E_r$ , in units of the half-width  $(\Gamma/2)$  of the resonance.

- **Fano  $q$  parameter:** This parameter determines the overall profile of the cross section, ranging from a near-Lorentzian ( $q \rightarrow \infty$ ), to a window-like ( $q \rightarrow 0$ ), and up to a completely asymmetric resonance ( $q \rightarrow \pm 1$ ).
- In JAC, no attempt has been made so far to calculate the Fano profiles explicitly for selected resonances, although this is possible quite readily by combining proper calls to functions from the modules `PhotoIonization`, `PhotoExcitation` as well as `Auger`.

### Total photoionization amplitude and cross sections across the resonance level $(\alpha_r \mathbb{J}_r)$ :

- The photoexcitation and (subsequent) autoionization of atoms and ions obviously contributes to the photoionization and, hence, to its amplitudes and cross sections.
- **Total photoionization amplitudes across the resonance level  $(\alpha_r \mathbb{J}_r)$ :**

$$\begin{aligned} \mathcal{M}(\omega; (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t, \alpha_r \mathbb{J}_r, \alpha_i \mathbb{J}_i) \\ = \langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{O}^{(\mathbb{M}, \text{photoionization})} \parallel \alpha_i \mathbb{J}_i \rangle + \frac{\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t \parallel \mathbb{O}^{(\text{Auger})} \parallel \alpha_r \mathbb{J}_r \rangle \langle \alpha_r \mathbb{J}_r \parallel \mathbb{O}^{(\mathbb{M}, \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle}{E_i + \omega - E_r + i \Gamma_r/2} \end{aligned}$$

In this notation of the **resonant photoionization**, we assume the photoelectron to escape by means of the partial wave  $|\varepsilon \kappa\rangle$  with kinetic energy  $\varepsilon = E_i + \omega - E_f$  and with well-defined angular momentum and parity.

- Apart from the *direct* photoionization amplitude (first term), the total photoionization amplitude also contains the photoexcitation & autoionization amplitudes (second term).

- From these amplitudes, the **total photoionization cross section (intensity)** is obtained as before by the summation over all the possible scattering states of the final system ‘photoion + electron’:

$$\sigma(\omega; \alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) = \frac{4\pi^2 \alpha \omega}{3(2J_i + 1)} \sum_{\alpha_r \mathbb{J}_r \kappa \mathbb{J}_t} |\mathcal{M}(\omega; (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J}_t, \alpha_r \mathbb{J}_r, \alpha_i \mathbb{J}_i)|^2,$$

This includes both, the summation over all relevant resonances as well as the summation over the partial waves of the photoelectron and the total angular momenta and parities of the total scattering states  $|\alpha_t \mathbb{J}_t\rangle$ .

- In JAC, no attempt has yet been made to calculate and tabulate the resonant photoionization cross sections or angular anisotropy parameters, although this will be possible since all required many-electron matrix elements are internally quite readily available.

### Angular distribution of resonantly emitted Auger electrons:

- Of course, the angular distribution of the emitted Auger electrons critically depend on the (properties of the) prior excitation process; **in this PhotoExcitationAutoion module, we assume a photoexcitation of the atoms or ions for calculating subsequent properties of Auger electrons. We here also assume that the direct photoionization is negligible near to the considered resonance level  $(\alpha_r \mathbb{J}_r)$ .**
- If the resonantly-excited level  $(\alpha_r \mathbb{J}_r)$  is axially symmetric along the  $z$ -axis,  $\mathcal{A}_{kq}(\alpha_r \mathbb{J}_r) \sim \delta_{q0}$ , the angular distribution only depends on the angle  $\vartheta$  between the symmetry ( $z$ -) axis and the linear momentum of the ejected electron. Then, the angular distribution simplifies to

$$W(\vartheta; \alpha_r \mathbb{J}_r \rightarrow \alpha_f \mathbb{J}_f) = \frac{A_a(r \rightarrow f)}{4\pi} \left[ 1 + \sum_{k=2,4,\dots}^{k_{\max}} \alpha_k(\alpha_r \mathbb{J}_r \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{k0}(\alpha_r \mathbb{J}_r) P_k(\cos \vartheta) \right].$$

- In JAC, no attempt has been made so far to tabulate the angular distribution  $W(\vartheta; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)$  explicitly for selected scenarios; cf. section 8.1.e.
- **Photoexcitation of initially unpolarized atoms within the dipole approximation:** For the photoexcitation of initially unpolarized atoms the Auger angular distribution further simplifies to

$$W(\vartheta; \alpha_r \mathbb{J}_r \rightarrow \alpha_f \mathbb{J}_f) = \frac{A_a(r \rightarrow f)}{4\pi} [1 + \beta_2(r \rightarrow f) P_2(\cos \vartheta)] \equiv \frac{A_a(r \rightarrow f)}{4\pi} [1 + \alpha_2(\alpha_r \mathbb{J}_r \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{20}(\alpha_r \mathbb{J}_r) P_2(\cos \vartheta)].$$

In this case, the overall form of the angular distribution for the photoinduced Auger emission coincides with those for the (direct) photoelectron emission, although the asymmetry parameter  $\beta$  is now a product of two factors:  $\beta_2(r \rightarrow f) = \alpha_2(\alpha_r \mathbb{J}_r \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{20}(\alpha_r \mathbb{J}_r)$ . However, this factorization of the  $\beta_2$  anisotropy parameter is only valid if the initial level is (sufficiently) well isolated.

- The angular distribution of the emitted Auger electrons is sensitive to the phase difference between the Auger amplitudes, in contrast to the total probability  $A(i \rightarrow f)$ . Since the coefficients are symmetric with regard to an interchange  $\kappa \leftrightarrow \kappa'$  in the summation of the angular distribution, this distribution is invariant also with respect to the inversion:  $\vartheta \rightarrow \pi - \vartheta$ ,  $\varphi \rightarrow \varphi + \pi$ , simply because it only contains the spherical harmonics of even rank.

### Spin polarization of resonantly emitted Auger electrons:

- The spin polarization of Auger electrons is usually described by an polarization vector  $\mathbf{P}$ . The three components of  $\mathbf{P}$  can be expressed in terms of the statistical tensors of the initial level as well as the intrinsic anisotropy parameters of the considered Auger transition.
- Two coordinate systems,  $S(XYZ)$  and  $S'(X'Y'Z')$  are often employed in order to characterize the spin polarization of Auger electrons; cf. the figure below and Kabachnik *et al.* (2007).

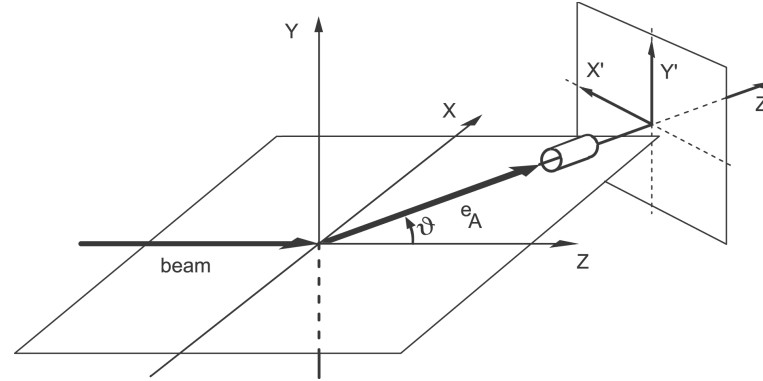


Figure 8.1.: The coordinate systems that are usually utilized for describing the Auger electron spin polarization. From Kabachnik *et al.* (2007).

- (Longitudinal) spin component of the emitted Auger electrons: If the initial level  $(\alpha_i \mathbb{J}_i)$  is produced by photoabsorption of unpolarized target atoms with monochromatic plane-wave photons, the (longitudinal) spin component of the emitted Auger electrons along their propagation direction can be written as:

$$P_{z'} = \frac{\mathcal{A}_{10}(\alpha_i \mathbb{J}_i) \delta_1 \cos \vartheta}{1 + \alpha_2(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{20}(\alpha_i \mathbb{J}_i) P_2(\cos \vartheta)}.$$

- **Transverse spin component:** The transverse spin component within the  $(x - z)$  reaction plane  $P_{x'}$  and the transverse component perpendicular to the reaction plane  $P_{y'}$  take the form

$$P_{x'} = \frac{\mathcal{A}_{10}(\alpha_i \mathbb{J}_i) \xi_1 \sin \vartheta}{1 + \alpha_2(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{20}(\alpha_i \mathbb{J}_i) P_2(\cos \vartheta)}, \quad P_{y'} = P_y = \frac{\mathcal{A}_{20}(\alpha_i \mathbb{J}_i) \xi_2 \sin 2\vartheta}{1 + \alpha_2(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \mathcal{A}_{20}(\alpha_i \mathbb{J}_i) P_2(\cos \vartheta)},$$

- **For the photoionization by unpolarized or linearly polarized light**, the photo ion is aligned along the beam direction or photon polarization direction, respectively. From these expressions above for the components of the spin-polarization vector, it follows then that the spin of the Auger electron can be oriented only perpendicular to the (reaction) plane that contains the alignment axis and the electron emission direction. This has been called **dynamic polarization** (Klar 1980, Kabachnik 1981).
- **For the photoionization by circularly-polarized light, the photon ion is not only aligned but also oriented.** In this case, the spin components of the Auger electrons in the reaction plane do not vanish. This is an example of an **polarization transfer** process (Klar 1980).

## 8.2. In JAC partly-implemented processes

### 8.2.a. Rayleigh & Compton scattering of light (RayleighCompton)

#### Process, notation & application:

- Rayleigh or Compton scattering of photons at an atom or ion:  $A + \hbar\omega_i \longrightarrow A^{(*)} + \hbar\omega_f$  ... including  $\omega_i = \omega_f$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i M_i\rangle + \hbar\omega_i(\mathbf{k}_i, \lambda_i; \{\mathbb{M}_i\}) \longrightarrow |\alpha_f \mathbb{J}_f M_f\rangle + \hbar\omega_f(\mathbf{k}_f, \lambda_f; \{\mathbb{M}_f\})$   
 $\omega_i = \omega_f$  ... for elastic Rayleigh scattering
- Using JAC: Perform an `Atomic.Computation(.., process=Compton, processSettings=RayleighCompton.Settings(..), ..)` or call directly functions from the module `RayleighCompton`.

#### Motivation:

- The elastic scattering of light by the bound electrons of an atom or ion is commonly known as **Rayleigh scattering** and has been found a versatile tool in the past for studying the electronic structure of atoms and their (chemical) environment.
- The **inelastic (Compton or Raman) scattering of light** on atoms, ions or molecules is associated in contrast with an excitation of the target and has also been explored since the 1920s, both experimentally and theoretically.
- First theoretical investigations on the elastic scattering of photon by bound electrons date back to the mid-1930s. While initially rather simple approximations were applied, for instance based on atomic form factors, a more rigorous quantum-electrodynamical (QED) approach was developed later in terms of the relativistic second-order S-matrix amplitude.
- **Rayleigh scattering:** The Rayleigh scattering of incident light by the atomic electrons is the **dominant elastic scattering mechanism for all photon energies below 2 MeV**, while the nuclear Thomson, nuclear resonance and low-energy Delbrück (virtual pair) scattering is negligible for these photon energies.
- In JAC, the angular-differential cross sections for the elastic Rayleigh and inelastic Compton scattering are calculated and tabulated for all selected levels of  $(i \rightarrow f)$  line.



## Second-order scattering amplitude

- **Compton scattering amplitude:** In second-order perturbation theory, the elastic Rayleigh and inelastic Compton process can be described in terms of the **two-photon transition amplitudes** for a transition from substates  $|\alpha_i \mathbb{J}_i M_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  owing to the absorption and emission of photons with well-defined wave vectors  $\mathbf{k}_{i,f}$  and polarization vectors  $\boldsymbol{\epsilon}_{i,f}$ . This amplitude is given in terms of the electron-photon interaction operator by (Jahrsetz *et al.*, 2015)

$$\mathcal{M}_{fi}^{(\text{Compton})}(\alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i; \mathbf{k}_f, \boldsymbol{\epsilon}_f, \mathbf{k}_i, \boldsymbol{\epsilon}_i) = \sum_{\alpha_\nu \mathbb{J}_\nu M_\nu} \left[ \frac{\langle \alpha_f \mathbb{J}_f M_f | \hat{R}^\dagger(\mathbf{k}_f, \boldsymbol{\epsilon}_f) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | \hat{R}(\mathbf{k}_i, \boldsymbol{\epsilon}_i) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega_i - E_\nu} + \frac{\langle \alpha_f \mathbb{J}_f M_f | \hat{R}(\mathbf{k}_i, \boldsymbol{\epsilon}_i) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | \hat{R}^\dagger(\mathbf{k}_f, \boldsymbol{\epsilon}_f) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i - \omega_f - E_\nu} \right].$$

Here, the energies of the photons involved are related by  $\omega_f = \omega_i - E_f + E_i$  to each other and to the energies of the initial and final states of the atoms or ions.

- Owing to the time-ordering in (time-dependent) perturbation theory, there are obviously two contributions to this second-order amplitude for the *absorption-emission* and *emission-absorption* of the two photons involved.
- Although these second-order amplitudes can be readily written down, they are less useful for practical computations as they are based on different representations of the atomic and photon state(s); we therefore first need to perform a multipole expansion of the electron-photon interaction operators and to do all necessary simplifications.
- **Compton (scattering) amplitude for the scattering of photons with well-defined helicity and multipolarity:**

$$\mathcal{M}_{fi}^{(\text{Compton})}(\alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i; \mathbb{M}_f, \lambda_f, \mathbb{M}_i, \lambda_i) = \dots \frac{\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}_f, \text{emission})} || \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu || \mathbb{O}^{(\mathbb{M}_i, \text{absorption})} || \alpha_i \mathbb{J}_i \rangle}{E_i + \omega_f - E_\nu} + \dots$$

### Angle-differential and total cross sections:

- **Angle-differential cross section for the Compton scattering of unpolarized light by initially unpolarized atoms:** For unpolarized incident plane-wave photons and if the polarization of the scattered photons as well as the magnetic sublevel population of the residual ions both remain unobserved, the angle-differential cross section is given by

$$\begin{aligned} & \frac{d\sigma^{(\text{Compton})}}{d\Omega}(\vartheta; \omega_i) \\ &= \frac{1}{2} \frac{\omega_f}{\omega_i} \frac{1}{2J_i + 1} \sum_{\lambda_i \lambda'_i} \sum_{\lambda_f \lambda'_f} c_{\lambda_i \lambda'_i} \mathcal{M}_{fi}^{(\text{Compton})}(\alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i; \mathbb{M}_f, \lambda_f, \mathbb{M}_i, \lambda_i) \mathcal{M}_{fi}^{(\text{Compton})}(\alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i; \mathbb{M}_f, \lambda'_f, \mathbb{M}_i, \lambda'_i) \end{aligned}$$

Unfortunately, there is no simple parametrization of this angle-differential cross section  $\frac{d\sigma^{(\text{Compton})}}{d\Omega}(\vartheta; \omega_i)$ .

- The angle-differential Rayleigh cross sections can be obtained from the formulas above by using  $|\alpha_f \mathbb{J}_f\rangle = |\alpha_i \mathbb{J}_i\rangle$  in the two-photon amplitudes and irreducible tensors.
- In JAC, the angle-differential Rayleigh and Compton scattering cross sections are calculated by default for all selected initial levels and ( $i \rightarrow f$ ) lines, if a proper spectrum is specified in `RayleighCompton.Settings.spectrum`.

### 8.2.b. Multi-photon excitation and decay (MultiPhotonDeExcitation)

#### Process, notation & application:

- **Multi-photon excitation** of an atom or ion:  $A + n \hbar \omega \longrightarrow A^*$
- **Multi-photon decay** of an atom or ion:  $A^* \longrightarrow A + n \hbar \omega$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar \omega_1(\mathbf{k}_1, \lambda_1; \{\mathbb{M}_1\}) + \hbar \omega_2(\mathbf{k}_2, \lambda_2; \{\mathbb{M}_2\}) + \dots + \hbar \omega_n(\mathbf{k}_n, \lambda_n; \{\mathbb{M}_n\}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle$   
or
- $$|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar \omega_1(\mathbf{k}_1, \lambda_1; \{\mathbb{M}_1\}) + \hbar \omega_2(\mathbf{k}_2, \lambda_2; \{\mathbb{M}_2\}) + \dots + \hbar \omega_n(\mathbf{k}_n, \lambda_n; \{\mathbb{M}_n\})$$

- In particular, the **two-photon decay of few-electron ions**  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega_1 + \hbar\omega_2$  has often been considered, both experimentally and theoretically. For this two-photon decay, the total decay rate, the spectral (energy) distribution as well as the angle-angle correlation function of the emitted photons have been explored.
- Using JAC: Perform an `Atomic.Computation(..., process=MultiPhoton, processSettings=MultiPhotonDeExcitation.Settings(...), ...)` or call directly functions from the module `MultiPhotonDeExcitation`.
- In JAC, only the initial and final levels are tabulated by default, together with their symmetry and total transition energy, while some proper flags must be set in `MultiPhotonDeExcitation.Settings` for all further cross section information.
- Using JAC: Different multi-photon (de-) excitation processes are distinguished in `MultiPhotonDeExcitation.Settings(...)` by an (abstract) type `process::AbstractMultiPhotonExcProcess` that (currently) takes the values `TwoPhotonAbsorptionMonochromatic(...)`, `TwoPhotonEmission(...)`, ...
- Using JAC: Different multi-photon properties are distinguished in `process::AbstractMultiPhotonExcProcess` by choosing one or several `properties::ArrayAbstractMultiPhotonExcProperty,1`. Currently defined subtypes of `AbstractMultiPhotonExcProperty` are: `TotalCsLinear()`, `TotalCsRightCircular()`, `TotalCsLinear()`, ..., although only some of these properties can be called for each selected multi-photon (de-) excitation process; cf. docstrings.
- Using JAC: The Green function (channels) have to be calculated before and passed to the computations by `MultiPhotonDeExcitation.Settings(..., green=greenFunction)`.
- *Ab-initio* calculations of two-photon-ionization cross sections for rare-gas atoms and their iso-electronic ions have shown that correlation effects may play an essential role in the multi-photon ionization of many-electron atoms.
- **Use of variational principles for multi-photon computations:** Variational principles are rarely applied for higher-order perturbative processes as for the multi-photon excitation or ionization. For an  $N$ -th order perturbative process, the major difficulty usually arises from the summation over the  $N - 1$  complete sets of intermediate states. However, there are several aspects in the theoretical description of  $N$ -th order perturbative processes which might benefit from a (variational) formulation due to the stability of variational computations.

### Monochromatic two-photon absorption amplitude and total rate:

- **Two-photon absorption of monochromatic light** (from the same beam) of an atom or ion:  $A + 2\hbar\omega \longrightarrow A^*$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbf{k}, \lambda_1; \{\mathbb{M}_1\}) + \hbar\omega(\mathbf{k}, \lambda_2; \{\mathbb{M}_2\}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle \quad E_f - E_i = 2\hbar\omega$

- **Final-state density matrix of the excited atom following the absorption of two monochromatic photons:** For a two-photon excitation (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  of an atom or ion by (two) monochromatic and equally-polarized photons (usually from the same beam), the final-state density matrix  $\langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M'_f \rangle$  of the excited atom can be expressed in terms of the initial-state density matrix  $\langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle$ , the photon density matrices  $c_{\lambda\lambda'}$  of the two photons as well as the two-photon transition amplitudes by (Hofbrucker 2020)

$$\begin{aligned}
& \langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M'_f \rangle \\
&= \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2, M_i M'_i} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle \mathcal{M}(\mathbf{k}, \lambda_2, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \mathcal{M}^*(\mathbf{k}, \lambda'_2, \lambda'_1; \alpha_i \mathbb{J}_i M'_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\
& \mathcal{M}(\mathbf{k}, \lambda_2, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\
&= \sum_{\alpha_f \mathbb{J}_f M_f} \frac{\langle \alpha_f \mathbb{J}_f M_f | R(\mathbf{k}, \mathbf{u}_{\lambda_2}) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | R(\mathbf{k}, \mathbf{u}_{\lambda_1}) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega - E_\nu} \\
&= 2\pi \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} (-1)^{J_f - M_f + K - q} \sqrt{[L_1, L_2]} [K] \begin{pmatrix} K & J_f & J_i \\ q & -M_f & M_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & K \\ \lambda_1 & \lambda_2 & -q \end{pmatrix} \\
& \quad \times \left\{ \begin{matrix} J_i & J_f & K \\ L_2 & L_1 & J_\nu \end{matrix} \right\} \sum_{\alpha_\nu} \frac{\langle \alpha_f \mathbb{J}_f || \mathbb{O}(\mathbb{M}_2, \text{absorption}) || \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu || \mathbb{O}(\mathbb{M}_1, \text{absorption}) || \alpha_i \mathbb{J}_i \rangle}{E_i + \omega - E_\nu} . \\
&= 2\pi \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} (-1)^{J_f - M_f + K - q} \sqrt{[L_1, L_2]} [K] \begin{pmatrix} K & J_f & J_i \\ q & -M_f & M_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & K \\ \lambda_1 & \lambda_2 & -q \end{pmatrix} \\
& \quad \times \mathcal{U}^{(K, \text{absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) .
\end{aligned}$$

➤ **Reduced two-photon absorption amplitude:**

$$\mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) = \left\{ \begin{matrix} J_i & J_f & K \\ L_2 & L_1 & J_\nu \end{matrix} \right\} \sum_{\alpha_\nu} \frac{\langle \alpha_f \mathbb{J}_f \parallel \mathbb{O}^{(\mathbb{M}_2, \text{absorption})} \parallel \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu \parallel \mathbb{O}^{(\mathbb{M}_1, \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle}{E_i + \omega - E_\nu}.$$

In the reduced amplitude  $\mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i)$  above, the summation  $\alpha_\nu$  runs over all the atomic states of given symmetry  $\mathbb{J}_\nu$ , i.e. over all the ASF as provided by a given **Green function channel of symmetry  $\mathbb{J}_\nu$** .

➤ **Total two-photon absorption cross sections:** For initially unpolarized atoms, the two-photon absorption cross section for the atomic excitation (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  and for the absorption of two arbitrary but equally-polarized photons with  $c_{\lambda\lambda'} = c_{\lambda\lambda'}(P_1, P_2, P_3)$  is given by (Hofbrucker 2020)

$$\begin{aligned} & \sigma^{(2\gamma \text{ absorption})}(\alpha_i \mathbb{J}_i + 2\omega \rightarrow \alpha_f \mathbb{J}_f) \\ &= \frac{8\pi^3 \alpha^2}{\omega^2 [J_i]} \sum_{M_i M_f} \langle \alpha_f \mathbb{J}_f M_f \mid \rho_f \mid \alpha_i \mathbb{J}_i M_i \rangle \\ &= \frac{8\pi^3 \alpha^2}{\omega^2 [J_i]} \sum_{M_i M_f} \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \mathcal{M}(\mathbf{k}, \lambda_2, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \mathcal{M}^*(\mathbf{k}, \lambda'_2, \lambda'_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\ &= \frac{32\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} \sqrt{[L_1, L_2]} \begin{pmatrix} L_1 & L_2 & K \\ \lambda_1 & \lambda_2 & -q \end{pmatrix} [K] \\ & \quad \times \sum_{\mathbb{M}'_1 \mathbb{M}'_2, \mathbb{J}'_\nu} (-i)^{L'_1 - p'_1 + L'_2 - p'_2} (-\lambda'_1)^{p'_1} (-\lambda'_2)^{p'_2} \sqrt{[L'_1, L'_2]} \begin{pmatrix} L'_1 & L'_2 & K \\ \lambda'_1 & \lambda'_2 & -q \end{pmatrix} \\ & \quad \times \mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) [\mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}'_2, \mathbb{J}'_\nu, \omega, \mathbb{M}'_1, \alpha_i \mathbb{J}_i)]^* . \end{aligned}$$

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- **Two-photon absorption cross section for linearly-polarized photons:** For linear-polarization ( $P_1 = 1$ ), the total two-photon amplitude contains a full summation over  $\lambda_1, \lambda_2$ , and the two-photon absorption cross section becomes (Hofbrucker 2020)

$$\sigma^{(2\gamma \text{ absorption, linear})}(\alpha_i \mathbb{J}_i + 2\omega \rightarrow \alpha_f \mathbb{J}_f) = \frac{8\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{Kq} \left| \sum_{\lambda_1 \lambda_2} \sum_{\mathbb{M}_1 \mathbb{M}_2 \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} [L_1, L_2]^{1/2} \begin{pmatrix} L_1 & L_2 & K \\ \lambda_1 & \lambda_2 & -q \end{pmatrix} [K] \mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) \right|^2.$$

- **Two-photon absorption cross section for right-circularly polarized photons:** For right-circularly polarized light ( $P_3 = 1$ ), the two-photon absorption cross section is given by

$$\sigma^{(2\gamma \text{ absorption, } \odot)}(\alpha_i \mathbb{J}_i + 2\omega \rightarrow \alpha_f \mathbb{J}_f) = \frac{8\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{Kq} \left| \sum_{\mathbb{M}_1 \mathbb{M}_2 \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} [L_1, L_2]^{1/2} [K] \begin{pmatrix} L_1 & L_2 & K \\ 1 & 1 & -q \end{pmatrix} \mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) \right|^2.$$

- **Two-photon absorption cross section for unpolarized photons:** For unpolarized light ( $P_1 = P_2 = P_3 = 0$ ), the summation over  $\lambda_1, \lambda_2$  occurs *outside* of the modulus (of the amplitude), and the two-photon absorption cross section becomes

$$\sigma^{(2\gamma \text{ absorption, unpolarized})}(\alpha_i \mathbb{J}_i + 2\omega \rightarrow \alpha_f \mathbb{J}_f) = \frac{8\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{Kq} \sum_{\lambda_1 \lambda_2} \left| \sum_{\mathbb{M}_1 \mathbb{M}_2 \mathbb{J}_\nu} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} [L_1, L_2]^{1/2} [K] \begin{pmatrix} L_1 & L_2 & K \\ \lambda_1 & \lambda_2 & -q \end{pmatrix} \mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega, \mathbb{M}_1, \alpha_i \mathbb{J}_i) \right|^2.$$

## Bichromatic two-photon absorption amplitude and total rate:

- **Two-photon absorption of bichromatic light** (from differently oriented beams) of an atom or ion:  $A + \hbar\omega_1 + \hbar\omega_2 \longrightarrow A^*$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega_1(\mathbf{k}_1, \lambda_1; \{\mathbb{M}_1\}) + \hbar\omega_2(\mathbf{k}_2, \lambda_2; \{\mathbb{M}_2\}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle \quad E_f - E_i = \hbar(\omega_1 + \omega_2) .$

- **Final-state density matrix of the excited atom following the absorption of two photons:** For a two-photon excitation (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  of an atom or ion by two photons  $\gamma_1 = (\omega_1, \mathbf{k}_1, \lambda_1; \{\mathbb{M}_1\})$  and  $\gamma_2 = (\omega_2, \mathbf{k}_2, \lambda_2; \{\mathbb{M}_2\})$  with well-defined frequency, propagation direction and helicity (as well as for a given set of multipolarities), the final-state density matrix  $\langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M'_f \rangle$  of the excited atom can be expressed in terms of the initial-state density matrix  $\langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle$ , the directions  $\mathbf{k}_1 = \mathbf{k}_1(\omega_1, \vartheta_1, \varphi_1)$ ,  $\mathbf{k}_2 = \mathbf{k}_2(\omega_2, \vartheta_2, \varphi_2)$ , the photon density matrices  $c_{\lambda_1 \lambda'_1}$  and  $c_{\lambda_2 \lambda'_2}$  of the two photons as well as the two-photon transition amplitudes by (Hofbrucker 2020)

$$\begin{aligned} & \langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M'_f \rangle \\ &= \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle \mathcal{M}(\mathbf{k}_2, \lambda_2, \mathbf{k}_1, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \mathcal{M}^*(\mathbf{k}_2, \lambda'_2, \mathbf{k}_1, \lambda'_1; \alpha_i \mathbb{J}_i M'_i \rightarrow \alpha_f \mathbb{J}_f M'_f) \end{aligned}$$

$$\begin{aligned}
& \mathcal{M}(\mathbf{k}_2, \lambda_2, \mathbf{k}_1, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\
&= \sum_{\alpha_\nu \mathbb{J}_\nu M_\nu} \frac{\langle \alpha_f \mathbb{J}_f M_f | R(\mathbf{k}_2, \mathbf{u}_{\lambda_2}) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | R(\mathbf{k}_1, \mathbf{u}_{\lambda_1}) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega_1 - E_\nu} \\
&\quad + \sum_{\alpha_\nu \mathbb{J}_\nu M_\nu} \frac{\langle \alpha_f \mathbb{J}_f M_f | R(\mathbf{k}_1, \mathbf{u}_{\lambda_1}) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | R(\mathbf{k}_2, \mathbf{u}_{\lambda_2}) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega_2 - E_\nu} \\
&= \pi \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} \sum_{M_1 M_2} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} (-1)^{J_f - M_f + K - q} \sqrt{[L_1, L_2]} [K] \begin{pmatrix} K & J_f & J_i \\ q & -M_f & M_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & K \\ M_1 & M_2 & -q \end{pmatrix} \\
&\quad \times D_{M_1, \lambda_1}^{(L_1)}(\vartheta_1, \varphi_1) D_{M_2, \lambda_2}^{(L_2)}(\vartheta_2, \varphi_2) \\
&\quad \times \left( \left\{ \begin{matrix} J_i & J_f & K \\ L_2 & L_1 & J_\nu \end{matrix} \right\} \sum_{\alpha_\nu} \frac{\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}_2, \text{absorption})} || \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu || \mathbb{O}^{(\mathbb{M}_1, \text{absorption})} || \alpha_i \mathbb{J}_i \rangle}{E_i + \omega_1 - E_\nu} \right. \\
&\quad \left. + (-1)^{L_1 + L_2 + K} \left\{ \begin{matrix} J_i & J_f & K \\ L_1 & L_2 & J_\nu \end{matrix} \right\} \frac{\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}_1, \text{absorption})} || \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu || \mathbb{O}^{(\mathbb{M}_2, \text{absorption})} || \alpha_i \mathbb{J}_i \rangle}{E_i + \omega_2 - E_\nu} \right) \\
&= \pi \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} \sum_{M_1 M_2} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} (-1)^{J_f - M_f + K - q} \sqrt{[L_1, L_2]} [K] \begin{pmatrix} K & J_f & J_i \\ q & -M_f & M_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & K \\ M_1 & M_2 & -q \end{pmatrix} \\
&\quad \times D_{M_1, \lambda_1}^{(L_1)}(\vartheta_1, \varphi_1) D_{M_2, \lambda_2}^{(L_2)}(\vartheta_2, \varphi_2) \mathcal{U}^{(K, \gamma + \gamma' \text{ absorption})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i)
\end{aligned}$$



➤ **Reduced two-photon absorption amplitude:**

$$\begin{aligned} & \mathcal{U}^{(K, \gamma + \gamma' \text{ absorption})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) \\ &= \mathcal{U}^{(K, 2\gamma \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) + (-1)^{L_1 + L_2 + K} \mathcal{U}^{(K, 2\gamma' \text{ absorption})}(\alpha_f \mathbb{J}_f, \mathbb{M}_1, \mathbb{J}_\nu, \omega_2, \mathbb{M}_2, \alpha_i \mathbb{J}_i). \end{aligned}$$

➤ **Total two-photon absorption cross sections:** For initially unpolarized atoms, the two-photon absorption cross section for the transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  and for the absorption of two photons with well-defined frequency  $\omega_1, \omega_2$ , propagation directions  $(\vartheta_1, \varphi_1), (\vartheta_2, \varphi_2)$  and photon density matrices  $c_{\lambda_s \lambda'_s} = c_{\lambda_s \lambda'_s}(P_1, P_2, P_3)$ ,  $s = 1, 2$  is given by (Hofbrucker 2020)

$$\begin{aligned} & \sigma^{(\gamma + \gamma' \text{ absorption})}(\alpha_i \mathbb{J}_i + \omega + \omega' \rightarrow \alpha_f \mathbb{J}_f) \\ &= \frac{8\pi^3 \alpha^2}{\omega^2 [J_i]} \sum_{M_i M_f} \langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M_f \rangle \\ &= \frac{8\pi^3 \alpha^2}{\omega^2 [J_i]} \sum_{M_i M_f} \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \mathcal{M}(\mathbf{k}_2, \lambda_2, \mathbf{k}_1, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \mathcal{M}^*(\mathbf{k}_2, \lambda'_2, \mathbf{k}_1, \lambda'_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\ &= \frac{8\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{\lambda_1 \lambda'_1, \lambda_2 \lambda'_2} c_{\lambda_1 \lambda'_1} c_{\lambda_2 \lambda'_2} \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} \sum_{M_1 M_2} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} \sqrt{[L_1, L_2]} \begin{pmatrix} L_1 & L_2 & K \\ M_1 & M_2 & -q \end{pmatrix} [K] \\ & \quad \times \sum_{\mathbb{M}'_1 \mathbb{M}'_2, \mathbb{J}'_\nu} \sum_{M'_1 M'_2} (-i)^{L'_1 - p'_1 + L'_2 - p'_2} (-\lambda'_1)^{p'_1} (-\lambda'_2)^{p'_2} \sqrt{[L'_1, L'_2]} \begin{pmatrix} L'_1 & L'_2 & K \\ M'_1 & M'_2 & -q \end{pmatrix} \\ & \quad \times D_{M_1, \lambda_1}^{(L_1)}(\vartheta_1, \varphi_1) D_{M_2, \lambda_2}^{(L_2)}(\vartheta_2, \varphi_2) [D_{M'_1, \lambda'_1}^{(L'_1)}(\vartheta_1, \varphi_1) D_{M'_2, \lambda'_2}^{(L'_2)}(\vartheta_2, \varphi_2)]^* \\ & \quad \times \mathcal{U}^{(K, \gamma + \gamma' \text{ absorption})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) [\mathcal{U}^{(K, \gamma + \gamma' \text{ absorption})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}'_2, \mathbb{J}'_\nu, \omega_1, \mathbb{M}'_1, \alpha_i \mathbb{J}_i)]^*. \end{aligned}$$

➤ **Total two-photon absorption cross sections for photons from co-linear beams:** For initially unpolarized atoms, the two-photon absorption

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cross section for the transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  and for the absorption of two photons with well-defined frequency  $\omega_1, \omega_2$ , propagation directions  $(\vartheta_1, \varphi_1) = (\vartheta_2, \varphi_2) = (0, 0) \parallel \mathbf{e}_z$ , and photon density matrices  $c_{\lambda_s \lambda'_s} = c_{\lambda_s \lambda'_s}(P_1, P_2, P_3)$ ,  $s = 1, 2$  is given by (Hofbrucker 2020)

??

- **Total two-photon absorption cross sections for photons from perpendicular beams:** For initially unpolarized atoms, the two-photon absorption cross section for the transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  and for the absorption of two photons with well-defined frequency  $\omega_1, \omega_2$ , propagation directions  $(\vartheta_1, \varphi_1) = (0, 0) \parallel \mathbf{e}_z$  and  $(\vartheta_2, \varphi_2) = (\pi/2, 0) \parallel \mathbf{e}_x$ , and photon density matrices  $c_{\lambda_s \lambda'_s} = c_{\lambda_s \lambda'_s}(P_1, P_2, P_3)$ ,  $s = 1, 2$  is given by (Hofbrucker 2020)

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### Two-photon decay amplitude and total rate:

- **Two-photon emission of an atom or ion:**  $A^* \longrightarrow A + \hbar\omega_1 + \hbar\omega_2$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega(\mathbf{k}_1, \lambda_1; \{\mathbb{M}_1\}) + \hbar\omega(\mathbf{k}_2, \lambda_2; \{\mathbb{M}_2\})$   $E_i - E_f = \hbar(\omega_1 + \omega_2)$ .
- **Final-state density matrix of the de-excited atom following the emission of two photons:** For the two-photon decay (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  of an initially-excited atom or ion, the total final-state density matrix  $\langle \alpha_f \mathbb{J}_f M_f | \rho_f | \alpha_f \mathbb{J}_f M'_f \rangle$  of the atom or ion *plus* the two photons with well-defined wave vectors  $\mathbf{k}_1, \mathbf{k}_2$  and helicities  $\lambda_1, \lambda_2$  can be expressed in terms of the initial-state density matrix  $\langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle$  of the atom as well as the two-photon emission amplitudes by (Hofbrucker 2020)

$$\begin{aligned} & \langle \alpha_f \mathbb{J}_f M_f, \mathbf{k}_1 \lambda_1, \mathbf{k}_2 \lambda_2 | \rho_f | \alpha_f \mathbb{J}_f M'_f, \mathbf{k}_1 \lambda'_1, \mathbf{k}_2 \lambda'_2 \rangle \\ &= \sum_{M_i M'_i} \langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle \mathcal{M}(\mathbf{k}_2, \lambda_2, \mathbf{k}_1, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \mathcal{M}(\mathbf{k}_2, \lambda'_2, \mathbf{k}_1, \lambda'_1; \alpha_i \mathbb{J}_i M'_i \rightarrow \alpha_f \mathbb{J}_f M'_f) \end{aligned}$$

$$\begin{aligned}
& \mathcal{M}(\mathbf{k}_2, \lambda_2, \mathbf{k}_1, \lambda_1; \alpha_i \mathbb{J}_i M_i \rightarrow \alpha_f \mathbb{J}_f M_f) \\
&= \sum_{\alpha_\nu \mathbb{J}_\nu M_\nu} \left( \frac{\langle \alpha_f \mathbb{J}_f M_f | R(\mathbf{k}_2, \mathbf{u}_{\lambda_2}) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | R(\mathbf{k}_1, \mathbf{u}_{\lambda_1}) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega_1 - E_\nu} \right. \\
&\quad \left. + \frac{\langle \alpha_f \mathbb{J}_f M_f | R(\mathbf{k}_1, \mathbf{u}_{\lambda_1}) | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | R(\mathbf{k}_2, \mathbf{u}_{\lambda_2}) | \alpha_i \mathbb{J}_i M_i \rangle}{E_i + \omega_2 - E_\nu} \right) \\
&= \pi \sum_{Kq} \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} \sum_{M_1 M_2} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} (-1)^{J_f - M_f + K - q} [K] \begin{pmatrix} K & J_f & J_i \\ q & -M_f & M_i \end{pmatrix} \begin{pmatrix} L_1 & L_2 & K \\ M_1 & M_2 & -q \end{pmatrix} D_{M_1, \lambda_1}^{(L_1)}(\vartheta_1, \varphi_1) \\
&\quad \times D_{M_2, \lambda_2}^{(L_2)}(\vartheta_2, \varphi_2) \left[ \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) + (-1)^{L_1 + L_2 + K} \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_1, \mathbb{M}_1, \mathbb{J}_\nu, \omega_2, \mathbb{M}_2, \alpha_i \mathbb{J}_i) \right].
\end{aligned}$$

➤ **Reduced two-photon emission amplitude:** (Hofbrucker 2020)

$$\mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) = \left\{ \begin{matrix} J_i & J_f & K \\ L_2 & L_1 & J_\nu \end{matrix} \right\} \sum_{\alpha_\nu} \frac{\langle \alpha_f \mathbb{J}_f || \mathbb{O}^{(\mathbb{M}_2, \text{ emission})} || \alpha_\nu \mathbb{J}_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu || \mathbb{O}^{(\mathbb{M}_1, \text{ emission})} || \alpha_i \mathbb{J}_i \rangle}{E_i + \omega_1 - E_\nu}.$$

In the reduced amplitude  $\mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i)$  above, the summation  $\alpha_\nu$  runs again over all the atomic states of given symmetry  $\mathbb{J}_\nu$ , i.e. over all the ASF as provided by a given **Green function channel of symmetry  $\mathbb{J}$** .

➤ **Two-photon angle-angle-differential emission rate:** For the two-photon decay (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  of an initially unpolarized atom or ion, the angle-angle-differential emission rate, if neither the polarization of the photons nor the polarization of the atom is observed, can

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be written as

$$\begin{aligned}
& \frac{d^2 W^{(2\gamma \text{ emission})}}{d\Omega_1 d\Omega_1}(\omega_1; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \\
&= \frac{\alpha^2}{(2\pi)^3} \omega_1 \omega_2 d\omega_1 \sum_{M_f} \sum_{\lambda_1, \lambda_2} \langle \alpha_f \mathbb{J}_f M_f, \mathbf{k}_1 \lambda_1, \mathbf{k}_2 \lambda_2 | \rho_f | \alpha_f \mathbb{J}_f M_f, \mathbf{k}_1 \lambda_1, \mathbf{k}_2 \lambda_2 \rangle \\
&= \frac{\alpha^2}{8\pi^3 [J_i]} \omega_1 \omega_2 d\omega_1 \sum_{\lambda_1 \lambda_2, Kq} [K] \\
&\quad \times \sum_{\mathbb{M}_1 \mathbb{M}_2, \mathbb{J}_\nu} \sum_{M_1 M_2} i^{L_1 - p_1 + L_2 - p_2} (-\lambda_1)^{p_1} (-\lambda_2)^{p_2} [L_1, L_2]^{1/2} \begin{pmatrix} L_1 & L_2 & K \\ M_1 & M_2 & -q \end{pmatrix} D_{M_1, \lambda_1}^{(L_1)}(\vartheta_1, \varphi_1) D_{M_2, \lambda_2}^{(L_2)}(\vartheta_2, \varphi_2) \\
&\quad \times \sum_{\mathbb{M}'_1 \mathbb{M}'_2, \mathbb{J}'_\nu} \sum_{M'_1 M'_2} (-i)^{L'_1 - p'_1 + L'_2 - p'_2} (-\lambda'_1)^{p'_1} (-\lambda'_2)^{p'_2} [L'_1, L'_2]^{1/2} \begin{pmatrix} L'_1 & L'_2 & K \\ M'_1 & M'_2 & -q \end{pmatrix} [D_{M'_1, \lambda'_1}^{(L'_1)}(\vartheta_1, \varphi_1) D_{M'_2, \lambda'_2}^{(L'_2)}(\vartheta_2, \varphi_2)]^* \\
&\quad \times \left[ \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) + (-1)^{L_1 + L_2 + K} \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_1, \mathbb{M}_1, \mathbb{J}_\nu, \omega_2, \mathbb{M}_2, \alpha_i \mathbb{J}_i) \right] \\
&\quad \times \left[ \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}'_2, \mathbb{J}'_\nu, \omega_1, \mathbb{M}'_1, \alpha_i \mathbb{J}_i) + (-1)^{L_1 + L_2 + K} \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_1, \mathbb{M}'_1, \mathbb{J}'_\nu, \omega_2, \mathbb{M}'_2, \alpha_i \mathbb{J}_i) \right]^* .
\end{aligned}$$

➤ **Two-photon energy-differential emission rate:** For the two-photon decay (transition)  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$  of an initially unpolarized atom, the energy-differential emission rate can be written as

$$\begin{aligned}
& \frac{dW^{(2\gamma \text{ emission})}}{d\omega_1}(\omega_1; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) \\
&= \frac{2\pi\alpha^2}{[J_i]} \omega_1 \omega_2 \sum_{\mathbb{M}_1 \mathbb{M}_2 \mathbb{J}_\nu} \left| \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_1, \mathbb{M}_1, \mathbb{J}_\nu, \omega_2, \mathbb{M}_2, \alpha_i \mathbb{J}_i) + (-1)^{L_1 + L_2 + K} \mathcal{U}^{(K, 2\gamma \text{ emission})}(\alpha_f \mathbb{J}_f, \omega_2, \mathbb{M}_2, \mathbb{J}_\nu, \omega_1, \mathbb{M}_1, \alpha_i \mathbb{J}_i) \right|^2
\end{aligned}$$

➤ Total two-photon decay rate:

$$W^{\text{total}}(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \int d\omega_1 \frac{dW^{(2\gamma \text{ emission})}}{d\omega_1}(\omega_1; \alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)$$

### 8.2.c. Multi-photon ionization (MultiPhotonIonization)

#### Process, notation & application:

- Multi-photon ionization: of an atom or ion  $A + n \hbar \omega \longrightarrow A^{(*)} + e_p^-$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar \omega_1(\mathbb{M}_1) + \hbar \omega_2(\mathbb{M}_2) + \dots + \hbar \omega_n(\mathbb{M}_n) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon \kappa\rangle$
- If the photon energy is smaller than the ionization threshold of the atom, it can still be ionized due to its simultaneous interaction with several photons. However, the probability generally decreases rapidly with the number of photons  $N$ , that are required to overcome the ionization threshold.
- Multi-photon ionization is studied mainly by means of intense, pulsed lasers. The ionization probability is for moderate intensities proportional to the  $N$ -th power of the intensity,  $I^N$ , while this power law breaks down at high intensities due to the ac-Stark effect.
- In first strong-field laser experiments, a rather large probability was found for a multiple ionization of atoms, relative to single-ionization probability, and gave rise to various speculation about *collective modes* in the electronic motion of atoms and ions.

#### Two-photon ionization with monochromatic light:

- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar \omega(\mathbb{M}_1) + \hbar \omega(\mathbb{M}_2) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon \kappa\rangle$ ;      equally-polarized photons
- Final-state density matrix of the ‘photo-ion + photo-electron’: For the two-photon ionization with monochromatic and equally-polarized photons (typically from the same beam), the photoion is found in the final level  $(\alpha_f \mathbb{J}_f)$ , while the *free* photoelectron is emitted with

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asymptotic linear momentum  $\mathbf{p}$  and spin projection  $m_s$ . In a basis of well-defined angular momenta  $\mathbb{J}_i, \mathbb{J}_f$ , the initial-state density matrix is  $\langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle$ , and the final-state density matrix can be written as:

$$\begin{aligned} \langle \alpha_f \mathbb{J}_f M_f, \mathbf{p} m_s | \rho_f | \alpha_f \mathbb{J}_f M'_f, \mathbf{p}, m'_s \rangle &= \sum_{\lambda_1 \lambda'_1 \lambda_2 \lambda'_2} \langle \mathbf{k} \lambda_1 | \rho_\gamma | \mathbf{k} \lambda'_1 \rangle \langle \mathbf{k} \lambda_2 | \rho_\gamma | \mathbf{k} \lambda'_2 \rangle \langle \alpha_i \mathbb{J}_i M_i | \rho_i | \alpha_i \mathbb{J}_i M'_i \rangle \\ &\times \sum_{\nu} \frac{\langle \alpha_f \mathbb{J}_f M_f, \mathbf{p} m_s | \sum_j \alpha_j \mathbf{u}_{\lambda_{2j}} e^{i\mathbf{k} \cdot \mathbf{r}_j} | \alpha_\nu \mathbb{J}_\nu M_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu M_\nu | \sum_n \alpha_n \mathbf{u}_{\lambda_{1j}} e^{i\mathbf{k} \cdot \mathbf{r}_j} | \alpha_i \mathbb{J}_i M_i \rangle}{E_{\alpha_i \mathbb{J}_i} + \omega - E_{\alpha_\nu \mathbb{J}_\nu}} \\ &\times \sum_{\nu'} \frac{\langle \alpha_f \mathbb{J}_f M'_f, \mathbf{p} m'_s | \sum_j : \alpha_n \mathbf{u}_{\lambda'_{2j}} e^{i\mathbf{k} \cdot \mathbf{r}_j} | \alpha'_\nu \mathbb{J}'_\nu M'_\nu \rangle \langle \alpha'_\nu \mathbb{J}'_\nu M'_\nu | \sum_n \alpha_n \mathbf{u}_{\lambda'_{1j}} e^{i\mathbf{k} \cdot \mathbf{r}_j} | \alpha_i \mathbb{J}_i M'_i \rangle}{E_{\alpha_i \mathbb{J}_i} + \omega - E_{\alpha'_\nu \mathbb{J}'_\nu}}. \end{aligned}$$

- **Total two-photon ionization cross sections for initially unpolarized atoms** For initially unpolarized atoms and equally-polarized plane-wave photons with wave vector  $\mathbf{k} \parallel \mathbf{e}_z$  and Stokes parameters  $P_1, P_2, P_3$ , the total two-photon ionization cross sections for the transition  $|\alpha_i J_i\rangle \rightarrow |\alpha_f J_f\rangle$  is given by:

$$\begin{aligned} \sigma(\alpha_i J_i \rightarrow \alpha_f J_f) &= \frac{32\pi^5 \alpha^2}{\omega^2 [J_i]} \sum_{M_i} \sum_{\lambda_1 \lambda'_1 \lambda_2 \lambda'_2} \langle \mathbf{k} \lambda_1 | \rho_\gamma | \mathbf{k} \lambda'_1 \rangle \langle \mathbf{k} \lambda_2 | \rho_\gamma | \mathbf{k} \lambda'_2 \rangle \sum_{J_t M_t \kappa} \mathcal{M}_{\kappa \mathbb{J}_t M_t}^{\lambda_1 \lambda_2} \mathcal{M}_{\kappa \mathbb{J}_t M_t}^{\lambda'_1 \lambda'_2 *} \\ \mathcal{M}_{\kappa \mathbb{J} M}^{\lambda_1 \lambda_2} &= \sum_{\mathbb{M}_1 \mathbb{M}_2} \sum_{\mathbb{J}_\nu M_\nu} i^{L_1+L_2} \frac{[L_1, L_2]^{1/2}}{[J_\nu, J]^{1/2}} (i\lambda_1)^{p_1} (i\lambda_2)^{p_2} \langle J_i M_i, L_1 \lambda_1 | J_\nu M_\nu \rangle \langle J_\nu M_\nu, L_2 \lambda_2 | J M \rangle \\ &\times \frac{\langle (\alpha_f \mathbb{J}_f, \varepsilon \kappa) \mathbb{J} \parallel \mathbb{O}^{(\mathbb{M}_1, \text{photoionization})} \parallel \alpha_\nu J_\nu \rangle \langle \alpha_\nu \mathbb{J}_\nu \parallel \mathbb{O}^{(\mathbb{M}_2, \text{absorption})} \parallel \alpha_i \mathbb{J}_i \rangle}{E_{\alpha_i \mathbb{J}_i} + \omega - E_{\alpha_\nu \mathbb{J}_\nu}}. \end{aligned}$$

- **Total two-photon ionization cross sections for initially unpolarized atoms and unpolarized light:** For initially unpolarized atoms and unpolarized plane-wave photons with wave vector  $\mathbf{k} \parallel \mathbf{e}_z$ , the total two-photon ionization cross sections for the transition  $|\alpha_i J_i\rangle \rightarrow |\alpha_f J_f\rangle$  is given by:

$$\sigma(\alpha_i J_i \rightarrow \alpha_f J_f) = \dots$$

### 8.2.d. Coulomb excitation (CoulombExcitation)

#### Process, notation & application:

- Coulomb excitation of an atom or ion by fast, heavy ions:  $A + Z_p \longrightarrow A^* + Z_p$  (projectile remains unaffected)
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + Z_p(\beta_p) \longrightarrow |\alpha_f \mathbb{J}_f\rangle, \quad \beta_p = \frac{v_p}{c}$
- Using JAC: Perform an `Atomic.Computation(.., process=CoulExc, processSettings=CoulombExcitation.Settings(..), ..)` or call directly functions from the module `CoulombExcitation`.

#### Motivation

- In Coulomb excitation processes, one often assumes that a single electron from a (fast-moving) projectile ion with relative velocity  $\beta_p = v_p/c$  (with regard to the target) is excited by a target nucleus at rest.
- Of course, an analogue process occurs also when we consider the excitation of the target that may occur due to a fast-moving (bare) projectile ion, and in which case the role of the projectile and target need simply to be interchanged in all formulas below.
- The Coulomb excitation or ionization of the projectile (ion) will be affected, in addition, also by the target electrons (or, *vice versa*, the projectile electrons) but such rather small effects are often not considered in detail.
- The Coulomb excitation of few-electron ions in fast ion-atom collisions leads to the formation of excited ionic states. In typical ion-atom collision experiments, a *preferred* direction is hereby defined for the overall systems, both at storage rings and the EBIT, and this typically results in an *alignment of the excited ions* along this distinct direction.
- The first step in calculating energy- and angle-differential as well as total Coulomb excitation cross sections usually refers to determining the *impact-parameter dependence of the excitation probability  $P(b)$* . The weighted *K*-shell Coulomb excitation probability  $2\pi b P(b)$  is known to have a maximum in the vicinity of the *K*-shell radius. This is quite similar as for the Coulomb ionization probabilities.
- In JAC, the partial and total Coulomb excitation cross sections are calculated and tabulated by default for all selected pairs of initial and final levels.

## Coulomb excitation amplitude of few-electron projectile ions in position space

- **Coulomb (excitation) amplitude for the excitation of a (single) projectile electron:** If a one-electron projectile moves at a trajectory with impact parameter  $b$ , the amplitude for an excitation from level  $i \rightarrow f$  is given by Eichler & Meyerhof (1995, Eq. 6.2)

$$\mathcal{M}_{fi}^{(\text{Coul})}(b) = i \frac{\gamma Z_t e^2}{\hbar} \int dt \exp\left(\frac{i}{\hbar} (E_f - E_i) t\right) \int d^3r \psi_f^\dagger(\mathbf{r}) \frac{(1 - \beta_p \alpha_z)}{r'(t)} \psi_i(\mathbf{r}),$$

$$r'(t) = \sqrt{(x-b)^2 + y^2 + \gamma^2 (z - vt)^2}, \quad \beta_p = \frac{v_p}{c},$$

where  $\mathbf{r}$  is the coordinate of the projectile electron,  $r'(t)$  its (time-dependent) distance from the target nucleus, and where  $\psi_f(\mathbf{r})$  and  $\psi_i(\mathbf{r})$  denote the final- and initial-state eigenfunctions of the projectile electron with energies  $E_f$  and  $E_i$ .

- **Coulomb (excitation) amplitude for the excitation of a many-electron projectile (ion):** For an Coulomb excitation of a many-electron projectile from the sublevel  $|\alpha_i \mathbb{J}_i M_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$ , the excitation amplitude for given impact parameter  $b$  can then be written in first-order perturbation theory and natural units ( $\hbar = m_e = c = 1$ ) as:

$$\mathcal{M}_{fi}^{(\text{Coul})}(b; \alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i) = i \gamma \alpha Z_t \int dt e^{i(E_f - E_i)t} \left\langle \alpha_f \mathbb{J}_f M_f \left| \sum_{k=1}^N \frac{1 - \beta_p \hat{\alpha}_z(k)}{r'_k(t)} \right| \alpha_i \mathbb{J}_i M_i \right\rangle.$$

- From this transition amplitude, the cross section for an excitation of the projectile from (sub-) level  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  can be obtained by integrating over all the impact parameters  $b$  and by taking the average over the initial magnetic sublevels  $M_i$ .
- In JAC, we do not use the Coulomb excitation amplitude in position space but make use of a representation of this amplitude in momentum space instead, see below.

## Coulomb excitation amplitude of few-electron projectile ions in momentum space:

- **Coulomb (excitation) amplitude for the excitation of a (single) projectile electron:** To evaluate Coulomb excitation cross sections for one- and many-electron atoms, it is often more convenient to work in momentum space and to express all properties in terms of the



**Fourier transform of the Coulomb excitation amplitude in position space.** If we make use of the momentum transfer  $\mathbf{q} = (\mathbf{q}_b, q_z)$ , the time-integration in this Coulomb (excitation) amplitude can be carried out explicitly (Eichler & Meyerhof 1995, Eq. 6.4)

$$\mathcal{M}_{fi}^{(\text{Coulex})}(b) = \frac{i \nu_p}{\pi} \int \frac{d^2 q_b}{q_b^2 + (1 - \beta^2) q_0^2} e^{-i \mathbf{q}_0 \cdot \mathbf{b}} \mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q}); \quad \mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q}) = \langle \psi_f(\mathbf{r}) | (1 - \beta \alpha_z) e^{i \mathbf{q} \cdot \mathbf{r}} | \psi_i(\mathbf{r}) \rangle.$$

This formula removes the complicated time dependence in  $r'(t)$  and replaces it instead by an explicit wave number (momentum transfer) dependence.

- Note, that in momentum space, the (momentum-space) Coulomb excitation amplitude  $\mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q})$  does no longer depend on the impact parameter  $b$  but now simply contains an integration over the momentum transfer  $\mathbf{q}$ , and which starts from the **minimum momentum transfer for the excitation** of the initial ion from level  $|i\rangle \rightarrow |f\rangle$ :  $q_0 = (E_f - E_i)/v_p$ .
- In momentum space, indeed, most Coulomb excitation cross sections can be expressed directly in terms of the momentum-space Coulomb excitation amplitude  $\mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q})$ .
- **(Momentum-space) Coulomb excitation amplitude for many-electron projectiles:** This amplitude can be further simplified by using the Wigner-Eckert theorem (Surzhykov and Fritzsche, 2008)

$$\begin{aligned}
\mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q}; \alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i) &= \left\langle \alpha_f \mathbb{J}_f M_f \left| \sum_k^N (1 - \beta \alpha_z(k)) e^{i \mathbf{q} \cdot \mathbf{r}_k} \right| \alpha_i \mathbb{J}_i M_i \right\rangle \\
&= \sum_{LM} i^L Y_{LM}^*(\arccos(q_0/q), 0) \left\langle \alpha_f \mathbb{J}_f M_f \left| \sum_{k=1}^N (1 - \beta_p \hat{\alpha}_z(k)) j_L(q r_k) Y_{LM}(\vartheta_k, \varphi_k) \right| \alpha_i \mathbb{J}_i M_i \right\rangle, \\
&= \sum_t \frac{1}{\sqrt{2J_f + 1}} \langle J_i M_i, t (M_f - M_i) | J_f M_f \rangle \sum_L i^L Y_{L, M_f - M_i}^*(\arccos(q_0/q), 0) \left\langle \alpha_f \mathbb{J}_f \left\| H_{tL}^{(\text{Coulex})}(q) \right\| \alpha_i \mathbb{J}_i \right\rangle \\
&= \sum_t \frac{1}{\sqrt{2J_f + 1}} \langle J_i M_i, t (M_f - M_i) | J_f M_f \rangle \sum_L i^L Y_{L, M_f - M_i}^*(\arccos(q_0/q), 0) \\
&\quad \times (\delta_{tL} \langle \alpha_f \mathbb{J}_f \left\| \mathbb{K}^{(L, \text{Coulex}, jY)} \right\| \alpha_i \mathbb{J}_i \rangle - \beta_p \langle LM, 10 | tM \rangle \langle \alpha_f \mathbb{J}_f \left\| \mathbb{K}^{(t, \text{Coulex}, jT)} \right\| \alpha_i \mathbb{J}_i \rangle)
\end{aligned}$$

- In JAC, these (momentum-space) Coulomb excitation amplitudes  $\mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q}; \alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i)$  are implemented explicitly and the integration over  $q$  is typically performed by a Gauß-Legendre integration.

### Coulomb excitation operators and interaction strength:

- **Coulomb excitation (interaction) strength:** The (full) Coulomb excitation amplitude in momentum space above combines two kinds of reduced (many-electron) matrix elements due to the two interaction operators:  $\sum_{k=1}^N j_L(q r_k) Y_L(\vartheta_k, \varphi_k)$  of rank  $L$  as well as  $\sum_{k=1}^N j_L(q r_k) \hat{\alpha}(k) \cdot \mathbf{T}_{tL}(\vartheta_k, \varphi_k)$  of rank  $t$ , respectively. These two reduced matrix elements are the actual building blocks that are needed in order to represent and to explore the properties of the target or projectile excitation process.
- **Coulomb excitation (interaction) strength:** The building blocks for the computation of the Coulomb excitation and ionization amplitudes

are given by the reduced matrix elements

$$\begin{aligned}\langle \alpha_f \mathbb{J}_f \parallel \mathbb{K}^{(L, \text{Coulex}, jY)} \parallel \alpha_i \mathbb{J}_i \rangle &= \left\langle \alpha_f \mathbb{J}_f \parallel \sum_{k=1}^N j_L(q r_k) Y_L(\vartheta_k, \varphi_k) \parallel \alpha_i \mathbb{J}_i \right\rangle \\ \langle \alpha_f \mathbb{J}_f \parallel \mathbb{K}^{(t, \text{Coulex}, jT)} \parallel \alpha_i \mathbb{J}_i \rangle &= \left\langle \alpha_f \mathbb{J}_f \parallel \sum_{k=1}^N j_L(q r_k) \hat{\boldsymbol{\alpha}}(k) \cdot \mathbf{T}_{tL}(\vartheta_k, \varphi_k) \parallel \alpha_i \mathbb{J}_i \right\rangle\end{aligned}$$

### Energie-differential, partial and total Coulomb excitation cross sections:

- **Partial Coulomb excitation cross section:** If the Fourier transformation from the position to momentum coordinates is performed, the integrals over the time  $t$  and the impact parameter  $b$  can be evaluated *analytically*. Then, the partial (excitation) cross section for the Coulomb excitation from (sub-) levels  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f M_f\rangle$  can be written as (Surzhykov and Fritzsche, 2008)

$$\begin{aligned}\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f M_f) &= \frac{2\pi}{2J_i + 1} \sum_{M_i} \int_0^\infty db \, b \left| \mathcal{M}_{fi}^{(\text{Coulex})}(b; \alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i) \right|^2 \\ &= 2\pi \left( \frac{8\pi Z_t \alpha}{\beta_p} \right)^2 \frac{1}{2J_i + 1} \sum_{M_i} \int_{q_0}^\infty dq \frac{q}{(q^2 - q_0^2 \beta_p^2)^2} \left| \mathcal{K}_{fi}^{(\text{Coulex})}(\mathbf{q}; \alpha_f \mathbb{J}_f M_f, \alpha_i \mathbb{J}_i M_i) \right|^2.\end{aligned}$$

### Alignment of Coulomb-excited ions:

- **Alignment of Coulomb-excited ions in level  $(\alpha_f \mathbb{J}_f)$ :** For a well-defined ion-atom collision axis, a Coulomb-excited ion in level  $(\alpha_f \mathbb{J}_f)$  is generally aligned; this alignment depends on the partial Coulomb cross sections  $\sigma(\alpha_f \mathbb{J}_f M_f)$  can be described in terms of one (or several)

parameters  $\mathcal{A}_k(\alpha_f \mathbb{J}_f)$ :

$$\mathcal{A}_k(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f) = \frac{\sqrt{2J_f + 1}}{\sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f)} \sum_{M_f} (-1)^{J_f - M_f} \langle J_f M_f J_f - M_f | k 0 \rangle \sigma(\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f M_f),$$

### 8.2.e. Photoionization & fluorescence (PhotoIonizationFluor)

#### Process, notation & application:

- **Photoionization** of an atom or ion with subsequent fluorescence emission:  $A + \hbar\omega \longrightarrow A^* + e_p^- \longrightarrow A^{(*)} + e_p^- + \hbar\omega'$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega \longrightarrow |\alpha_e \mathbb{J}_e\rangle + |\varepsilon\kappa\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon\kappa\rangle + \hbar\omega_f(\mathbb{M})$
- Apart from astrophysical interest, emphasis on the photoionization of inner-shell electrons from multiple and highly charged ions and its subsequent photon emission arises also from the diagnostics of various *laboratory* plasmas.

#### Density operator of the fluorescence photon $\hbar\omega_f(\mathbb{M})$ :

- After the inner-shell photoionization, the photoion appears to be in an excited level  $(\alpha_e \mathbb{J}_e)$  that decays subsequently to some energetically lower level  $(\alpha_f \mathbb{J}_f)$  by the emission of a characteristic photon.
- **Characteristic photon density matrix in the helicity representation:** For this characteristic photon, the density matrix can be expressed in the form  $\langle \mathbf{k}_0 \lambda | \rho_\gamma | \mathbf{k}_0 \lambda' \rangle$ , in which  $\mathbf{k}_0 \equiv (\vartheta_0, \varphi_0)$  denotes the wave vector along the propagation direction of the fluorescence photon and  $\lambda = \pm 1$  its helicity. Note that the helicity representation of this density matrix also describes the photon polarization.

#### Stokes parameter of the fluorescence photon $\hbar\omega_f(\mathbb{M})$ :

- The density matrix of the fluorescence photon  $\hbar\omega_f(\mathbb{M})$  is usually parametrized in terms of the so-called Stokes parameters (Blum 1981; Balashov *et al.*, 2001)

$$\langle \mathbf{k}_0 \lambda | \rho_{\omega_f} | \mathbf{k}_0 \lambda' \rangle \equiv c_{\lambda, \lambda'} = \frac{1}{2} \begin{pmatrix} 1 + P_3 & -P_1 + iP_2 \\ -P_1 - iP_2 & 1 - P_3 \end{pmatrix},$$

and which are utilized to characterize both the degree of linear ( $P_1$  and  $P_2$ ) and circular ( $P_3$ ) polarization of the light.

- Apart from the population of the excited sublevels  $|\alpha_e \mathbb{J}_e M_e\rangle$  and the angle  $\vartheta$  of the emitted photon, the degree of linear polarization of the characteristic x-ray radiation also depends on the total angular momenta of the excited level ( $\alpha_e \mathbb{J}_e$ ) and the final level ( $\alpha_f \mathbb{J}_f$ ) of the characteristic transition as well as on its *multipolarity*.

### 8.2.f. Photoionization & autoionization (PhotoIonizationAutoIon)

#### Process, notation & application:

- **Photo ionization** of an atom or ion with subsequent autoionization:  $A + \hbar\omega \longrightarrow A^{+,*} + e_p^- \longrightarrow A^{(*)} + e_p^- + e_a^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) \longrightarrow |\alpha_r \mathbb{J}_r\rangle + |\varepsilon_p \kappa_p\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_p \kappa_p\rangle + |\varepsilon_a \kappa_a\rangle$

#### Photo-Auger electron coincidence spectrometry:

- Photo-Auger electron coincidence spectrometry has been found a versatile tool for studying the structure and dynamics of atoms, molecules and solids. In atomic physics, for example, it has been utilized to **realize a so-called complete experiment in the photoionization of atoms as well as for exploring small effects of coherence and post-collision interactions in photo-induced Auger processes**.
- For a full analysis of the photoionization and subsequent autoionization process, both electrons should be detected in coincidence by measuring the energy and angular distributions, i.e. the **photo-Auger electron correlation function**.
- The **photoionization and subsequent autoionization process differs from the direct double photoionization** due to the formation of a (well-defined) intermediate ionic state and, thus, the emission of the two electrons can usually be considered within a two-step model.
- Investigations of the **magnetic circular dichroism in the photoemission from solids have been found useful for studying the magnetic properties of solids**.

#### Photo-Auger electron correlation function:

- **Sequential ionization of polarized targets:** There are three relevant directions that need to be distinguished in the sequential ionization of polarized targets: the direction of the photoelectron  $\mathbf{n}_p = (\vartheta_p, \varphi_p)$ , those of the Auger electron  $\mathbf{n}_a = (\vartheta_a, \varphi_a)$  and the direction of the

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target polarization  $\mathbf{n}_t = (\vartheta_t, \varphi_t)$ . Because of these three relevant but independent directions, the (triple-differential) cross sections can be expanded in terms of **tripolar spherical harmonics**

$$\{\mathbb{Y}_{k_0}(\mathbf{n}_t) \otimes \{\mathbb{Y}_{k_1}(\mathbf{n}_p) \otimes \mathbb{Y}_{k_2}(\mathbf{n}_a)\}_k\}_{k'q'} = \langle \dots | \dots \rangle \langle \dots | \dots \rangle Y_{k_0 q_0}(\vartheta_t, \varphi_t) Y_{k_1 q_1}(\vartheta_p, \varphi_p) Y_{k_2 q_2}(\vartheta_a, \varphi_a)$$

### 8.2.g. Dielectronic recombination & fluorescence (DielectronicFluores)

#### Process, notation & application:

➤ **Dielectronic recombination** of an atom or ion with subsequent fluorescence:

$$A^{q+} + e_s^- \longrightarrow A^{(q-1)+*} \longrightarrow A^{(q-1)+(*)} + \hbar\omega \longrightarrow A^{(q-1)+(*)} + \hbar\omega + \hbar\omega'$$

➤ **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_s \kappa_s\rangle \longrightarrow |\alpha_r \mathbb{J}_r\rangle \longrightarrow |\alpha_d \mathbb{J}_d\rangle + \hbar\omega_d(\mathbb{M}_d) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega_d(\mathbb{M}) + \hbar\omega_f(\mathbb{M}_f)$

### 8.2.h. Electron-impact (de-) excitation (ImpactExcitation)

#### Process, notation & application:

➤ **Electron-impact excitation** of an atom or ion:  $e_s^- + A \longrightarrow A^* + e_s^{-'}$

➤ **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle$  or  $|\alpha_i \mathbb{J}_i\rangle + |\mathbf{p}_i m_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\mathbf{p}_f m_f\rangle$

➤ Electron-impact excitation is formally an inelastic scattering process in which a free incident electron  $|\varepsilon_i \kappa_i\rangle$  is scattered at the atom and leaves as final electron  $|\varepsilon_f \kappa_f\rangle$ .

➤ Electron-impact ionization cross sections are required in different field, for example, for calculating level populations and spectral line intensities of non-local-thermodynamic-equilibrium (non-LTE) plasmas.

## Computation of electron-impact processes:

- **Approaches for electron-impact excitation cross sections:** Different approaches have been implemented and applied in order to compute electron-impact cross sections for atoms and ions. Two main approaches refer to (1) the use of the first-order Born approximation and (2) the close-coupling approximation. The close-coupling (CC) equations enable one to incorporate, at least partly, the coupling of the different excitation channels due to the impact of free electrons as well as resonances in the cross sections. To a good approximation, such CC equations are implemented in various R-matrix codes; cf. the BSR code.
- **First-Born approximation:** The second (standard) method for the computation of electron-impact excitation cross sections apply the first-order Born approximation and **assumes that the excitation into different (excited) states are independent of each other**. Apart from the (simple) plane-wave first-Born approximation, the Coulomb- or distorted-wave (DW) Born approximation accounts for the modification of the emitted electron waves due to the Coulomb *or* the effective many-electron potential of the excited atom or ion. In particular, the DW Born approximation includes the realistic electronic structure of the atoms and provides significantly better results than all simpler versions of the (first-) Born approximation.
- The electron-impact excitation of atoms is often described in first-order Born approximation, in which one can easily distinguish individual excitation channels. This approximation neglects however the coupling of the *continuum channels*, but which can later be incorporated perturbatively.
- **Distorted-wave Born approximation (DWBA):** We here make use of the DWBA that accounts for the distortion of the continuum orbitals due to (local) potential of the nucleus and all the electrons of the target. The DWBA typically gives better results than the *pure* Born or the Coulomb-Born approximation. The current implementation is similar to the codes by Zhang *et al.*(1989) as well as to the FAC code (Gu 2008).
- For a reliable evaluation of plasma parameters, such as temperature, density or level populations, the excitation cross sections need to be known quite accurately.
- **Computational methods for electron-impact excitation & ionization:** Three methods are commonly used in the literature to calculate electron-impact excitation and ionization cross sections: i) Coulomb-Born (CB) approximation, where the continuum orbital just represent a free electron in a Coulomb potential; ii) distorted-wave (DW) approximation that includes a more realistic potential for the continuum orbitals; iii) close-coupling (CC) approximation. **In the first two approximations, all excitation channels are treated independently and give overall rise to a scattering matrix which is not necessarily unitary.**

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- **Electron-impact excitation in plasma diagnostics:** In plasma-diagnostics measurements, the population of the excited states, relevant for plasma diagnostics, is largely driven by the direct electron-impact excitation of the ground and low-lying metastable states, and followed by their radiative decay.

### Collision strength and cross sections:

- **Collision strength:** The name *collision strength* was first suggested by Seaton (1953). For a given (atomic target) transition  $\alpha_i \mathbb{J}_i \rightarrow \alpha_f \mathbb{J}_f$ , the collision strength is related to the cross section  $Q$  by

$$\Omega(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) = \frac{4\pi g_i}{\lambda_i^2} Q(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f),$$

if the continuum orbitals are normalized per unit energy. The statistical weight  $g_i$  of level  $|\alpha_i \mathbb{J}_i\rangle$  ensures the detailed-balance relation  $\Omega(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) = \Omega(\alpha_f \mathbb{J}_f, \alpha_i \mathbb{J}_i)$ .

- **Collision strength:** If  $|\varepsilon_i, \kappa_i\rangle$  and  $|\varepsilon_f, \kappa_f\rangle$  denote the partial waves of the incident and scattered electrons, the collision strength is given by

$$\Omega_{if} = 2 \sum_{\kappa_i, \kappa_f} \sum_{\mathbb{J}_t} [J_t] \left| \langle (\mathbb{J}_f, \epsilon_f, \kappa_f) \mathbb{J}_t M_t | V^{(e-e)} | (\mathbb{J}_i, \epsilon_i, \kappa_i) \mathbb{J}_t M_t \rangle \right|^2.$$

- In the JAC program, the standard decomposition of the electron-electron interaction matrix elements is utilized to compute the collision strength.
- **Normalization of continuum orbitals:** A continuum orbital is said to be **normalized per unit energy** if it has an asymptotic amplitude  $\sqrt{k/\varepsilon}$  (or,  $\sqrt{2/k}$  in the non-relativistic limit) or, equivalently, if it fullfills, equivalently,

$$\int dr [P_\varepsilon(r) P_{\varepsilon'}(r) + Q_\varepsilon(r) Q_{\varepsilon'}(r)] = \pi \delta(\varepsilon - \varepsilon').$$

- For electron-impact processes, the collision strength  $\Omega(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f)$  is typically of the order of unity, though still large variation may still occur owing to its dependence on the particular ion as well as the transition and impact energy. Therefore, it is usually not justified to assume  $\Omega = 1$  as sometimes done in astrophysical codes.
- **Simplification for heavy ions with open  $d$ - and  $f$ -shells:** For heavy and ionized atoms with open  $d$ - and  $f$ -shells, the fine-structure of just (mixed) single initial- and final-state configurations may give rise to thousands of (fine-structure) transitions, for which the radial integrals



often depend only weakly on the transition energy. For such transition arrays, the total cross section computations can be simplified considerably by either neglecting the weak dependence of the radial integrals or by some simple interpolation.

- Accurate calculations of electron-impact excitation of atom and ions are overall still a challenge for contemporary electronic methods, such as convergent close-coupling, R-matrix close-coupling or time-dependent close-coupling scheme, and even by using the largest (parallel) computers.

### Electron-impact excitation of magnetic sublevels:

- **Electron-impact excitation by an incident electron beam:** If the electron-impact is made by a *beam* of electrons, the excited target atoms are generally **aligned** and the subsequently emitted radiation becomes polarized. This alignment of the (electron-impact) excited atoms can be either expressed in terms of the atomic density matrix or by means of magnetic sublevel dependent cross sections. Both schemes require **electron-impact transition amplitudes** with well-defined angular momenta of the initial and final-bound states as well the coupling of the partial waves to define scattering states of proper symmetry.
- **Electron-impact excitation by an incident electron beam:** Theoretical computations of the alignment and magnetic sublevel-dependent electron-impact cross sections can be applied, for instance, to beam-plasma interactions in solar flares, for the diagnostics tokamak plasmas, or to analyze experiments with electron-beam-ion-traps (EBIT).

### Collisional-excitation rate coefficients:

- The rate coefficient of collisional excitation is given by

$$\alpha^{(\text{impact:excitation})} = \int_{\Delta E}^{\infty} dv f(v) \sigma^{(\text{impact-excitation})}(v)$$

where  $f(v)$  is velocity distribution of electrons which is typically assumed to have a Maxwellian distribution with electron temperature  $T_e$ ,  $\sigma^{(\text{impact-excitation})}(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f)$  is the electron-impact excitation cross-section from level  $i \rightarrow f$  at velocity  $v$ , and  $\Delta E = E_f - E_i$  is the excitation energy.

- For a given energy of the incident electrons, the collisional-excitation rate coefficient can be expressed also as

$$\alpha^{(\text{impact-excitation})} = \sqrt{\frac{\pi}{E}} \int_{\Delta E}^{\infty} dE E \sigma^{(\text{impact-excitation})}(E) \exp\left(-\frac{E}{T_e}\right).$$

**8.2.i. Electron-impact excitation & autoionization** (ImpactExcitationAutoIon)Process, notation & application:

- Electron-impact excitation with subsequent autoionization of an atom or ion:  $A + e_s^- \longrightarrow A^* + e_s^{-'} \longrightarrow A^{+(*)} + e_s^{-'} + e_a^-$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_r \mathbb{J}_r\rangle + |\varepsilon_r \kappa_r\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_r \kappa_r\rangle + |\varepsilon_a \kappa_a\rangle$
- Electron-impact excitation with subsequent autoionization occurs frequently in plasma and has been utilized to study the autoionization of atoms and ions.

**8.2.j. Radiative-Augur decay** (RadiativeAuger)Process, notation & application:

- Radiative-Augur (autoionization) of an atom or ion:  $A^{q+*} \longrightarrow A^{(q+1)+,(*)} + (e_a^- + \hbar\omega)$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega(\mathbb{M}) + |\varepsilon_a \kappa_a\rangle$
- The radiative Auger process results in the simultaneous emission of an electron and photon, and mainly occurs for inner-shell excited atoms and ions. There are no characteristic electron or photon lines associated with this process, since the transition energy is shared between the photon and the electron.

**8.2.k. Multi-photon double ionization** (MultiPhotonDoubleIon)Process, notation & application:

- Multi-photon double ionization: of an atom or ion:  $A + n \hbar\omega \longrightarrow A^{(*)} + e_{p_1}^- + e_{p_1}^-$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega_1(\mathbb{M}_1) + \hbar\omega_2(\mathbb{M}_2) + \dots + \hbar\omega_n(\mathbb{M}_n) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle$
- The energy of several photons together can also lead to the emission of two electrons: This emission can occur either sequential, direct (non-sequential) or via some given resonances of the atom.

- In this section, we only consider the direct (non-sequential) multi-photon double ionization in which the energy of all photons is continuously shared by the two emitted electrons:  $n \hbar \omega = E_f - E_i + \varepsilon_1 + \varepsilon_2$ .

### 8.2.1. Internal conversion (InternalConversion)

#### Process, notation & application:

- **Internal conversion** of an atom or ion:  $A^{q+} + \text{nucleus}^* \longrightarrow A^{(q+1)+*} + e_c^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \text{nucleus}^*(\{\mathbb{M}\}, \mathcal{E}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + e_c^-(\mathbf{p}, m_s)$  or  $|\alpha_i \mathbb{J}_i\rangle + \text{nucleus}^*(\{\mathbb{M}\}, \mathcal{E}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon \kappa\rangle$ ,  $\varepsilon = \mathcal{E} - (E_i - E_f)$
- Here, the excited nucleus decays under the release of the energy  $\mathcal{E}$  by (several) multipoles  $\{\mathbb{M}\}$  and , leading to an emitted electron with well-defined kinetic energy  $\varepsilon$ .
- **Internal conversion:** formally refers to the decay an excited nucleus to its ground or some lower-lying level, and where the excitation energy is given to a (bound) electron, leading to an ionization of the atom or ion. In general, the internal (energy) conversion competes with the gamma-ray emission as well as the formation of a electron-positron pair for nuclear excitation energies above 1.022 MeV.
- Often, the continuum wave of the outgoing electron has been calculated in the (final-state) atomic potential with a vacancy in the inner shell. Sometimes, however, this hole has been disregarded, leading to differences in the internal conversion coefficients as large as  $\sim 15\%$  for low kinetic energies  $\varepsilon \sim 1$  keV and  $L = 5$  transitions.

#### Nuclear decay by internal conversion:

- The internal conversion is more than a simple photoionization process, in which an emitted  $\gamma$  photon leads to the emission of electrons, but refers to an **alternative de-excitation of excited nuclei**.
- **Electron conversion coefficient:** In the internal conversion process, an atomic electron is ejected from one of the atomic shells. The electron conversion coefficient is defined as the probability ratio for emitting an atomic electrons from shell  $x$  to the emission of a  $\gamma$ -ray,  $a_x = P_x / P_\gamma$ .
- The kinetic energy of the emitted electron  $\varepsilon = \Delta E_{\text{nuc}} - E_b$  can be deduced from the nuclear transition energy, the binding energy of the atomic electron and the recoil energy of the emitting atom, which is typically very small. Transitions involving conversion electrons are only possible if  $\varepsilon > 0$ .

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- The internal conversion process (ICP) has been found a versatile tool for studying nuclear structure. In particular, the measurement and analysis of **conversion electron spectra reveal possible transitions between nuclear levels**. From the comparison of these spectra with calculated internal conversion coefficients, it is **often possible to assign a unique multipolarity to the nuclear gamma radiation** and, hence, a total angular momentum and parity to the excited nuclear states.
- The internal conversion coefficients can provide detailed information about the atomic nucleus if theoretical and experimental values are compared for transitions of different multipolarity and mixing ratios. A detailed knowledge of these coefficients is needed, for instance, for deriving absolute transition rates and for the normalization of decay schemes, for Mössbauer spectroscopy, for nuclear reaction computations as well as for the calculation of the decay heat of the fuel cells of nuclear reactors.
- **The internal conversion process is largely independent of the nuclear structure, although a non-zero probability requires a finite nuclear size and a finite probability of the electron to be found inside of the nucleus**. For highly suppressed transitions, this finite-size effect can become quite significant. For these transitions, Pauli developed formulae to correct the theoretical conversion coefficient for both, the electric and magnetic multipolarities.

### General theory:

- The internal conversion can be described as QED process by the retarded interaction of charges.
- In particular, the internal conversion is a second-order quantum-electrodynamical process in which a virtual photon is exchanged between the nucleus (proton) and an electron.
- **Internal conversion amplitude:** The (single-electron) matrix element of the conversion transition can be written in terms of the Hamiltonian (Listengarten 1961; Band *et al.*, 2002)

$$\langle f | \mathbb{H}^{(\text{conversion})} | i \rangle = -e \int d^3\mathbf{r} \psi_f^*(\mathbf{r}) [\Phi(\mathbf{r}) + \boldsymbol{\alpha} \cdot \mathbf{A}(\mathbf{r})] \psi_i(\mathbf{r}),$$

where  $\Phi(\mathbf{r})$  and  $\mathbf{A}(\mathbf{r})$  are the time-independent parts of the scalar and vector potentials of the electro-magnetic field that arise due to the **nuclear transition charges and currents**, and by including the retardation of these interactions.

➤ The retarded potentials in the internal conversion amplitude above are

$$\begin{aligned}\Phi(\mathbf{r}, t) &= e^{-i\omega t} \Phi(\mathbf{r}), & \Phi(\mathbf{r}) &= \int d^3\mathbf{R} \frac{\rho(\mathbf{R})}{|\mathbf{r} - \mathbf{R}|} e^{ik|\mathbf{R} - \mathbf{r}|} = \sum_{LQ} \Phi_{LQ}(\mathbf{r}) \\ \mathbf{A}(\mathbf{r}, t) &= e^{-i\omega t} \mathbf{A}(\mathbf{r}), & \mathbf{A}(\mathbf{r}) &= \frac{1}{c} \int d^3\mathbf{R} \frac{\mathbf{J}(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|} e^{ik|\mathbf{R} - \mathbf{r}|} = \sum_{LQ} \mathbf{A}_{LQ}(\mathbf{r})\end{aligned}$$

with the wavenumber  $k = \omega/c = \mathcal{E}/\hbar c$ , and where  $\mathbf{r} = (r, \vartheta, \varphi)$  and  $\mathbf{R}$  are the coordinates of the electron and nucleus (proton), respectively.

➤ Here, we shall not go into further details for the representation of these potentials but just note that these interaction potentials can be written as a sum over multipole contributions as well as in terms of the nuclear charge density  $\rho(\mathbf{R})$  and current density  $\mathbf{J}(\mathbf{r})$  of the bound electrons, respectively.

### Internal conversion coefficients:

➤ **Internal conversion coefficient:** The internal conversion coefficient is defined as the ratio of the number of electrons  $N_e$  ejected from the atomic shell  $(n\ell)$  to the number of gamma quanta  $N_\gamma$  leaving the atom during the same time:

$$\alpha^{(\text{conversion})}(n\ell) = \frac{N_e}{N_\gamma}, \quad \alpha^{(\text{conversion})}(\alpha_i \mathbb{J}_i) = \sum_f \alpha^{(\text{conversion})}(n\ell)$$

The total internal conversion coefficient of a given (initial) level  $\alpha^{(\text{conversion})}(n\ell)$  of the nucleus is the sum of partial conversion coefficient associated with all possible ionization channels (lines) of the atom or ion.

➤ Internal conversion coefficients have been tabulated in a larger number of tables and compilations; in these tabulations, the screening of the nuclear electric field by the atomic electrons was often treated in the framework of either some statistical Thomas-Fermi-Dirac or Dirac-Fock-Slater models.

➤ For different  $x_\alpha$  pre-factors in the Dirac-Fock-Slater (type) potentials, the differences in the calculated conversion coefficients are typically small  $\sim 1\%$  for  $K$ -shell electrons but may increase to  $\sim 70\%$  for outer electrons or even larger for low kinetic energies of the conversion electron ( $\leq 1$  keV). The question of whether the electronic hole should be taken into account into the atomic potential has been explored previously but seem to have a minor role only.

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- A new internal conversion coefficient database BRICC has been developed that includes various tabulations of internal electron conversion (IECC), internal electron-positron pair conversion coefficients (IPCC) as well as the *electronic* factors  $\Omega(E0)$ .
- Theoretical conversion coefficients  $\alpha^{(\text{internal-conversion})}$  are associated with two kinds of uncertainties: (i) due to the physics model that is used in the computations and (ii) due to the spline interpolation that is frequently used in order to generate the tabulations. The physics model is typical based on assumptions about the atomic nucleus and the electron density.

### 8.2.m. Electron capture with nuclear decay

#### Process, notation & application:

- **Electron capture** of an atom or ion by nuclear decay:  $A(Z+1) + e^- \longrightarrow A(Z) + \nu_e$
- **Quantum notations used in the formulas below:**  $E_\nu = Q^+ - E_f - E_b > 0$
- Here, the nucleus decays by capturing an atomic electron (often from the K-shell), and under the emission of an electron neutrino. Here,  $Q^+$  is the energy difference due to the rest masses of the parent and daughter nucleus,  $E_f$  the energy of the final nuclear state of the daughter nucleus and  $E_b$  the binding energy of the captured electron. The release energy  $E_\nu$  will be shared between the emitted neutrino and, possible, some bremsstrahlungs photon or the shake-up/shake-off of a valence electron.
- For allowed nuclear transitions, nearly all vacancies occur in the  $ns$  shells of the atoms or ions, i.e. in the K,  $L_1$ ,  $M_1$ , ... shells.

## 8.3. Further processes, not yet considered in JAC

### 8.3.a. Coulomb ionization (CoulombIonization)

#### Process, notation & application:

- Coulomb ionization by fast, heavy ions:  $A^{(q+1)+} + Z_p \longrightarrow A^{(q+1)+(*)} + e^- + Z'_p$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + Z_p(\dots) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + e^-$
- The Coulomb ionization of projectile ions by target atoms leads to a different charge state of the ions and often determines their lifetime in storage rings.
- If one of the projectile electrons is ionized, the ion is lost from the ring since it will be misbent by subsequent steering magnets.

#### Perturbative calculation of ionization cross sections:

- Semi-relativistic treatment of the Coulomb ionization: In their semi-relativistic treatment, Anholt and Becker (1987) distinguish three contributions to the ionization cross sections due to Coulomb ionization, transverse ionization, and the ionization due to the spin-flip of the ionized electron. These three contributions have different asymptotic behaviour in ultra-relativistic collisions. — In this approach, the Coulomb ionization cross section is the same as in the plane-wave Born approximation for nonrelativistic projectiles.
- The Coulomb part is dominant at nonrelativistic energies, while the transverse part mainly arise from the magnetic interactions at large impact parameters.
- The cross section for the (projectile) ionization of a  $1s$  electron increases as  $\ln \gamma$  due to the transverse interaction for high projectile energies and if the target screening is neglected. This transverse interaction is however screened and reduced if the charge of the projectile is smaller than those of the target,  $Z_p < Z_t$ .
- For fast collisions and for impact parameters  $b$  comparable with, or larger than the ionic  $K$ -shell radius, the perturbation of the target atom by the projectile can be treated in first-order time-dependent perturbation theory, even for high- $Z$  projectiles.
- Perturbation theory breaks generally down for high- $Z$  projectiles (or high- $Z$  targets). For these high- $Z$  projectiles, an approximate scaling rule for the ionization probability at high relativistic energies ( $\gamma > 5$ ) and fixed impact parameters has been established by numerical calculations. For  $b = 0$ , for example, the ionization probability  $P(b = 0) = 1.8 \times 10^{-4} Z_p^2$  is independent of the target charge within about  $\pm 10\%$  up to the heaviest elements.

### 8.3.b. Bremsstrahlung (BremsStrahlung)

#### Process, notation & application:

- Bremsstrahlung emitted by an electron in the field of an atom or ions  $A^{q+} + e_i^- \longrightarrow A^{(q)+*} + e_f^- + \hbar\omega$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle + \hbar\omega(\mathbb{M})$
- Bremsstrahlung arises generally if a charged particle is decelerated or deflected by another charged particle, often an electron or nucleus, and if parts of its kinetic energy is converted into radiation.
- More generally speaking, bremsstrahlung or braking radiation refers to any radiation that arises due to the deceleration of charged particle, including synchrotron radiation from relativistic particles or cyclotron radiation from non-relativistic particles.
- In atomic physics, bremsstrahlung often refers to the radiation from electrons that are slowed down in matter.
- Atomic bremsstrahlung: This term sometimes refers also to the polarized radiation that arise from the Coulomb field of the incident charged particle.
- Bremsstrahlung has a continuous spectrum and a peak intensity that shifts toward higher frequencies with an increasing energy transfer from the decelerated particles.

### 8.3.c. Inverse bremsstrahlung

#### Process, notation & application:

- Inverse bremsstrahlung of a charged particle in the field of an atom or ions  $\hbar\omega + A^{q+} + e_i^- \longrightarrow A^{(q)+} + e_f^-$
- Quantum notations used in the formulas below:  $\hbar\omega(\mathbb{M}) + |\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle$
- In the inverse bremsstrahlung process, a free electron gains kinetic energy due to the absorption of a photon.



### 8.3.d. Radiative recombination & fluorescence

#### Process, notation & application:

- Radiative recombination & fluorescence of an ion:  $A^{q+} + e_s^- \longrightarrow A^{(q-1)+,*} + \hbar\omega_r \longrightarrow A^{(q-1)+} + \hbar\omega_r + \hbar\omega_f$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_r \mathbb{J}_r\rangle + \hbar\omega_r(\mathbb{M}_r) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega_r(\mathbb{M}_r) + \hbar\omega_f(\mathbb{M}_f)$
- In the photorecombination & fluorescence process, also known radiative recombination (RR) or radiative electron capture (REC), an electron is captured by the ion into an excited state that subsequently decay under fluorescence emission.

### 8.3.e. Resonant two-color (two-photon, single-electron) ionization

#### Process, notation & application:

- Resonant two-color (two-photon, single-electron) ionization of an ion:  $A + \hbar\omega + \hbar\omega' \longrightarrow A^* + \hbar\omega' \longrightarrow A^{+*} + e_p^-$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) + \hbar\omega'(\mathbb{M}') \longrightarrow |\alpha_r \mathbb{J}_r\rangle + \hbar\omega'(\mathbb{M}') \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon \kappa\rangle$
- In the resonant two-color photoionization, an atom or ion is resonantly excited by one photon and subsequently ionized by a second photon of the same or some different frequency.

### 8.3.f. Interference of multi-photon ionization channels (MultiPhotonInterference)

#### Process, notation & application:

- Interference of *non-resonant* one-photon ( $2\omega$ ) and *resonant* two-photon ( $\omega$ ) ionization of an atom or ion:

$$A + \left[ \begin{array}{c} \hbar(2\omega) \\ \hbar\omega + \hbar\omega \end{array} \right] \longrightarrow A^{+(*)} + e_p^-$$

- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \left[ \begin{array}{c} \hbar(2\omega) \\ \hbar\omega + \hbar\omega \end{array} \right] \longrightarrow |\alpha_i \mathbb{J}_i\rangle + |\varepsilon \kappa\rangle$
- The two-pathway quantum interference has been explored in order to better understand the quantum control of atoms and ions.
- Such quantum control studies were initially stimulated by the small fraction of the second harmonic that typically arise at XFEL and that cannot so easily be filtered out, though it may strongly influence the experimental from two-photon ionization experiments. Despite of the rather small intensity of the second harmonic, the ionization by photons with frequency  $2\omega$  (second harmonic, first-order process) can readily compete with, or even dominate, the two-photon ionization by photons with frequency  $\omega$ .

### Interference of non-res. one-photon ( $2\omega$ ) and resonant two-photon ( $\omega$ ) ionization:

- Experimental signals: For a linearly-polarized bichromatic beam, the interference due to different quantum paths manifests itself in an asymmetry of the photoelectron angular distributions (PAD) with respect to the plane that is perpendicular to the electric field of the incident radiation; cf. Grum-Grzhimailo *et al.*(2015).
- Photoelectron angular distribution (PAD): In the dipole approximation and for an isotropic target, this angular distribution must be axially symmetric with regard to the polarization direction

$$\frac{dW}{d\Omega} = \frac{W_o}{4\pi} \left[ 1 + \sum_{k=1}^K \beta_k P_k(\cos \vartheta) \right]$$

where  $\vartheta$  is the angle of the photoelectron with regard to the polarization direction (**E**-field) and  $\beta_k$  the corresponding anisotropy parameters, which can expressed in terms of the photoionization amplitudes.

- For the interference of one-photon and two-photon ionization paths, all terms with  $k = 1, 2, 3, 4$  must be taken into account in the PAD above. The odd polynomials arises from the photoelectron partial waves with opposite parities due to the ininteraction of the atom with the fundamental and second harmonic of the radiation.
- The quantum interference of absorption amplitudes with an even and odd number of photons, such as  $(\omega + 2\omega)$  photoionization, does not modify the total yield but only affect the angle-resolved observations. The interference between an even or odd number of photons lead to photoelectron partial waves with opposite parities.
- Interference in photoionization: Many photoionization experiments have been performed in order to better understand the concept of quantum-mechanical interference. Interference in photoionization occurs since the phase of the incident photons is eventually imprinted upon

the wave of the emitted electron. Apart from cross sections, this phase imprint enables one to extract the phases from the measurements, and which could not be derived for classical particles.

- **Interference in photoionization:** Using a seeded free-electron laser, first coherent optical experiments have been performed also at short wavelengths; in these experiments, high xuv harmonics have been utilized to coherently control the outcome of experiments by controlling the electron beam in the accelerator. Such a control requires to precisely know both, the amplitude and phase of each harmonic.
- **Time-dependent electric field in two-color experiments:** In two-color experiments, the field is often approximated by (DiFraia *et al.*, 2019)

$$\mathcal{E}(t) = \sqrt{I_\omega(t)} \cos \omega t + \sqrt{I_{2\omega}(t)} \cos(2\omega t - \phi), \quad \boldsymbol{\mathcal{E}}(t) = \mathcal{E}(t) \mathbf{e}_z,$$

and where  $I_\omega(t)$ ,  $I_{2\omega}(t)$  are the envelopes of the two pulses and  $\phi$  the relative phase between the  $\omega - 2\omega$  pulses. In this definition, the larger  $\phi$  as more the  $2\omega$  pulse is delayed.

### 8.3.g. Two-color multi-photon interference ionization (TwoColorInterferenceIon)

#### Process, notation & application:

- **Two-color multi-photon interference ionization** of an ion:  $A + m\hbar\omega + n\hbar\omega' \longrightarrow A^{+*} + e_p^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + m\hbar\omega(\mathbb{M}) + n\hbar\omega'(\mathbb{M}') \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon\kappa\rangle$
- In the two-color multi-photon interference ionization, an atom or ion emits an electron whose angular distribution is affected by the interference of different ionization paths.

### 8.3.h. Two-photon above-threshold ionization (ATI) (TwoColorInterferenceIon)

#### Process, notation & application:

- **Two-photon above-threshold ionization** of an ion:

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➤ Quantum notations used in the formulas below:

➤ Petrov *et al.* (2019) considered the two-photon  $3p$  ionization of argon:  $\text{Ar } 3p^6 + 2\gamma \longrightarrow 3p^5 \varepsilon \kappa$  with  $\varepsilon > \hbar\omega$ .

### 8.3.i. Double photoionization (DoublePhotoIonization)

#### Process, notation & application:

➤ Simultaneous double photoionization of an atom or ion:  $A^{q+*} + \hbar\omega \longrightarrow A^{(q+2)+(*)} + (e_{p_1}^- + e_{p_2}^-)$

➤ Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle$

➤ The (direct) double photoionization of atoms has attracted much interest during the last decades as the emission of a second electron is caused by the electron-electron interaction.

➤ The recent advancements of free electron lasers (FEL) has lead to intense short pulses with rather high photon energies, and which may help investigate the (direct) double photoionization process for multiply charged ions.

#### Cross sections:

➤ Triple-differential cross section for the double ionization of polarized atoms: If one expresses the cross section in terms of the solid angles  $\Omega_{1,2}$  of the two electrons as well as the energy  $E_1$  of one of the emitted electrons, this (five-fold differential) cross section can be written as trace over the final-state density matrix  $\rho_f$

$$\frac{d^3 \sigma}{d\Omega_1 d\Omega_2 dE_1} = c \text{Tr} \rho_f = c \text{Tr} (R \rho_i R^+) = c \text{Tr} (D \rho^\gamma \rho_i R^+),$$

where  $\rho^\gamma$  is the photon density matrix and  $c$  just a kinematically determined normalization constant. Usually, this expression is evaluated in a basis with well-defined symmetry  $\mathbb{J}$ .

➤ Within the density matrix and the statistical tensor formalism, the triply differential cross section for single-photon double ionization from above can be written as (Berakdar and Kabachnik, 2005)

$$\frac{d^3 \sigma}{d\Omega_1 d\Omega_2 dE_1} = c \sum_{\alpha\alpha' \mathbb{J}\mathbb{J}' kq} \rho_{kq}^f(\alpha\mathbb{J}, \alpha'\mathbb{J}') \epsilon_{kq}^*(\alpha\mathbb{J}, \alpha'\mathbb{J}')$$

where  $\rho_{kq}^f(\alpha\mathbb{J}, \alpha'\mathbb{J}')$  is the final-state statistical tensor of the “ion + two electrons” with symmetries  $\mathbb{J}$  and  $\mathbb{J}'$  and where  $\epsilon_{kq}(\alpha\mathbb{J}, \alpha'\mathbb{J}')$  denotes the efficiency tensor of the detector system to record these final states. Here, the summation over  $\alpha, \alpha'$  refers to all other quantum numbers which remain unobserved.

- **Final-state density matrix:** The final-state density matrix of the “photoion + two free electrons” can be expressed in terms of the statistical tensors of the total initial state “atom + photon” as well as the reduced electron-photon (photoionization) amplitudes (Berakdar and Kabachnik, 2005)

$$\begin{aligned} \rho_{kq}^f(\alpha\mathbb{J}, \alpha'\mathbb{J}') &= \sum_{k_o q_o k_\gamma q_\gamma} [k_o, k_\gamma]^{1/2} \langle k_o q_o, k_\gamma q_\gamma | kq \rangle \begin{Bmatrix} J_o & 1 & J \\ J_o & 1 & J' \\ k_o & k_\gamma & k \end{Bmatrix} \rho_{k_o q_o}(\alpha_o \mathbb{J}_o) \rho^\gamma(P_1, P_2, P_3) \\ &\quad \times \langle \alpha\mathbb{J} || \mathbb{O}^{(\text{photoionization})} || \alpha_o \mathbb{J}_o \rangle \langle \alpha'\mathbb{J}' || \mathbb{O}^{(\text{photoionization})} || \alpha_o \mathbb{J}_o \rangle^*. \end{aligned}$$

- Although such expressions for the (triple-differential) cross sections appear to be rather complex, they can be handle quite easily in JAC.

### Single-photon multiple ionization:

- **Single-photon multiple ionization:** The direct multiple ionization of atoms and ions by single photons is perhaps the simplest many-body process. Such a simultaneous release of two or more electrons is caused by interelectronic correlations and is very different from the (typical) inner-shell excitation or ionization of atoms and the subsequent autoionization. Therefore, the direct double (multiple) ionization is sensitive to details of the electron-electron interaction, and this applies especially for negative ions.
- **Direct multiple ionization:** While a direct multiple photoionization has been observed for both, positive and negative ions, a clear separation of the direct and sequential ionization processes is often difficult.

### 8.3.j. Double-Auger decay (DoubleAuger)

#### Process, notation & application:

- **Simultaneous double Auger electron emission (autoionization)** of an atom or ion:  $A^{q+*} \longrightarrow A^{(q+2)+(*)} + (e_{a_1}^- + e_{a_2}^-)$

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- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle$
- An autoionization of an atom may occur also via the simultaneous emission of two electrons which share the overall excess energy.
- The (direct) double Auger (DA) emission is an important second-order processes in which two electrons are ejected simultaneously from an inner-shell excited atom. A first evidence of the direct DA was found in *K*-shell photoionization experiments of neon with photon energies between 867 and 913 eV by Krause and coworkers (1965) as well as for argon.
- For the decay of a Ne 1s-hole, already Carlson and Krause (1965) found an about 8 % portion of Ne<sup>3+</sup> ions due to the simultaneous double Auger decay. This portion occurs in contrast to the  $\lesssim 1$  % prediction from a simple shake-off model.

### 8.3.k. Positron-annihilation-induced autoionization

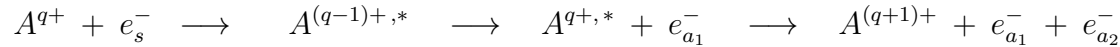
#### Process, notation & application:

- Positron-annihilation-induced autoionization of an ion: ...
- Quantum notations used in the formulas below:
- Positron-annihilation-induced Auger electron spectroscopy (PAES): This positron-induced autoionization help explore surface structures and the observation of segregation processes. The time-dependent PAES has been utilized as a novel technique for the selective investigation of, e.g. heterogeneous catalysis, corrosion, or surface alloying.
- Mayer *et al.* (2010) applied the time-resolved PAES for the first time in order to determine the time constant for segregation as well as the final segregated configuration at the surface. For Cu-Pd alloys, for example, the amount of Cu atoms and their exact position was found to strongly affect the mechanical stability and the catalytic properties of Pd membranes. These authors also investigated the stability and dynamics of thin Cu layers on the surface of poly-crystalline Pd. When compared with the electron-induced Auger electron spectroscopy, the PAES appears intrinsically to be sensitive to the topmost atomic layer of a sample. These experiments were performed by means of the high intensity neutron-induced positron source Munich (NEPOMUC) which delivers about 10<sup>9</sup> monoenergetic positrons per second.
- Positron affinity: PAES is a highly selective technique for selecting specific atoms at surfaces because of the quite different positron affinities of the surface atoms. If more than a single element is present at some surface, the positrons are attracted to and annihilated with those atoms that have a higher relative positron affinity. Because of the high positron affinities of Pd, the positron will likely annihilate with electrons from Pd atoms in a Cu-Pd alloy, if such atoms are within the diffusion length of the positron at the surface.

### 8.3.l. Resonant excitation with sequential double autoionization (RESDA):

#### Process, notation & application:

- Resonant excitation with sequential double autoionization (RESDA) of an ion: ...



- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_m \mathbb{J}_m\rangle \longrightarrow |\alpha_n \mathbb{J}_n\rangle + |\varepsilon_1 \kappa_1\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle$
- Lithium-like ions are perhaps the simplest ions in which a RESDA can occur. This process can be observed by measuring the ratio of the numbers of trapped ions of two neighbouring charge states as a function of electron energy within an electron beam ion trap.

### 8.3.m. Resonant excitation with direct double autoionization (REDDA):

#### Process, notation & application:

- Resonant excitation with direct double autoionization (REDDA) of an ion: ...



- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_m \mathbb{J}_m\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle$
- In the REDDA process, an electron is resonantly captured into a (doubly) excited level that subsequently decays by the simultaneous emission of two electrons, a so-called double autoionization, and where the two electrons share the overall excess energy.

### 8.3.n. Radiative double electron capture

#### Process, notation & application:

- Radiative double electron capture (RDEC) of an ion:  $A^{q+*} + e_1^- + e_2^- \longrightarrow A^{(q-2)+} + \hbar\omega$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_1 \kappa_1\rangle + |\varepsilon_2 \kappa_2\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega(\mathbb{M})$
- The radiative double electron capture (RDEC) is the time-reversed process of the single-electron direct double photoionization; it includes the transfer of two target electrons into a bound state of the projectile under the simultaneous emission of a single photon. Indeed, RDEC can be considered as the simplest and (almost) background-free tool for studying electron-electron correlations in high- $Z$  ions.
- Experimental evidence: Simon *et al.* (2010) have presented experimental evidence of radiative double electron capture in the collision of 38 MeV  $O^{8+}$  with a carbon foil. When compared to theoretical cross sections, the experiments suggest a 5 times larger cross sections. This discrepancy may arise from the fact that no capture into excited states were included into the computations and that the electrons were considered as quasi-free in all computations.
- The (non-resonant) radiative electron capture is known to be dominant for fast collisions of heavy ions with light target atoms and shows a rather weak dependence on the inter-electron interaction between the projectile and target ions. The RDEC is a single-step process where the energy of two correlated captured electrons are converted into the energy and momentum of one emitted photon (Chernovskaya *et al.*, 2011).
- The RDEC can be described as the inverse process to double photoionization. Indeed, RDEC can be seen as a prominent tool for investigating the role of interelectronic interactions in the process of ion-atom collisions.

### 8.3.o. Generalized oscillator strengths (GOS)

#### Process, notation & application:

- Inelastic scattering of high-energetic photons or electrons The generalized oscillator strengths has been utilized to describe the inelastic scattering of high-energetic photons or fast electrons at atoms. This inelastic scattering has been discussed quite early by Bethe (1931) but has received less attention afterwards.
- Inelastic scattering of a fast electron by an atom or ion:  $A^{q+} + e_s^- \longrightarrow A^{r+} + e_s^{-'}$  with  $r \geq q$ .



- The notion of GOS has been introduced if only the effective scattering cross section (strength) is of interest and if all the other released electrons are neglected from the theoretical treatment.

### GOS expressions:

- **Fast electron impact:** The GOS for an excitation of the atom by fast electrons has been expressed as (Zhu *et al.*, 2006)

$$f(E, K) = \frac{E}{2} \frac{p_i}{p_f} K^2 \frac{d\sigma}{d\Omega} = \frac{2E}{K^2} |\langle \alpha_f \mathbb{J}_f M_f | T_1(\mathbf{K}) | \alpha_i \mathbb{J}_i M_i \rangle|^2,$$

where  $E$  is the excitation energy,  $K$  the momentum transfer,  $p_i, p_f$  the incident and scattered electron momenta, while  $\frac{d\sigma}{d\Omega}$  refers to the differential scattering cross section of the incident electron.

### 8.3.p. Electron-impact ionization (ImpactIonization)

#### Process, notation & application:

- **Electron-impact ionization** of an atom or ion:  $e_s^- + A \longrightarrow A^* + e_s'^- + e^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle + |\varepsilon_c \kappa_c\rangle$  where  $|\varepsilon_c \kappa_c\rangle$  is the initially bound *atomic* electron.
- The electron-impact ionization process is important in all (high-temperature) plasma, both in astro and plasma physics, and elsewhere. It is the inverse process to the three-body recombination,  $A + e^- \longleftrightarrow A^+ + e_1^- + e_2^-$ .
- We refer to the three *free* electrons, that are involved in this process, as **incident, (final-) scattered and additional (-ly released) electron**, and with the corresponding indices above.
- **Electron-impact ionization cross sections:** In the distorted-wave approximation, the differential (in energy) electron-impact ionization cross sections can be obtained from the formulas of the electron-impact excitation cross section, if the excited bound electron is replaced by another continuum electron. Unfortunately, such a replacement increases the number of ionization channels considerably, since now formally two *free* electrons need to be coupled to the final state of the residual ion and since a summation has to be made over all (total) angular momenta of the scattering states with two free electrons. Here, a clean notation for all incoming and outgoing electron waves is crucial to retain the application of such electron-impact ionization for different physical scenarios. Until the present, most derivation have been made with specific assumptions about the electron-impact ionization cross sections, and often in a rather intransparent notation.

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- **Total electron-impact ionization cross sections:** The total ionization cross section is obtained by integrating over the energy-differential cross section up to the threshold energy  $\varepsilon^{(\text{threshold})} = \varepsilon_i - (E_f - E_i)$

$$\sigma(\varepsilon_i) = \int_0^{\varepsilon^{(\text{threshold})}} d\varepsilon \frac{d\sigma}{d\varepsilon}(\varepsilon, \varepsilon_i).$$

Since the energies  $\varepsilon_i, \varepsilon$  enter also all the radial integrals, these integrals must often be interpolated/extrapolated in order to keep the computation of electron-impact ionization cross sections feasible at all.

- **Direct ionization rate coefficients:** Mazotta *et al.* (1998) display a parametrization of the direct (electron-impact) ionization rate coefficients as function of the electron temperature

$$\alpha^{(\text{direct ionization})}(T_e; \alpha_i \mathbb{J}_i) = \frac{6.69 \cdot 10^7}{T_e^{3/2}} \sum_j \frac{\exp(-x_j)}{x_j} F(x_j), \quad x_j = \frac{I_p(n_j) [\text{eV}]}{T_e [\text{eV}]}, \quad [\text{cm}^3/\text{s}].$$

Here, the summation runs over all occupied shells  $j$ , and the ionization potentials are assumed to be given in eV. Although Mazotta *et al.* (1998) display the function  $F(x_j)$  is displayed, no further remarks are made about the validity of this parametrization. Very likely, this direct ionization rate coefficients just accounts for the electron-impact ionization but no photoionization contributions. A parametrization of these ionization rate coefficients are available for selected ions and combined with interpolations.

### Cross sections:

- **Electron-impact ionization cross section:** These cross sections are obtained rather similarly as the electron-impact excitation cross sections but by allowing an **ionizing transition between fine-structure levels**  $\alpha_i \mathbb{J}_i(N) \rightarrow \alpha_f \mathbb{J}_f(N-1)$  (Fontes *et al.* 2015)

$$\sigma^{(\text{ionization})}(\alpha_i \mathbb{J}_i, \alpha_f \mathbb{J}_f) = \frac{8}{k_i^2 g_i} \sum_{\mathbb{J}_c, \mathbb{J}_t} (2J_s + 1) \sum_{\kappa_i \kappa_f \kappa_e} \int_0^{\varepsilon_i - I_p} \varepsilon' \left| \langle ((\alpha_f \mathbb{J}_f, \epsilon_c \kappa_c) \mathbb{J}_c), (\epsilon_f \kappa_f) \mathbb{J}_t \parallel \mathbb{V}^{(e-e)} \parallel (\alpha_i \mathbb{J}_i, \epsilon_i \kappa_i) \mathbb{J}_t \rangle \right|^2$$

- This cross section contains a summation over all possible values  $\mathbb{J}_t$  of the initial ion and the (incoming) incident electron in the partial wave  $|\varepsilon_i \kappa_i\rangle$ .

### 8.3.q. Electron-impact multiple ionization

#### Process, notation & application:

- **Electron-impact multiple ionization** of an atom or ion:  $e_s^- + A \longrightarrow A^* + e_s'^- + e_a^- + e_b^- + \dots$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle + |\varepsilon_a \kappa_a\rangle + |\varepsilon_b \kappa_b\rangle + \dots$   
 where  $|\varepsilon_a \kappa_a\rangle$ ,  $|\varepsilon_b \kappa_b\rangle$ , ... refer to the initially bound *atomic* electrons.
- To describe the **multiple ionization in electron-impact processes**, one needs to consider the (electron-impact) excitation, ionization as well as several resonant excitation processes. This is usually done in the **isolated resonance approximation**, in which all the processes are treated independently. The multiple ionization is then obtained from a proper summation over individual decay pathways and branching ratios.
- **Charge state distribution (CSD) in plasma:** Electron-impact double and multiple ionization plays a central role upon the charge state distribution of a plasma if the electron temperature changes rapidly either in time or space.
- For a plasma in a **collisional-ionization equilibrium**, the CSD is determined by the balance between electron-ion recombination and electron-impact – single and multiple – ionization. Therefore, accurate electron-impact excitation and ionization cross sections are important for plasma diagnostics over a wide range of plasma (electron) temperatures, electron densities and elemental abundancies.

### 8.3.r. Three-body recombination

#### Process, notation & application:

- **Three-body recombination** of an ion:  $A^{q+} + e_i^- + e_c^- \longrightarrow A^{(q-1)+} + e_f^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle + |\varepsilon_c \kappa_c\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle$
- The three-body recombination of an ion is the inverse process of the electron-impact ionization.
- The three-body recombination combination of an electron results in the capture of an electron by an positive ion due to energy and momentum transfer of the (captured) free electron to another free electron in the neighborhood of the atom or ion.
- **Three-body recombination:** For low-temperature afterglow and recombination-laser plasmas, the three-body collisional recombination to higher levels and deexcitation between higher levels are often dominant.

### 8.3.s. Elastic scattering of electrons and ions

#### Process, notation & application:

- **Elastic scattering of electrons and positrons** by atoms and ions of an ion:  $A^{q+} + e_i^- \longrightarrow A^{q+} + e_f^-$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle^+$
- **Potential scattering of relativistic electrons and positrons:** The scattering of relativistic electrons or positrons by a – real or complex – central-field  $V(r)$  is **completely described by the direct scattering amplitude  $f(\vartheta)$  and the spin-flip scattering amplitude  $g(\vartheta)$** , which are both complex functions of the polar scattering angle  $\vartheta$ .
- These scattering amplitudes are derived from the asymptotic behaviour for  $r \rightarrow \infty$  of the distorted plane-wave solutions of the Dirac equation *plus* an outgoing spherical wave.

#### Static scattering potentials:

- **Static-field approximation:** This approximation only includes the (electro-) static potential *plus* approximate local exchange potential for the interaction between the incoming or outgoing electron and the (target) ion. For electrons with kinetic energies  $E_{\text{kin}} \lesssim 10$  keV, moreover, one often includes optionally a semi-empirical correlation-polarization potential in order to account for the dynamically induced polarization of the target.
- **Local exchange potential:** For electron scattering processes, three simple analytical approximations for a local exchange potential refer to the Thomas-Fermi, Furness-McCarthy as well as the Riley-Truhlar potential (Salvat *et al.*, 2005).
- **Absorption potential:** For the calculation of elastic scattering cross sections, it is sometimes helpful to optionally include an imaginary (absorptive) part into the static potential in order to account for the coupling with inelastic channels.
- **Exchange potential:** For in- and/or outgoing electrons, a possible exchange with a bound electron need to be taken into account as it occurs naturally if all electrons are treated together by an (antisymmetrize) Slater determinant. In general, however, these exchange terms in the Dirac-Hartree-Fock equations are difficult to deal with and are often approximated in some suitable form.

### Scattering amplitudes and cross sections:

- **Partial-wave expansion of the scattering amplitudes:** For a projectile with wave number  $k = \hbar/p$  and kinetic energy  $E$ , the direct and spin-flip scattering amplitudes are given by

$$f(\vartheta) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} \{ (\ell+1) [\exp(2i\delta_{\kappa=-\ell-1}) - 1] + \ell [\exp(2i\delta_{\kappa=\ell}) - 1] \} P_{\ell}(\cos \vartheta)$$

$$g(\vartheta) = \frac{1}{2ik} \sum_{\ell=0}^{\infty} [\exp(2i\delta_{\kappa=\ell}) - \exp(2i\delta_{\kappa=-\ell-1})] P_{\ell}^1(\cos \vartheta), \quad (c\hbar k)^2 = E(E + 2mc^2),$$

and where  $P_{\ell}^1(x)$  is an associated Legendre function. The scattering amplitudes above apply for both, electrons and positrons if the sign of their charges is taken into account, and which turns an attractive potential into a repulsive potential and *vice versa*.

- Analogue to non-relativistic theory, **attractive potentials are generally associated with positive phase shifts and repulsive potentials with negative phase shifts.**
- **Elastic differential and total CS:** (Salvat *et al.*, 2005)

$$\frac{d\sigma^{(\text{elastic})}}{d\Omega} = |f(\vartheta)|^2 + |g(\vartheta)|^2, \quad \sigma^{(\text{elastic})} = \int d\Omega \frac{d\sigma^{(\text{elastic})}}{d\Omega} = 2\pi \int_0^{\pi} d\vartheta \sin \vartheta \frac{d\sigma^{(\text{elastic})}}{d\Omega}.$$

### Spin-polarization of elastically scattered electrons:

- **Sherman function:** This function describes the degree of spin polarization of electrons or positrons as function of the scattering angle  $\vartheta$  for an initially unpolarized beam

$$S(\vartheta) \equiv i \frac{f(\vartheta) g^*(\vartheta) - f^*(\vartheta) g(\vartheta)}{|f(\vartheta)|^2 + |g(\vartheta)|^2}.$$

### Applications of elastic scattering:

- **Application of differential elastic cross sections  $\frac{d\sigma^{(\text{elastic})}}{d\Omega}$ :** Accurate differential cross sections (DCS) for the elastic scattering of electrons and positrons by atoms and molecules are required in surface science, electron microscopy, electron-probe microanalysis, the design of radiation detectors, radiation protection, radiation-therapy planning and at several places elsewhere (Salvat *et al.*, 2005). Moreover, DCS for the elastic scattering by positive ions are needed also in order to describe the electron transport in plasmas.

## 8.3.t. Negative-continuum dielectronic recombination

### Process, notation & application:

- **Negative-continuum dielectronic recombination** of an ion:  $A^{q+} + e_s^- \longrightarrow A^{(q-2)+*} + e^+$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_i \kappa_i\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_f \kappa_f\rangle^+$
- The capture of an electron by a bare heavy nucleus may occur non-resonantly via the creation of a free-positron-bound-electron pair. This process is referred to as **negative-continuum dielectronic recombination** since it leads to the capture of (two) electrons into a bound state while a positron is released.

## 8.4. More processes, not yet considered in JAC

### 8.4.a. Nonradiative electron capture (NRC)

#### Process, notation & application:

- **Non-radiative electron capture** of an ion:  $\dots A^{q+} + e^- + Z_t \longrightarrow A^{(q-1)+, (*)} + Z'_t$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_f \kappa_f\rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle$
- The nonradiative electron capture of a quasi-free electron by a projectile ion mainly occurs if the electron and ion velocities match to each other.
- The nonradiative capture is often described within the eikonal approximation, which enables one to estimate the capture from any filled shell of the target to any shell of the projectile.
- In high-Z targets, the nonradiative electron capture into excited states of the projectile is dominant, as predicted by the eikonal calculations and confirmed by measurements.

#### Nonrelativistic capture cross sections:

- In the nonrelativistic theory, the (nonradiative electron capture) cross section of a stationary bare nucleus to capture an electron with energy  $E = \frac{m}{2} v^2$  is given by (Spitzer, 1956)

$$\sigma^{(\text{NRC, non-rel})}(E) = A \sum_{n=1}^{\infty} \frac{\varepsilon_g}{\hbar \omega_n E n^3} g_n,$$

where  $A = 32\pi/\sqrt{27} \hbar e^2/(m^2 c^3) \approx 2.11 \times 10^{-22} \text{ cm}^2$ ,  $\varepsilon_g$  is the ground-state binding energy of the hydrogenic projectile and  $\hbar \omega_n = E - \varepsilon_n$  the emitted photon energy for capture into level  $n$ . The factor  $g_n \approx 1$  is a correction factor which is typically not specified in detail for most computations.

- For  $g_n = 1$ , this cross section can be written

$$\sigma^{(\text{NRC, non-rel})}(E) = A \left( \frac{\varepsilon_g}{E} \right) \sum_{n=1}^{\infty} \frac{1}{n(n^2 + \frac{\varepsilon_g}{E})} = \frac{A \varepsilon_g}{2E} \left\{ \psi \left( 1 + i \sqrt{\frac{\varepsilon_g}{E}} \right) + \psi \left( 1 - i \sqrt{\frac{\varepsilon_g}{E}} \right) + 2\gamma_E \right\}$$

where  $\psi(z) = \frac{1}{\Gamma(z)} \frac{d}{dz} \Gamma(z)$  is the digamma function and  $\gamma_E \approx 0.57772$  is Euler's constant.

## 8. Atomic processes

➤ Using the asymptotic form of  $\psi(z)$ , the cross sections can then be approximated as

$$\sigma^{(\text{NRC, non-rel})}(E) = A \left( \frac{\varepsilon_g}{E} \right) \left[ \gamma_E + \ln \sqrt{\frac{\varepsilon_g}{E}} \right].$$

### Velocity distributions:

➤ Two velocity distributions have been frequently applied to study nonradiative electron capture processes at proton and heavy-ion storage rings.

➤ **Maxwell distribution:**  $f(E) = \frac{1}{(2\pi kT/m)^{3/2}} \exp\left(-\frac{E}{kT}\right).$

➤ **'Flattened' Maxwell distribution:**  $f(E) = \frac{1}{(2\pi kT/m)} \exp\left(-\frac{E}{kT}\right) \delta(v_{\text{ex}})$

which is obtained by suppressing one of the components of velocity.

➤ **Nonradiative electron-capture rates:** By using the asymptotic form of the digamma function in the nonradiative electron capture cross section above but different velocities distributions for the electrons to capture, **various approximations for the capture rates** can be derived. From the capture cross section  $\sigma^{(\text{NRC, non-rel})}(E)$ , the averaged coefficient  $\alpha_r$  can be evaluated analytically for different velocity distributions

$$\alpha_r^{(\text{NRC, non-rel})}(\text{Maxwell}) = \frac{\sqrt{2} A \varepsilon_g}{\sqrt{m, kT}} \frac{2}{\sqrt{\pi}} \left\{ \gamma_1 + \frac{\gamma_E}{2} + \Gamma\left(\frac{4}{3}\right) \gamma_2 \left(\frac{kT}{\varepsilon_1}\right)^{1/3} + \ln \sqrt{\frac{\varepsilon_1}{kT}} \right\}$$

$$\alpha_r^{(\text{NRC, non-rel})}(\text{flattened}) = \frac{\sqrt{2} A \varepsilon_g}{\sqrt{m, kT}} \sqrt{\pi} \left\{ \gamma_1 + \frac{\gamma_E}{2} + \Gamma\left(\frac{5}{6}\right) \frac{\gamma_2}{\sqrt{\pi}} \left(\frac{kT}{\varepsilon_g}\right)^{1/3} + \ln \left(2 \sqrt{\frac{\varepsilon_1}{kT}}\right) \right\}.$$



### Semi-relativistic capture cross sections:

- Cross section calculations for nonradiative electron capture in relativistic heavy-ion collisions are often based on an eikonal approximation. Anholt (1985) adapted some prior form of the asymmetric eikonal theory in order to calculate total nonradiative electron capture cross sections from any filled target shell to any projectile shell by just scaling the nuclear charges  $Z_t$  and  $Z_p$  by the principal quantum numbers  $n_t$  and  $n_p$ . In general, this approximation was found to become better for high-energetic ions and can be applied confidently also for ultra-relativistic collisions.

### 8.4.b. Vacuum-electron capture

#### Process, notation & application:

- **Vacuum electron capture** of an ion:  $\dots A^{q+} + Z_t + e^- + e^+ \longrightarrow A^{(q-1)+, (*)} + Z'_t + e^+$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon_- \kappa_- \rangle + |\varepsilon_+ \kappa_+ \rangle \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon_+ \kappa_+ \rangle$
- The vacuum electron capture process refers to the capture of an electron by fast projectiles due to the creation of an electron-positron pair and under the emission of the positron.
- In the vacuum electron capture, the target is considered to act as an perturbing potential that help create an electron-positron pair in the field of the projectile nucleus. While the electron is captured in one of the bound states (predominantly into  $1s$ ), the positron is emitted.
- The creation of an electron-positron pair from the vacuum is similar to the Coulomb ionization process of the projectile ion, except that the relative momentum of the ion is imparted into the vacuum instead of exciting an electron into a higher state of the projectile.

### Semi-relativistic capture cross sections:

- Due to the high value of momentum transfer, which is needed to excite an electron-positron pair from the vacuum, **vacuum-electron capture takes place predominantly at small impact parameters**, where the screening of the target nucleus by the target electrons is unimportant.
- **Vacuum-capture cross sections** The vacuum-capture process involves a momentum transfer from the target nucleus to the vacuum followed by an electron capture into the projectile K-shell. Therefore, the vacuum capture cross section is  $\sim Z_t^2$ , similar to most momentum transfer processes like excitation and ionization, and also  $\sim Z_p^5$  as typical for projectile electron capture processes. For large  $\gamma$ , the cross sections increases as  $\ln \gamma$  by they vanish for  $v \ll c$  unlike for projectile ionization.

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- Anholt and Becker (1987, table I) provide (reduced) vacuum capture cross sections for any combination of target-projectile and for  $\gamma \geq 10$ . For these large values of  $\gamma$ , the cross section is approximately

$$\sigma^{(\text{VAC})} = Z_p^5 Z_t^2 a \ln \left( \frac{\gamma}{\gamma_0} \right) \quad (\gamma > \gamma_0)$$

where  $a(Z_p)$  is a slowly varying function between 0.4 and 2.7 and  $\gamma_0$  is an offset. As the capture into higher shells than the K-shell varies as  $n^{-3}$ , the cross section for 1s has been multiplied by 1.2 by Anholt and Becker to provide an estimate for the total capture. For  $\gamma > 10$ , these cross sections are expected to be accurate within approximately 20 %.

- The capture of an electron into the 1s shell of the projectile under the simultaneous emission of a positron has been calculated by Becker *et al.* (1987) and by Bertulani and Bauer (unpublished).

### 8.4.c. Positron-bound-electron pair annihilation with single-photon emission (PairAnnihilation1Photon)

#### Process, notation & application:

- Positron-bound-electron pair annihilation with single-photon emission from an atom or ion:  $A^{q+} + e^+ \longrightarrow A^{(q+1)+*} + \hbar\omega$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon \kappa\rangle^+ \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega(\mathbb{M})$
- A positron can annihilate with a bound electron from an atom or ion under the emission of one, two or more photons. Here, we consider the emission of a single photons which is possible only due to the presence of the atom.

### 8.4.d. Positron-bound-electron pair annihilation with two-photon emission (PairAnnihilation2Photon)

#### Process, notation & application:

- Positron-bound-electron pair annihilation with two-photon emission from an atom or ion:  $A^{q+} + e^+ \longrightarrow A^{(q+1)+*} + \hbar\omega_1 + \hbar\omega_2$
- Quantum notations used in the formulas below:  $|\alpha_i \mathbb{J}_i\rangle + |\varepsilon \kappa\rangle^+ \longrightarrow |\alpha_f \mathbb{J}_f\rangle + \hbar\omega_1(\mathbb{M}_1) + \hbar\omega_2(\mathbb{M}_2)$

- A positron can annihilate with a bound electron from an atom or ion under the emission of one, two or more photons. Here, we consider the emission of two photons.
- **Positron-emission tomography:** A detailed understanding of the angular distribution of photon pairs from the  $(e^-, e^+)$  annihilation determines the spatial resolution of tomography and the defect analysis of tissue and materials. A good quantitative understanding of this emission is relevant also for upcoming positron facilities, e.g. at the Lawrence Livermore National Laboratory.

### Cross section for positron-bound-electron annihilation:

- **Differential cross section for positron-bound-electron annihilation:** The differential cross section for the annihilation of a positron with energy  $\varepsilon_i$  and velocity  $v_i$  by a bound electron with energy  $\varepsilon_a$  via the simultaneous emission of a photon pair is given (in relativistic units) by (Zaytsev *et al.*, 2019)

$$\frac{d^2 \sigma}{d\mathbf{k}_1 d\mathbf{k}_2} = 4\alpha^2 \frac{(2\pi)^6}{v_i} |\mathcal{M}|^2 \delta(\varepsilon_a + \varepsilon_i - \omega_1 - \omega_2)$$

$$\mathcal{M} = - \sum_n \left( \frac{\langle (-p_i \mu_i) | \boldsymbol{\alpha} \cdot \mathbf{A}_{\mathbf{k}_2 \lambda_2}^* | n \rangle \langle n | \boldsymbol{\alpha} \cdot \mathbf{A}_{\mathbf{k}_1 \lambda_1}^* | a \rangle}{\varepsilon_a - \omega_1 - \varepsilon_n (1 - i 0)} + \frac{\langle (-p_i \mu_i) | \boldsymbol{\alpha} \cdot \mathbf{A}_{\mathbf{k}_1 \lambda_1}^* | n \rangle \langle n | \boldsymbol{\alpha} \cdot \mathbf{A}_{\mathbf{k}_2 \lambda_2}^* | a \rangle}{\varepsilon_a - \omega_2 - \varepsilon_n (1 - i 0)} \right)$$

Here,  $\sum_n$  implies the summation over the complete spectrum of the single electron, including the summation over the positive and negative parts of the continuum.  $\mu_i$  is the helicity of the incident positron. Both, the double-differential cross section and the amplitude follow standard lines from the QED formalism.

- **Differential cross section for positron-bound-electron annihilation:** In practice, one typically needs to consider only the **double differential angular cross section**

$$\frac{d^2 \sigma}{d\Omega_1 d\Omega_2} = \int d\omega_1 d\omega_2 \omega_1^2 \omega_2^2 \frac{d^2 \sigma}{d\mathbf{k}_1 d\mathbf{k}_2},$$

and which needs to be further averaged over the angular momentum and spin projections of the bound electron and positron as well as (to be summed over) the polarization of the emitted photons.

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### 8.4.e. Positron-bound-electron pair production by a photon (PairProduction)

#### Process, notation & application:

- **Positron-bound-electron pair production by a (single) photon** of an atom or ion:  $A^{q+} + \hbar\omega \longrightarrow A^{(q-1)+*} + e^+$
- **Quantum notations used in the formulas below:**  $|\alpha_i \mathbb{J}_i\rangle + \hbar\omega(\mathbb{M}) \longrightarrow |\alpha_f \mathbb{J}_f\rangle + |\varepsilon \kappa\rangle^+$
- At high photon energies, the electron-photon interaction can lead to the creation of an electron-positron from which the electron is eventually bound by a multiply or highly-charged ion.

### 8.4.f. Thomson scattering

#### Process, notation & application:

- **Thomson scattering** generally refers to the elastic scattering of photons by charged particles (electrons, nuclei, etc.). This elastic scattering is one of the most fundamental interaction processes in electrodynamics that frequently occurs in different laboratory and astrophysical sources of high-energy x-rays. While the *linear* Thomson scattering has been explored for many decades, the *nonlinear* Thomson scattering regime became accessible only recently due the development of high-intensity laser with sufficiently high electromagnetic field strengths.
- **Role of normalized vector potential  $a_o$ :** In the (low-field) linear Thomson scattering regime ( $a_o \ll 1$ ), the electrons oscillate non-relativistically along the field and scatter the light in the dipole-radiation pattern at the (same) frequency of the incident field. Modern, high-intensity lasers now support field strength upto  $a_o \gtrsim 10 \gg 1$  in the nonlinear regime, in which the contribution of the electric and magnetic field to the (Lorentz) force become comparable.
- **Thomson scattering at fast electron beams:** Already in classical electrodynamics, Thomson scattering of short (laser) pulses at charged particles (electrons) gives rise to well-defined and readily tunable (monochromatic) x-ray beams. Hereby, the quasi-monochromatic scattering is closely related to the short wiggling period of the electrons in the incident laser pulses and, hence, to the pulse length itself. For a near head-on collision of a laser pulse with frequency  $\omega$  with an relativistic electron bunch, the backscattered photons have the frequency

$$\omega' = \omega \frac{2(1 + \beta \cos \vartheta) \gamma^2}{1 + a_o^2/2 + \gamma^2 \vartheta_o^2} \approx \omega \frac{4\gamma^2}{1 + a_o^2/2 + \gamma^2 \vartheta_o^2}$$

Here,  $a_o$  is the (frequency-) normalized vector potential,  $\vartheta$  the interaction angle and  $\vartheta_o$  the observation angle, both taken w.r.t. the velocity of the electron beam (quantization axis). As seen from this formula, the scattered radiation is monochromatic for well-collimated and monoenergetic electrons and laser beams, a (normalized) field strength  $a_o \ll 1$  and a small observation area (for instance, purely back-scattered light).

- **Relativistic quiver motion of electrons in intense fields:** In the relativistic regime, the electrons follow a **figure-8 motion that is analogue to the electromagnetic wiggler motion at synchrotrons**. This quiver motion of the electron also leads to a **red-shift of the scattered photon (spectrum)** as predicted by classical electrodynamics for an incident field of frequency  $\omega$ ,  $\omega' = \omega (1 + a_o^2/2)$ , as well as to elliptically-scattered multipole-radiation pattern. In most experiments, this red-shift is more than compensated by the (double) Doppler up-shift  $\omega'' \approx 4\gamma\omega'^2$ , where  $\gamma$  refers to the relativistic Lorentz factor of the electrons.
- **Number of back-scattered photons per pulse-collision:** For an head-on collision of an electron bunch with  $N_e$  electrons and (intense) laser pulse of  $N_c$  cycles, the number of back-scattered photons is approximately given by (Khrennikov *et al.*, 2015)

$$N' = \frac{\pi \alpha N_c N_e a_o^2}{3 \langle n \rangle} \left[ \frac{1 - \beta}{1 + \beta} + \frac{a_o^2 (1 - \beta)}{4 \gamma^2 (1 + \beta)^2} \right],$$

and where  $\langle n \rangle$  is the averaged number of scattered photons per electron (harmonic number); this number strongly depends on the intensity of the incident laser pulse.

- **Thomson scattering process:** The process can be described (to a large extent) either in classical ED *or* quantum ED, and often with very similar resultss. Prunty (2014) provides a pedagogical elaborate and very careful treatment of the Thomson scattering from the viewpoint of classical ED. The quantum description then leads in a natural way also to the **Compton effect**, which is considered to be negligible at classical (non-relativistic) wavelength of the incident light. In classical ED, moreover, the Thomson scattering process is first of all an *incoherent* process due to the elastic scattering light of light from different charges.
- **Thomson scattering of light in high-temperature plasmas:** Thomson scattering of light frequently occurs in high-temperature plasmas as generated by modern experiments. In such high-temperature plasmas, the strength of the scattered signal provides information on the electron density, while the width of the scattered spectrum provides information on the plasma temperature. In high-temperature plasmas, the electrons move with a substantial fraction of the speed of light and, hence, the scattering of light has to be treated *relativistically*. Both the relativistic theory and computations are then lengthy but may give rise to subtle differences.
- **Applications of Thomson scattering:** This process can be utilized for the diagnostics of high-temperature plasmas in magnetic fusion and for high-density plasmas in inertial confinement fusion. It also help develop a **new class of accelerator-driven x-ray (so-called Thomson or Compton) sources that are suitable for nuclear-physics studies and highly-charged ions**.

- **Application of Thomson scattering:** This scattering process is a powerful and *non-perturbing* diagnostic technique in plasma physics research that provides information on the electron (or ion) density and the electron (or ion) velocity distribution (and hence, temperature). Usually, a high-intensity monochromatic light beam (from a high-power Q-switched laser beam) passes through a plasma and enforces the (quasi-) free electrons near to the laser focus to oscillate at the incident laser frequency. This oscillation then causes the electrons to emit dipole radiation that can be recorded and analysed. In these recorded spectra, the Doppler-shifted laser frequencies, if integrated over all scattered wavelengths, is proportional to the electron density and the width of the Doppler-broadened peak provides information on the electron temperature. Indeed, the Thomson scattering diagnostic has been found as an important diagnostic tool since it provides a direct handle on the evolution of the plasma. However, because of the intrinsic small scattering cross-section, Thomson scattering diagnostics have become feasible with the development of short-pulse, high-power plasma.

### Nonlinear Thomson scattering:

- **High-order multiphoton Thomson scattering:** A high-intensity laser field enables the electron to scatter simultaneously multiple photons into a single high-energy photon with (harmonic) frequency  $\omega' = n\omega$ . Here,  $n$  refers to both, the order of the (non-linear) interaction and to the number of incident photons scattered per electron.

## 8.5. Other topics related to atomic processes

### 8.5.a. Atomic databases from the literature

#### CHIANTI: A database for emission lines:

- CHIANTI is a database of assessed atomic parameters and transition rates that are required and utilized for the simulation of line and continuum emission spectra from optically thin and collisionally-dominated plasma.
- CHIANTI was first released in 1996 and, since then, several new up-dates have been made available in order to expand the database and improve the quality of the data. Emphasis in developing this database has been given especially to the line identification and improvement of the reference wavelengths.
- For several ions, the wavelengths and identifications from CHIANTI are different from and considered to be more accurate than those of the NIST database. Therefore, CHIANTI is now often applied as a reference atomic database for ions and has been included into several other atomic codes and packages.
- In its last version (Del Zanna *et al.*, 2015), the CHIANTI database includes a large amount of new data which improve simulations for the soft x-ray, extreme UV (EUV) as well as UV spectral regions. These regions are currently covered by several space missions.

#### DREAM: A database for lanthanide spectra:

- **DREAM database** The Mons group (Biemont and coworkers) have calculated various neutral and near-neutral lanthanide spectra; these data are kept within the DREAM database. In these computations, they employed the least-squares fitting procedure in the Cowan code (Cowan 1981) together with a core-polarization potential in order to obtain spectroscopic quality radiative rates.

#### NIST-ESTAR:

- The ESTAR database provides (electron) stopping powers and ranges for incident electrons with energies between 10 keV and 1 GeV, and as derived from the so-called ICRU Report (Amako *et al.*, 2005). In particular, the associated ESTAR web-interface computes stopping power, density effect parameters, range, and radiation yield tables for electrons in various materials.
- **Collision stopping powers:** In the ESTAR database, such stopping powers have been calculated with Bethe's theory and by applying Sternheimer's correction due to density effects of the materials.

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- **Radiative stopping powers:** Radiative stopping powers are evaluated in the ESTAR database by means of theoretical Bremsstrahlung cross sections. While reasonably accurate numerical stopping powers were calculated just below 2 MeV, an approximate high-energy formula has been applied above 50 MeV.
- The user can select a material and (a range of) energies [in MeV] between 0.001 MeV to 10000 MeV.

### NIST-PSTAR:

- The PSTAR and ASTAR databases provide (proton) stopping powers and ranges for incident protons with energies between 1 keV – 10 GeV; they were derived from the so-called ICRU Report 49.
- The user can (again) select a material and (a range of) energies [in MeV] between 0.001 MeV to 10000 MeV.

### NIST-XCOM:

- The XCOM database provides photon scattering data and attenuation coefficients between 1 keV and 100 GeV for all the elements of the periodic table. It also lists total cross sections, attenuation coefficients and partial interaction coefficients for selected processes, such as Compton and Rayleigh scattering, photoelectric absorption as well as pair production (Amako *et al.*, 2005).

## 8.5.b. Codes from astro and plasma physics that require atomic data input

### AtomDB:

- **ATOMDB** is an atomic database and program environment for X-ray plasma spectral modeling. Its current version is primarily used for modeling the x-ray emission from collisional plasmas of hot electrons in collision with astrophysically abundant elements and ions. ATOMDB has been found useful also to model the absorption by elements and ions or even photoionized plasmas, if x-ray photons (often from a simple power-law source) interact with elements and ions and lead to quite complex spectra.
- ATOMDB calculates the x-ray/UV spectrum of a hot, collisionally-dominated optically-thin plasma, based on knowledge of the atomic transition rates and energies of the involved ions. This code also help analyse the interplay between the different rates. The line and continuum results of ATOMDB (<http://www.atomdb.org>) apply to an **optically-thin thermal plasma with astronomical abundances**; cf. Anders and Grevesse (1989).



- ATOMDB aims for to incorporate all relevant data, generated both from theoretical models and experiment, and to evaluate these data quite critically. Each revision of the critically evaluated database is given a version number to aid reference.
- ATOMDB provides improved spectral modeling capability by making use of additional emission lines as well as of accurate wavelengths for most strong x-ray transitions. These improvements refer to the x-ray grating data analysis and to improve the knowledge about spectra at moderate (CCD) resolution.

### CLOUDY:

- **CLOUDY** is an open-source, spectral synthesis code in order simulate interstellar matter under a broad range of conditions. In particular, it simulates astronomical clouds and their spectra.
- Astrophysical (spectral) observation can be used to directly measure the temperature, density, pressure or composition of a cloud of gas or a star, using a telescope and a spectrometer. Since the spectra are formed in highly non-equilibrium gas and dust, numerical simulations are generally required in order simulate the spectra.
- CLOUDY is a code that computes the ionization, chemistry, radiation transport, and dynamics simultaneously and self consistently, based on a good deal of atomic and molecular data.

### FLYCHK and GALAXY:

- FLYCHK uses a hydrogenic approximation in order to calculate energy levels and level populations in plasma. However, the results of GALAXY and FLYCHK largely deviate from measured ones.
- FLYCHK is based on the K-shell spectroscopy code FLY and has been developed in order to study hot dense plasmas. Its ease of use for the simulation of synthetic spectral has made the code attractive to both experimentalists and modelers. The goal of FLYCHK is to provide a simple and general capability for a wider range of plasmas. In practice, unfortunately, benchmark experiments or calculations are quite scarce and the limitations and validity ranges of FLYCHK are not well known.
- GALAXY employs an average-of-configuration approximation for the electronic states as well as screened hydrogenic wave functions for both, the collisional and radiative processes. This code also employs Hartree-Dirac-Slater or Kramers cross-sections for photoionization.

### LTE:

- **LTE code:** This code applies the Boltzmann and Saha equations in order to obtain the ionization and excitation state of each element. It assumes a local thermodynamic equilibrium and that all scattering processes are negligible.

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- The LTE code often applies atomic data from NIST to determine the relative strengths of the lines.

### MOOG:

- **MOOG code:** This code generates synthetic absorption spectra of photospheres in cool stars by assuming a local thermodynamic equilibrium. It requires an (externally given) model atmosphere in order to derive the temperature, gas pressure and electron density at different layers of the surface gas. The code also requires an atomic line list that comprises all data about the absorption transitions (at rest), oscillator strength as well as excitation (ionization) energies of the lower levels for the element or ion of interest.
- In the MOOG code, the strengths of the observed absorption features are obtained by solving the radiative transfer equations with a plane-like parallel treatment of the atmosphere, and where the velocity distribution of the ions is assumed to be Maxwellian. Moreover, the excitation and ionization processes of the ions in selective charge states are described by the Boltzmann and Saha equations.
- The MOOG code has often been applied with Kurucz' model atmosphere and with data from the NIST data base.
- **MOOG:** This code help perform a variety of LTE line analysis and spectrum synthesis tasks. In particular, MOOG assists to determine the chemical composition of a star. The implementation of MOOG hereby follows an earlier formulation of the line analysis by Edmonds, Jr. (1969, JQSRT).

### RCF:

- **Radiative-Collisional code based on FAC, RCF:** This code has been used to simulate steady-state plasmas under non-local thermodynamic equilibrium condition, and especially for photoionization-dominated plasmas. RCF takes almost all of the radiative and collisional atomic processes into account by rate equations in order to interpret the plasmas systematically. The Flexible Atomic Code (FAC) supplies all the atomic data that are needed for RCF in order to ensures completeness and consistency of the atomic data.
- **RCF** is a steady-state, collisionalradiative, optically thin model. Its rate-equation

$$\frac{dN_{i,j}}{dt} = \text{populating processes} - \text{depopping processes} = 0$$

where  $N_{i,j}$  is the density of the j-th level in the i-th charge state. RCF includes ionization and recombination between neighboring charge states as well as the excitation and de-excitation within the same charge state.

### TARDIS:

- **TARDIS code:** This is an open-source Monte Carlo radiative-transfer spectral synthesis code for 1D models of supernova ejecta. It has been designed for rapid spectral modelling of supernovae, cf. <https://tardis-sn.github.io/tardis/>
- **Radiative transfer** generally describes how the properties of the electromagnetic radiation field change as it passes through an ambient material. Because of the many and complex interactions of the photons with the matter (clouds), radiative transfer need to be studies numerically. Although different numerical techniques are available, Monte Carlo techniques have become a successful and elegant tool particularly for radiative transfer problems in supernovae.
- **Monte-Carlo Radiative Transfer** methods are probabilistic techniques that follows the interaction of individual photons in propagating through an ambient material. In particular, a quite large number of representative ‘machine photons’ are solved in a stochastic process.

### XSTAR:

- XSTAR is a command-driven, interactive, computer program for calculating the physical conditions and emission spectra of photoionized gases; cf. <http://ascl.net/9910.008>. It may be applied in a wide variety of astrophysical contexts. In particular, XSTAR computes the re-radiated light when the gas of a star absorbs energy.

### Further codes:

- In PHICRE, the energy levels and spontaneous decay rates are taken from the NIST database, and other rate coefficients are calculated by widely used formulas.
- **CRMModel code:** This code by Hartgers *et al.* (2001) support a variety of plasmas that consist out of just a single atomic species but with any (finite) number of excited states between the ground level and the ionization threshold of the ion. The code assumes however that the density of all excited states remains small when compared to the ground-state density. The flexibility of this code makes it useful to investigate the effects of different cross section expressions.
- **STiC:** de la Cruz Rodriguez *et al.* (2019) present and discuss the STockholm inversion COde (STiC) that enables one to model the spectral lines from different atoms simultaneously. It is based on partial redistribution effects (PRD) of scattered photons in angle and frequency as well as a so-called Levenberg-Marquardt algorithm. Until the present, however, it remains pretty unclear to which extent such a code might benefit from a good set of atomic data.

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- **NESSY:** The NLTE Spectral SYnthesis code (NESSY) code supports the computation of synthetic spectra for various solar regions, such as quiet and magnetically-dominated regions and domains of magnetically-driven variability. NESSY has been built upon the COde for Solar Irradiance (COSI) and can now be utilized for modeling of the entire — UV-, visible-, IR and radio — spectra of solar and stellar regions; moreover, this code is considered to be substantially faster than COSI and allows for reliable calculation of the entire solar spectrum (Tagirov *et al.*, 2017).

### 8.5.c. Radiative opacities

#### Spectral intensity and radiative opacity of a plasma:

- **Radiative opacity of a plasma:** The radiative opacity of a plasma is of great significance for various research fields, such as astro and stellar physics, inertial confinement fusion or the development of x-ray lasers. Therefore, the (so-called) **Opacity Project** calculated mean (and approximate) opacities for most astrophysically abundant elements and also generated a database of opacities.
- **Fraction of transmitted radiation** From the opacity of a plasma, the fraction of the incident radiation that is transmitted through a medium, can be expressed as:

$$F(\omega) = \exp(-\rho \eta' L), \quad \kappa = \kappa(\omega)$$

where  $L$  refers to the path length of the light through the medium (plasma),  $\rho$  the mass density and  $\kappa(\omega)$  the radiative opacity. The fraction of transmitted radiation can be readily determined, both experimentally and theoretically.

- **Opacity computations generally imply the accurate knowledge of different atomic data, such as level energies, oscillator strength, photoionization and several other cross sections for all ionic species in the plasma.** They also require an adequate equation of state in order to determine the ionization fractions and level populations of the ions as well as information about line broadening mechanisms.
- **Effective (expansion) opacities:** In an expanding object, the frequency of photons suffers from a continuous Doppler shift with regard to the rest frame of the material, similar to the redshift of photons in the expanding Universe. Therefore, each photon has also an increased probability for interacting with an atomic line. Karp *et al.*, (1977) showed that this enhanced interaction with the spectral lines of atoms and ions can be taken into account by just replacing the ordinary static opacity by an **effective opacity, also known as the expansion opacity, and by applying diffusion theory.**
- **Radiative opacity of iron plasma:** Since the radiative opacity of iron plasmas at high temperatures is important for astrophysics, various experiments have been carried out to accurately measure their radiative opacity during recent decades.

- **Radiative opacity of iron plasma:** Although the fraction of iron is typically quite small in most stellar environments, especially when compared with the high abundance of hydrogen and helium, the opacity of iron plays a significant role for understanding in particular the radiative transfer in astrophysical plasmas, such as the Sun.
- The radiative opacity is often analysed and displayed either as function of the mass density at given temperature or as function of temperature at given mass density.
- **Spectral intensity  $I_\lambda$ :** The (specific) light intensity of a plasma or light source describes the amount of electro-magnetic radiation with wavelengths between  $\lambda \dots \lambda + d\lambda$  that passes in the time interval  $dt$  through the area  $dA$  into the solid angle  $d\Omega = \sin \vartheta d\vartheta d\varphi$  (Pettini 2018),

$$W_\lambda d\lambda = I_\lambda(\vartheta, \varphi) d\lambda dt dA \cos \vartheta \sin \vartheta d\vartheta d\varphi = I_\lambda(\vartheta, \varphi) d\Omega d\lambda dt dA \cos \vartheta$$

In astrophysics, the spectral intensity is often measured in units:  $\text{erg s}^{-1} \text{cm}^{-2} \text{\AA}^{-1} \text{sr}^{-1}$ .

- **Spectral and total energy density  $u_\lambda$ :** The specific energy density refers to the energy per unit volume that is contained in the radiation field with wavelengths between  $\lambda \dots \lambda + d\lambda$ , and from which the total energy density is easily obtained

$$u_\lambda d\lambda = \frac{d\lambda}{c} \int d\Omega I_\lambda(\vartheta, \varphi) = \frac{4\pi}{c} J_\lambda d\lambda \quad \Rightarrow \quad u = \int_0^\infty d\lambda u_\lambda,$$

and where  $J_\lambda$  is the angle-averaged spectral intensity.

- **Photon mean free path:** In a plasma or gas, photons from a light beam with spectral intensity  $I_\lambda$  are absorbed or scattered along its differential path  $ds$  through the medium (of given density  $\rho$  and opacity  $\kappa(\omega)$ ). This attenuation of the spectral intensity  $I_\lambda$  is given by

$$dI_\lambda = -\mu I_\lambda ds = -\kappa_\nu \rho I_\lambda ds, \quad \mu = \frac{1}{\kappa(\omega) \rho} = \frac{1}{\sigma(\lambda) n}$$

where  $\mu$  is the attenuation coefficient,  $\sigma$  is the interaction cross section and  $n$  the number density of particles in the plasma.

- **Optical depth of photons  $\tau_\lambda$ :**  $\tau_\lambda = \int_0^s ds \kappa(\omega) \rho$ .

### Definition of mean and detailed radiative opacities:

- **Radiative opacity  $\kappa(\omega)$ :** For a plasma in a local thermodynamic equilibrium at temperature  $T$  and mass density  $\rho$ , the radiative opacity  $\kappa(\omega)$  is given by (Cheng and Jiaolong, 2008)

$$\rho \kappa(\omega) = [\mu^{(\text{bound-bound})}(\omega) + \mu^{(\text{bound-free})}(\omega) + \mu^{(\text{free-free})}(\omega)] \left(1 - \exp\left(-\frac{\omega}{k_B T}\right)\right) + \mu^{(\text{scattering})}(\hbar\omega),$$

where  $\mu^{(\text{bound-bound})}$ ,  $\mu^{(\text{bound-free})}$ ,  $\mu^{(\text{free-free})}$  and  $\mu^{(\text{scattering})}$  are the absorption coefficients due to bound-bound, bound-free, free-free and well as the scattering processes, respectively.

- **Rosseland mean opacity:** The radiative transfer in a plasma is mainly controlled by the Rosseland mean opacity and is often expressed in terms of the reduced photon energy  $u$

$$\frac{1}{\kappa^{(\text{Rosseland})}} = \left[\frac{dB}{dT}\right]^{-1} \left[\int_0^\infty d\omega \frac{1}{\kappa(\omega)} \frac{\partial B_\omega}{\partial T}\right] = \int_0^\infty du \frac{1}{\kappa(u)} \times g(u), \quad g(u) = \frac{15}{4\pi^4} u^4 \frac{\exp(-u)}{[1 - \exp(-u)]^2}, \quad u = \frac{\hbar\omega}{kT}.$$

- **Rosseland mean opacity:** The Rosseland opacity is defined as average over the energy density  $W^{(\text{Rosseland})}(u)$  by:

$$\frac{1}{\kappa^{(\text{Rosseland})}} = \int_0^\infty du \frac{W^{(\text{Rosseland})}}{\kappa(u)}, \quad W^{(\text{Rosseland})} = \frac{15}{4\pi^4} \frac{u^4 e^{-u}}{(1 - e^{-u})^2}, \quad u = \frac{\hbar\omega}{k_B T}.$$

- **Planck mean opacity:** Similarly, the Planck mean opacity is defined as average over the energy density  $W^{(\text{Planck})}(u)$  by:

$$\frac{1}{\kappa^{(\text{Planck})}} = \int_0^\infty du W^{(\text{Planck})} [\kappa(u) - \kappa^{(\text{scattering})}(u)]; \quad W^{(\text{Planck})} = \frac{15}{\pi^4} \frac{u^3 e^{-u}}{(1 - e^{-u})}, \quad u = \frac{\hbar\omega}{k_B T}.$$

- **Rosseland versus Planck mean opacities:** The spectrally-resolved Rosseland and Planck mean opacities of iron plasmas at different temperatures between a few to a few hundred eV have been found useful in studying the evolution of stars, such as the Sun. These studies refer to both, stellar envelopes as well as their interiors.
- **Rosseland versus Planck mean opacities:** The Rosseland and Planck mean opacities are required for many practical applications such as radiative transfer.

- **Gray opacity:** The gray opacity value just results from the Thomson-scattering opacity,  $\kappa^{(\text{Thomson})} = 0.4(\bar{Z}/A) \text{ cm}^2/\text{g}$ , i.e. by assuming and if one assumes a (fully) ionized material (medium) with  $\bar{Z} = Z$ . Here,  $A$  is the atomic weight and one often simply applies  $\bar{Z}/A \approx 1/2$  for most elements.
- **Radiative opacity  $\kappa(\omega)$ :** The total frequency-dependent opacity  $\kappa(\omega)$  can be calculated as the sum of different contributions due to: (i) photo-excitation  $\kappa^{(\text{bound-bound})}$ , (ii) photo-ionization  $\kappa^{(\text{bound-free})}$ , (iii) inverse Bremsstrahlung  $\kappa^{(\text{free-free})}$  as well as (iv) photon scattering  $\kappa^{(\text{scattering})}$ .

$$\kappa(\omega) = \kappa^{(\text{bound-bound})}(\omega) + \kappa^{(\text{bound-free})}(\omega) + \kappa^{(\text{free-free})}(\omega)$$

$$\kappa'(\omega) = \kappa(\omega) \left( 1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right) \right) + \kappa^{(\text{scattering})}(\omega)$$

- **Free-free opacity contributions:** The free-free transitions refer to the **inverse Bremsstrahlung** due to emitted radiation, if an electron slows down in the electromagnetic field of an ion.
- **Assumptions for deriving the radiative opacity  $\kappa(\omega)$ :** Two assumptions are typically made in order to obtain the radiative opacity  $\kappa(\omega)$  of a plasma: (i) All quantum states of a degenerate level are equally populated and (ii) the levels with different energy  $E$  are populated due to a Boltzmann statistics  $\sim \exp(-E/kT)$ .
- **Planck function  $B(\omega, T)$ :** The Rosseland mean opacity is often computed by applying an inverse, or harmonic, averaging scheme and with a weighting function  $\propto B n(T)/T$  that peaks approximately at a photon energy  $\hbar\omega = 4 k_B T$ , of four times the temperature.
- **Specific radiative intensity  $I_\nu$ :** This specific intensity is not much different from the Planck function  $B(\omega, T)$  for a plasma in a local thermodynamic equilibrium (LTE), while the photon flux  $\mathbf{F}$  is often estimated by assuming an diffusion approach

$$\mathbf{F} = -\frac{4\pi}{3\kappa^{(\text{Rosseland})}} \frac{dB}{dT} \nabla T, \quad \frac{dB}{dT} = \int_0^\infty d\omega \frac{\partial B(\omega, T)}{\partial T}.$$

## Computation of radiative opacities:

- **Opacity computation** can provide valuable information about a plasma, including the fractional distribution of the different ion stages and whether the plasma is in a local thermodynamic equilibrium (or not) as well as about the temperature gradient in plasma.

## 8. Atomic processes

- **Opacity of light elements ( $Z < 30$ ):** The atomic properties of the light elements are known reasonably well from experiment and many previous computations. In particular, Kurucz (1993) and Kurucz and Bell (1995) provide an extensive list of lines (with about 42 million lines and 500,000 line shifts) mainly from the iron group elements. These lists were generated by using the CATS code (Cowan 1981) and by tuning the theoretical energies semi-empirically in order to reproduce the extensive observed experimental level energies.
- **Computation of low- $Z$  opacities:** A low- $Z$  opacity model, which starts from the detailed computation of all atomic data, has been found to agree very well with experimental measurements of the frequency-resolved opacity of aluminium at the temperature  $T \approx 40$  eV, and for different plasma densities.
- **Opacities of iron-group elements:** Detailed supernova calculations suggest that blue wave-lengths bound-bound transitions from complex iron group elements dominate in a given frequency band over other forms of opacity, such as the electron-scattering, free-free, and photoionization contributions to the overall opacity. In the blue and ultra-violet region, indeed, millions of lines may contribute to the bound-bound opacity, and they often appear as a pseudo-continuum if these lines are Doppler-broadened due to the differential velocities of the remnants.
- **Opacity of lanthanides:** Barnes and Kasen (2013) applied the line data from the VALD database in order to study the opacity of the lanthanides and to demonstrate that these heavy elements may exhibit a much larger opacity. At present, however, the limitations of VALD does not allow to compute reliable  $r$ -process opacities over the wavelength and temperature range as required by realistic transport calculation. In particular, VALD contains almost no lines with wavelengths greater than  $1\ \mu\text{m}$  and, hence, cannot be applied to compute sensible infrared opacities or emissivities of the neutron-star merger.
- **Opacity of lanthanides:** A detailed modelling of the radiative properties of lanthanides and other high- $Z$  ions will be a long-term endeavor because of the (large) number of electrons and the shell structure of the lanthanides as well as most elements beyond.
- **Opacities of  $r$ -process elements:** Among other  $r$ -process elements, the lanthanide elements are expected to have rather high optical and NIR opacities. Therefore, if lanthanides occur, a rather red and faint emission is expected from the ejecta of neutron-star mergers while the emission spectra are (expected to be) blue and bright for lanthanide-free ejecta ('blue kilonova').
- **Opacity Project:** This project is an international collaboration of about 25 scientists from 6 countries which started around 1982. The atomic data from this project are available in the TOPbase database, while the monochromatic opacities and Rosseland mean opacities are available from the OPServer at the Ohio Supercomputer Center.
- **Opacity Project:** This project is perhaps a pioneering example of what is nowadays known as **collaborative big-data science** (Mendoza 2018). This project involved the computation of large data sets by several internationally distributed research groups, which were then compiled and stringently evaluated before they became part of TOPbase.



## Experimental determination of opacities:

- **Laboratory plasma:** All plasmas, that are produced in the laboratory, are generally quite far from local thermodynamic equilibrium (LTE). Therefore, the ion distribution of such laboratory plasma cannot be described by the usual Saha-Boltzmann equations, neither for selected ions nor for dealing with different charge states of the ions.
- **Z-pinch experiments:** In the laboratory, one often has a **steady-state plasma, far from equilibrium, that is formed by x-ray radiation from a Z-pinch**. In such plasma, the (incident) ambient radiation field is important in addition to the electron-collisional processes in order to determine the excitation and ionization dynamics. **Such photoionized plasmas are believed to occur also in various astrophysical situations;** in fact, Z-pinch experiments allow for the first time to compare numerical models of photoionized plasmas with experiment (Rose *et al.*, 2004).
- **Uniform plasma density:** For a uniform density, the transmission of the sample is usually measured

$$T(\omega) = \frac{I(\omega)}{I_o} = \exp(-\rho L \kappa(\omega)),$$

and where  $I(\omega)$  is the attenuated intensity of the probe (backlighter) radiation and  $I_o$  the reference intensity. This transmission is related also to opacity by the Beer-Lambert law if the re-absorption can be neglected within the homogeneous plasma. Here,  $\rho$  is the density of the material and  $L$  its thickness.

- **Iron opacity measurements:** Bailey *et al.* (2015) measured iron opacities at electron temperatures between 1.9 – 2.3 million kelvin and electron densities between  $(0.7 - 4.0) \times 10^{22} \text{ cm}^{-3}$  at the Z facility. In these measurements, the observed optical absorptions was found about  $\sim 30 - 400 \%$  higher than those predicted by currently applied opacity models.
- **Opacity measurements by Z-pinch radiation:** There are several benefits in resorting to Z-pinch radiation for opacity measurements, including relatively large cm-scale lateral sample sizes and the relatively long 3-5 ns duration of the experiments.
- **Tachocline of the Sun:** This (hyper-) surface refers to the boundary between the convective and the radiative zone of the Sun and is determined by the frequency-dependent opacity of the plasma in this region. The opacities of the Sun have been recently explored as the Z-machine at Sandia National Laboratory.
- **Tachocline of the Sun:** In the tachocline region, iron is responsible for about 25% of the total opacity. In 2005, a measurement of the opacity in the spectral region between 7 and 12.7 Å gave rise to values that are 30 to 400 % than those from the (best) codes.

### Average-atom model:

- **Average-atom model:** Typically opacity computations have considered a total of up to  $10^8$  radiative lines. Since these computations cannot so easily be extended towards high- $Z$  elements, the **average-atom model** has been found a valuable alternative.
- **Average-atom model:** The average-atom is not a real entity with an integer number of bound electrons but a rather fictitious quantum system with a non-integer number of electrons. These electrons are distributed continuously among the shells in order to handle the average occupation of the shells in a (astro-physical) plasma. The main difficulty arise from finding an approximate average-atom potential, from which a set of one-electron wavefunctions are obtained by the solution of the corresponding wave equation.
- **Average-atom model:** The average-atom model predicts an increase of the low- $Z$  opacities that has been found in line with observations of stellar pulsations. Because of the known **sensitivity of the Rosseland mean opacity with regard to some "window" in the photoabsorption spectrum**, however, this *averaged* method may be potentially inaccurate.
- **Validation of the average-atom model:** The validation of the average-atom model for plasma in different density and temperature regimes is (still) important since this model has been widely applied in radiation-hydrodynamic simulations of laboratory plasmas, and where the rate equations are coupled to the hydrodynamics both through collisional processes and through the radiation field.

### Material for distribution in this section:

- **Opacity:** The opacity of a (plasma) medium characterizes the transport of radiation through matter. Opacity computations generally require atomic data for a large number of processes involving the absorption and scattering of radiation (Seaton 1987).
- **Opacity model OPAL:** OPAL refers to a new astrophysical opacity model that has been developed at the Lawrence Livermore National Laboratory (LLNL). This model showed that  $\Delta n = 0$  transitions often result in many overlapping lines and in a significant increase of the opacity of the iron mixtures.
- **Application of opacities:** Opacities are frequently applied in various research fields, such as the standard solar model (SSM), helio and astero-seismology, non-LTE 3D hydrodynamic photospheric modeling, nuclear reaction rates, solar neutrino observations, computational atomic physics as well as in plasma experiments (Mendoza 2018).
- **Expansion opacity:** Most atomic computations are nowadays based on the formalism by Karp *et al.* (1977):

$$\kappa^{(\text{expansion,bb})} = \frac{1}{\rho c t} \sum_{\ell} \frac{\lambda_{\ell}}{\Delta \lambda} (1 - e^{-\tau_{\ell}}), \quad \tau_{\ell} = \frac{\pi e^2}{m c} f_{\ell} n_{\ell} \lambda_{\ell} t = \frac{\pi e^2}{m c} \left( \frac{n \lambda_{\ell} t}{g_o} \right) g_{\ell} f_{\ell} e^{-E_{\ell}/kT}.$$

In this expansion opacity,  $\rho$  and  $t$  refers to the density and time after the merger, while the summation runs over all lines  $\ell$  in the chosen wavelength bin ( $\Delta\lambda$ ), and where  $\lambda_\ell$  is the transition wavelength and  $\tau_\ell$  the (so-called) Sobolev optical line depth. Moreover,  $g_\ell$ ,  $E_\ell$ ,  $f_\ell$  refer to the statistical weight and the energy of the lower level as well as the oscillator strength of the transition.

- **Number density  $n_\ell$ :** For the number density  $n_\ell$  of levels at the energy of the lower levels, a Boltzmann distribution  $n_\ell = \frac{g_\ell}{g_o} n \exp(-E_\ell/kt)$  is often assumed, and where  $g_o$  just refers to the statistical weight of the ground level. In the formulation by Karp *et al.* (1977), moreover, the number density  $n$  is calculated from the Saha equations by assuming an LTE.
- **Sobolev's expansion approach to the radiative opacities:** This approximation is based on the assumption that the opacity can be modeled by just a rather small number of distinct strong lines. If one assumes that the photon is re-emitted at the same energy as it was absorbed before, we can treat each line as a scattering center. However, the **use of area-preserving line profiles produces frequency-dependent opacities that are one to two orders of magnitude larger than those obtained in Sobolev's expansion approximation.**
- **Planck mean opacities at different temperatures:** The opacity does generally not depend much on the temperature of the ejecta of matter clouds. If the density and time is kept constant, the **Planck mean opacities agree within a factor of 1.5 with each other for different temperatures.**
- **Planck mean opacities at different temperatures:** Radiative opacities are required for the modeling of astrophysically relevant plasmas under local thermodynamic equilibrium (LTE) conditions. For the computation of these opacities, the atomic structure calculations should be carried out for many (or even all) fine-structure levels and by including electronic correlations.
- **Early opacity computations** have often used data obtained from simple atomic models. However, already Simon (1982) suggested that such simple estimates are too small by factor of 2-3 for all elements heavier than helium.
- **Opacity calculations for lanthanides or actinides:** In previous opacity computations for the lanthanides or actinides, rather large uncertainties arose from the large number and uncertainties of the (yet unknown) atomic states and line strengths of these complex elements. Indeed, these high- $Z$  atoms still represent, both experimentally and theoretically, a major challenge for accurate atomic calculations; they often require the use of statistical models that need later to be calibrated to experimental data.
- **Opacity calculations for iron:** When compared to previous estimations, OPAL iron monochromatic opacities at density  $\rho = 6.82 \times 10^{-5} \text{ g cm}^{-3}$  and temperature  $T = 20 \text{ eV}$  indicate a rather large enhancement at photon energies around 60 eV, and which may arise from  $\Delta n = 0$  unresolved transition arrays in Fe. This enhancement is supported also by laboratory photoabsorption measurements.
- **Bound-bound opacity:** For nearly-neutral ions and neutral atoms, the **bound-bound opacity depend sensitively on the level density just above of the ground state.** This density increases with the electron occupation, until a shell is half-filled, and may become quite sizeable for several open shells. Moreover, a very large level density also occurs for open  $d$ - and  $f$ -shell elements, i.e. the  $3d$  and  $4d$  transition elements

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and lanthanides. In general, the energy-level density is slightly shifted towards higher excitation energies (above of the ground level) if the number of electrons increase in a given shell.

- **Bound-bound opacity:** For temperatures between  $T = 5,000 - 10,000$  K, Tanaka *et al.* (2019) estimate for a mixture of r-process elements an average opacity of  $\kappa \sim 20 - 30$  cm<sup>2</sup>/g for an electron yield  $Y_e \leq 0.2$ ,  $\kappa \sim 3 - 5$  cm<sup>2</sup>/g for an electron yield  $Y_e \sim 0.25 - 0.35$ , and  $\kappa \sim 1$  cm<sup>2</sup>/g for an electron yield  $Y_e \sim 0.4$ , respectively. These bound-bound opacities steeply decrease at lower temperature.

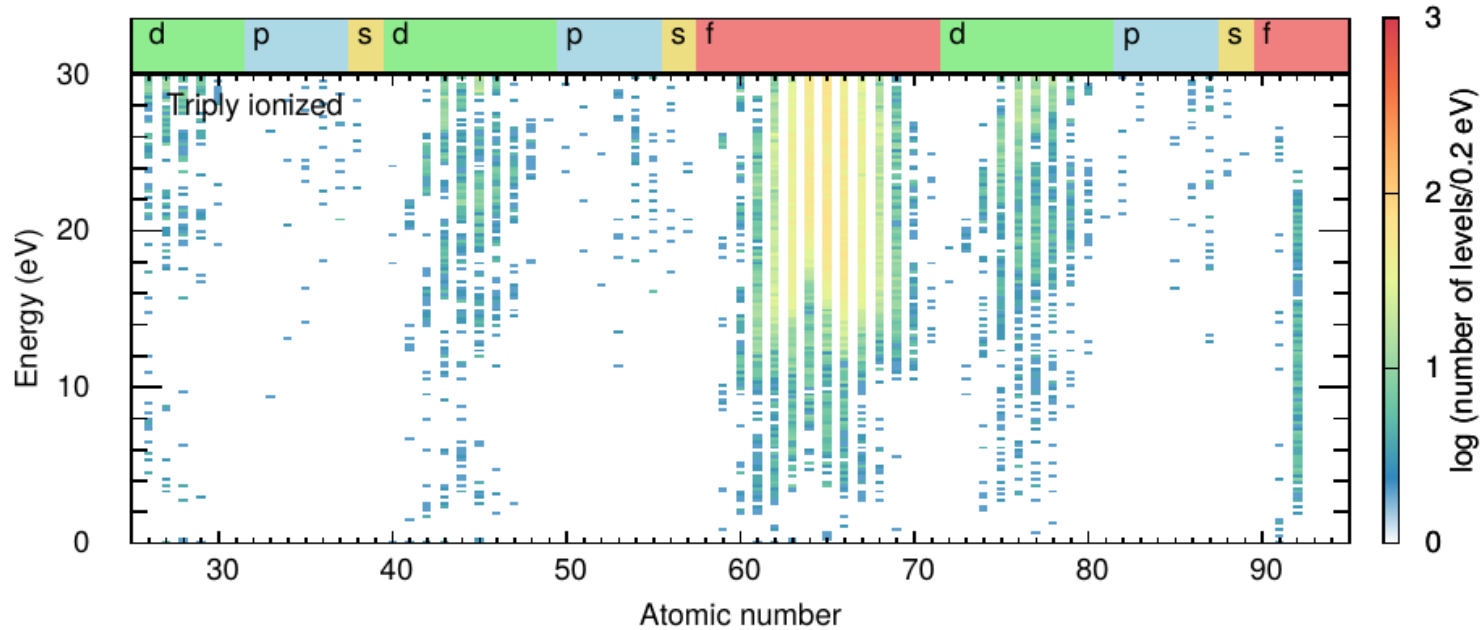


Figure 8.2.: Energy levels density of triply-ionized elements up to 30 eV above the ground level and collected in energy bins of 0.2 eV; taken from Tanaka *et al.* (2019).

- **Opacity calculations for the lanthanides:** For  $T \approx 5,000$  K, Tanaka *et al.* (2019) predict the largest Planck mean opacities among all lanthanide elements for Pr, Nd, and Pm ( $Z = 59, 60$ , and  $61$ ). For all elements with even more  $4f$  electrons, these Planck mean opacities then become smaller because the energy-level density decreases near to the ground level. More generally, the temperature dependence of

the Planck mean opacity has been found asymmetric with regard to half-filled shells, while the number of levels is symmetric with regard to a half-filled occupation and is determined *geometrically*.

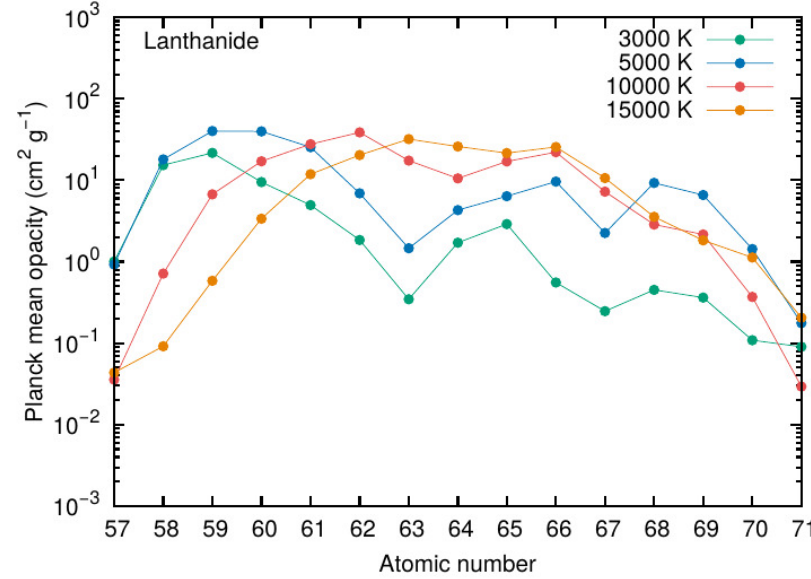


Figure 8.3.: Planck mean opacities of lanthanide elements as a function of atomic number and for selected temperatures. For lower temperature ( $T < 5,000K$ ), the opacity decrease with the nuclear charge  $Z$ , while the opacities are largest for elements with a half-filled  $f$ -shell at temperatures  $T > 10,000K$ ; taken from Tanaka *et al.* (2020).

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- **Opacity calculations for r-process elements:** Fontes *et al.* (2017) calculated radiative opacities for four r-process elements (cerium, neodymium, samarium and uranium) by using both, fully and semi-relativistic methods as well as for different amounts of configuration interaction in the atomic-structure computations.
- **Opacity computations:** For every given element, the opacity computations require atomic-structure data (energies, wavefunctions and oscillator strengths) and photoionization cross sections.
- **Opacity calculations for r-process elements:** Fontest *et al.* use the GIPPER ionization code in order to obtain the relevant photoionization

cross sections in the distorted-wave approximation. The photoionization data are used to generate the bound-free contributions to the opacity and are not expected to be too important for the present application because of the relevant photon energies.

### 8.5.d. Electro-magnetic transients & light curves from astrophysical matter clouds

#### Observation from astrophysical matter clouds:

- **Light curves from stars & temperature:** The light observed from a star typically originates from its atmosphere, i.e. a gas layer that surrounds some (more or less) opaque interior. In equilibrium, the photons from this atmosphere carry away (i) the gravitational energy that is released by the collapse of the matter cloud; (ii) the energy released from the thermonuclear reaction within the core of the star as well as (iii) the released cooling energy of, for instance, white dwarfs, once the thermonuclear reactions has stopped (Pettini 2018).
- **$\delta$  Cephei stars:** The so-called  $\beta$ -Cephei stars are hot blue-white stars of spectral class B. These stars have masses of  $8 \dots 20 M_{\odot}$  and their magnitude ranges from +3.16 to +3.27. These stars pulsate through the (so-called)  $\kappa$  mechanism that is related to the M-shell transitions of these elements. The Cepheid stars are known to be used in order to estimate stellar distances. These distances are now better understood after the opacities were revised by about a factor two for various species of atomic number  $Z > 2$ , and as confirmed also by recent measurements of absorption coefficients. The opacities of the iron group elements (Cr, Fe, Ni and Cu) for  $T \approx 2 - 3 \times 10^5$  K and  $\rho = 10^7 \dots 10^{-6}$  g/cm<sup>3</sup> have been found important for analyzing these stars.
- **Local Thermodynamic Equilibrium (LTE):** Despite the complexity of (and complications with) astrophysical plasma, one makes often use of the LTE approximation as long as the mean free path of the photons and particles is small compared to the scale over which the temperature changes significantly. This applies for instance to many stellar interiors because of the high density and temperature and, hence, quite small mean distances between collisions.

#### Temperature of stars in astrophysical matter clouds:

- **Temperature of stars:** The temperature can be defined in various different ways, namely as (Pettini 2018):
  1. **Effective temperature:** as defined in terms of the luminosity of the star and its radius;
  2. **Excitation temperature:** as given by the relative population of different excited levels of an atom or ion in the plasma, and by using Boltzmann's equation;

3. **Ionization temperature:** as defined by the relative population of different ionisation stages of an atom, and by using Saha's equation;
4. **Kinetic temperature:** as defined by the Maxwell-Boltzmann distribution:

$$n_v dv = n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} 4\pi v^2 dv$$

with the number density  $n_v$  (number of particles per unit volume) of particles with speeds between  $v \dots v + dv$  and the total number density  $n$  of all particles with the given mass  $m$ ;

5. **Color temperature:** as the temperature of the blackbody whose spectral energy distribution resembles most closely that of the given star.

### Photoionized, steady-state plasma:

- **Calculation of ion distributions:** The standard method for calculating the ion distribution in a non-LTE system is to solve the rate equations for all the important ionic states and by including different excitation and ionization channels due to the incident radiation. From the solutions of these rate equations, a time history of the electron temperature and density as well as the time evolution of the different charge states in the plasma can be evaluated. The **steady-state solution** is then obtained by following the time evolution until the populations do no longer change with time.
- **Calculation of ion distributions:** In non-LTE plasma, a major simplification in the calculation of ion distributions is achieved if only the shell populations is taken into account within the **average-atom model**. In this model, the shell distribution is averaged over the distribution of the ionic states. Indeed, this approach reduces the number of differential equations significantly, when compared to a detailed treatment of all charge states, although the shell occupancies are non-integers in the average-atom model.
- **Calculation of ion distributions:** The photoexcitation and photoionization as well as their inverse rates are often approximated by Kramers' (1923) simple expressions, convolved with the intensity of the ambient radiation field.

### Need of astrophysical opacities:

- **Applications of opacity calculations:** Three typical example applications for opacity calculations are: (i) The iron opacities at conditions of the solar convection zone, (ii) nickel opacities for modeling various stellar envelopes, and (iii) the samarium opacities for the modeling of light curves as produced by neutron star mergers.

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- **Frequency-dependent opacity:** In recent work, the frequency-dependent LTE opacity of iron has been studied for the conditions of the solar convection zone. These studies revealed rather large (30–400%) differences between experiment and theory for the monochromatic opacity of an neon-like iron plasma (or nearby charge states). Until the present, the source of this not yet fully understood and remains an active area of research.

## Gravitational-wave astronomy:

- **Discovery of gravitational waves (GW):** The discovery of GW from the inspiral and coalescence of binary black holes (BH) and/or neutron stars (NS) by the Laser Interferometer Gravitational Wave Observatory (LIGO) has opened a new window on the cosmos.
- **Discovery of gravitational waves (GW):** The discovery of electromagnetic signals in coincidence with a chirp at the gravitational-wave detectors leads to a better location and a much richer picture about the initially merger process. This may allow to extract directly information on the formation of the binary channels, the age of the stellar population as well as the dynamics of binary mergers.
- **Merger of black-hole binaries:** In general, the merger of BH binaries is not expected to produce luminous electro-magnetic emission because there is not enough baryonic matter in these systems.
- **Gravitational-wave (GW) astronomy:** The direct detection of GW opened a new era of (GW) astronomy. To further understand the astrophysical nature of GW sources, the **identification of their electromagnetic (EM) counterparts is crucial, since the GW detectors are generally not accurate enough to pin down the position of these GW sources.**
- **Sources of gravitational waves (GW):** Despite of a rather large number of expected BH-BH mergers during the next few years, a better synthesis and analysis of gravitational wave and the associated electro-magnetic signals will probably come from NS-NS or BH-NS mergers, i.e. if neutron stars are involved.
- **Sources of gravitational waves (GW):** While most detected GW sources are nowadays believed to arise from black-hole binaries, neutron star mergers are another major source of gravitational waves. **For these NS mergers, an electro-magnetic signal is expected to arise in two forms: gamma-ray bursts (GRB) or from kilonovae** (Metzger *et al.*, 2010). The GRB are expected to be short-lived with a jet-type signal, while the kilonovae are predicted to generate relatively isotropic signals.
- **Sources of gravitational waves:** In practice, it is not easy to precisely locate the sky position of GW sources since it needs to be determined by triangulation, i.e. from the arrival times of the GW signals at different detectors. At present, the uncertainties in this triangulation are quite large, although these uncertainties will be reduced to  $\approx 10 - 100 \text{ deg}^2$ , once Virgo in Italy and, eventually, KAGRA in Japan and LIGO-India will join the network (Metzger 2017). Initially, these uncertainties were  $\approx 850 \text{ deg}^2$  for GW15091 and with a later improvement to  $\approx 250 \text{ deg}^2$ ).



- **Sources of gravitational waves:** Even an localisation of the GW signals within  $10 - 100 \text{ deg}^2$  greatly exceeds the fields of view of most radio, optical and x-ray telescopes, and in particular the field of view of those telescopes that are sensitive enough to detect the electro-magnetic counterparts of NS-NS and BH-NS mergers.
- **$\gamma$ -ray bursts (GRB):** Although short GRB are (very) bright and high-energetic events, only a subset of these bursts will be observed on Earth since the most intense emission from a given merger will typically not intersect the line of sight from the Earth.
- **$\gamma$ -ray bursts (GRB):** Short GRB are commonly believed to be powered by the accretion of a massive remnant disk, following some BH and/or NS mergers. These GRB are typically expected to occur already within seconds of the GW chirp, providing an unambiguous temporal signature to the GW signal. Although such short GRB are likely the cleanest electro-magnetic counterparts to the GW signals, their measured rate will remain low within the Advanced LIGO detection volume. This rate is probably less than one observable event per year if the GW signal arises from NS-NS mergers since the  $\gamma$ -ray emission is beamed into a narrow solid angle not seen from Earth (Metzger 2017).
- **Electro-magnetic counterparts of GW:** NS-NS and BH-NS mergers are also predicted to be accompanied by a more isotropic counterpart, commonly known as kilonovae. These kilonovae provide both a robust electro-magnetic counterpart to the GW chirp, and which is expected to accompany a good fraction of BH-NS mergers and essentially all NS-NS mergers (Metzger 2017).
- **Sources of gravitational waves:** The single NS-NS merger event (GW170817, GRB170817A, AT2017gfo) made a big qualitative step for gravitational-wave astronomy since it showed that these mergers can be observed and are directly linked to gravitational waves, gamma-ray bursts, kilonovae as well as the generation of heavy elements (nucleosynthesis).
- **Role of neutrinos for neutron-star mergers:** The absorption of neutrinos can make the ejected material from neutron-star mergers less neutron-rich and can increase the so-called **electron fraction  $Y_e$ , e.g. the number of protons per nucleon**.
- **Simulation of neutron-star mergers:** While different (relativistic) simulations of NS mergers have predicted a wide ranges of electron fractions  $Y_e = 0.05, \dots, 0.45$ , although a detailed understanding of the electron distribution depends on the nuclear equations of state as well as the masses and mass ratio of the neutron stars. For the sake of simplicity, a flat mass distribution and an electron fraction  $Y_e = 0.1, \dots, 0.4$  are assumed to represent dynamical ejecta.
- **Spectra from AT2017gfo:** A series of spectra have been observed from this merger has enabled one to analyze the evolution of the kilonovas primary electromagnetic output from 1.5 days until 10 days after the event (Watson *et al.*, 2019). It is expected from rather simple estimates that a large number of moderate-to-weak lanthanide lines with unknown oscillator strengths dominate the observed spectra. For a spherically expanding ejecta, the line broadening should be then comparable to the expansion velocity of the gas. However, a more detailed analysis will require also additional knowledge about the geometry of the gas cloud and the wavelength-dependent opacities over a wide range of elements.

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- **Sources of gravitational waves:** The discovery of a kilonova in coincidence with a gravitational-wave signal from a binary neutron-star merger *and* with a short burst of  $\gamma$ -rays provides **striking evidence for the main theoretical picture of neutron-star mergers**. In particular, these detections confirm that binary neutron-star mergers produce kilonovae with emission properties in reasonable agreement with theoretical predictions.

### Neutron-star merger:

- **Opacities for ejecta from neutron-star mergers:** At the near-IR/optical frequencies, the dominant source of opacity arises from the many bound-bound transitions between the low-lying levels of the atoms and ions. **For this continuum of lines, the opacity is determined by the strength and wavelength density of all lines**, and which depend sensitively on the composition of the ejecta.
- **Opacities for ejecta from neutron-star mergers:** The opacity of the ejecta from NS mergers can significantly rise if they just contain a modest fraction of elements with a partially-filled  $f$ -shell, such as the elements from the lanthanide and actinide groups.
- **Plasma of neutron-star mergers:** Because of the rather cold ( $\sim 1$  eV) conditions in the plasma of a neutron-star merger, it is typically sufficient to include a small number of low-lying configurations for each ion stage in order to obtain a **converged set of fine-structure level populations, making use of a local-temperature equilibrium Saha-Boltzmann statistics**. Fontes *et al.* (2015) used such a small number of configurations and generated about  $10^5$  levels and  $3.3 \times 10^8$  lines.
- **Plasma of neutron-star mergers:** Results from a multi-dimensional ray-trace merger calculation for neutron-star ejecta suggest that the radioactively-powered heavy materials are more difficult to observe in the r-process, than it was previously believed (Fontes *et al.*, 2017).
- **Opacities of ejecta from neutron-star mergers:** At rather low plasma temperatures  $T \lesssim 10^3$  K of the neutron-star ejecta, a further uncertainty arise from a improved treatment of the (initially) gaseous to a solid-state phase. Until the present, **it remains unclear whether such r-process dust then increases or decreases the optical/UV opacity** as this will depend how the dust condenses and how quickly it grows in size.
- **Light emission from neutron-star mergers:** The light emission from the ejecta of neutron star mergers strongly depends on the ejecta material. Therefore, Tanaka *et al.* (2018) performed limited atomic structure calculations for the r-process elements: Se ( $Z = 34$ ), Ru ( $Z = 44$ ), Te ( $Z = 52$ ), Ba ( $Z = 56$ ), Nd ( $Z = 60$ ) and Er ( $Z = 68$ ). These computations confirmed, in particular, that the bound-bound (expansion) opacities of the two lanthanides Nd and Er with an open  $f$ -shell are significantly larger than those of the mid- $Z$  elements over a rather wide range of wavelengths. These authors focused especially on neutral atoms as well as on singly- and doubly-ionized ions which are expected to be most common at  $t = 1$  day after the merger.

- **Opacities for neutron-star mergers:** Because of the lack of atomic data for the  $r$ -process elements, one has often just applied the opacities of iron in order to simulate neutron-star mergers. However, in order to predict the emission properties of kilonova, (more) systematic atomic data for  $r$ -process elements are highly desirable.
- **Neutron stars:** These stars have been postulated already short after the discovery of the neutron as the **ultimate fate of massive stars which end in a supernova**. The existence of neutron stars was later shown in the 1960s following the observation of the first pulsars.
- **Distribution of neutron star masses:** Today, the equation of state and the distribution of neutron star masses are believed to be known reasonably well.
- **Material ejected from neutron-star mergers:** The material that is ejected during or immediately after the merger of two neutron stars may produce considerable amounts of heavy elements through the  $r$ -process. The subsequent radioactive decay of these (neutron-rich) nuclei can power transient electromagnetic emission similar to, but significantly dimmer than, an ordinary supernova (Kasen *et al.*, 2013). One goal of future observations of the electro-magnetic transients in gravitational-wave astronomy is to better understand the  $r$ -process and, hence, the astrophysical sources of gravitational waves.
- **Material ejected from neutron-star mergers:** A key in studying the matter outside of the remnant of the neutron-star merger is the release of neutron rich-matter and the cascade of nuclear reactions. These nuclear reaction gives then rise to **kilonova which can be observed on the time scale of hours, days and even months due to the radioactive decay of freshly synthesized, neutron-rich elements in the ejected matter**.
- **Mass of ejecta from neutron-star mergers:** This mass is predicted to be rather high and to reach from  $10^{-3} \dots 10^{-2} M_{\odot}$  for the overall  $r$ -process matter.
- **Light curves from neutron-star mergers:** Since very little is known about the optical properties of the heavy  $r$ -process elements, most previous light-curve models have adopted the opacities from the iron group elements. Barnes and Kasen (2013) considered first the opacities of lanthanides and concluded, that the opacity of the ejecta material from neutron-star mergers might be larger by several orders of magnitude. In further detail, Barnes and Kasen included these opacities into time-dependent, multi-wavelength radiative transport calculations in order to predict the broadband light curves for a range of masses and velocities of the ejecta.
- **Light curves from neutron-star mergers:** In neutron-star mergers, the light curves usually decline rapidly in the *optical* region, while they evolve more slowly in the *near-infrared* (NIR) region. Moreover, a high expansion velocity is expected if featureless spectra are observed.
- **Neutron star merger:** These mergers may give rise to both, short-duration gamma-ray bursts as well as the production of  $r$ -process elements in the universe.
- **Light curves from neutron-star mergers:** One current questions about neutron-star merger is of whether the emitted electro-magnetic radiation can be observed in the optical or infrared bands. In order to model the light curves and spectra produced by NS merger, it

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appears necessary to calculate the radiative opacities from heavy elements, such as the lanthanides. These elements are expected to be present due to the capture of rapid neutrons during the r-process.

- **Simulation of neutron-star mergers:** Metzger (2017) introduces a **vanilla model of lanthanide-rich ejecta** that is heated by radioactivity in a week-long transient state of the ejecta from the merger process. This transient matter state may lead to the emission of optical (blue) light due to basically Lanthanide-free components of the ejecta or, possibly, to an early UV-bright **precursor that is powered by the decay of free neutrons in the outermost layers of the ejecta** (Metzger 2017).
- **Numerical simulations of neutron-star mergers:** Such simulations are often considered as a cornerstone for understanding the multi-messenger signatures and nucleosynthesis in the ejecta of neutron-star mergers.
- **Binary neutron-star mergers:** These binary neutron-star mergers are excellent examples of multi-physics problems that combine knowledge and data from strong-field gravity, strongly interacting matter, relativistic (magneto-) hydrodynamics and neutrino transport (Arcavi *et al.*, 2018).
- **Nuclear reactions in neutron-star mergers:** The high neutron densities in ejected NS mergers permit a violent r-process, leading to a fission cycle that produces very heavy nuclei in regions far from (nuclear) stability.

### r-process:

- **Rapid neutron-capture in elements beyond iron:** Burbidge *et al.* (1957) and Cameron (1957) realized already more than 60 years ago that approximately half of the elements heavier than iron are synthesized via the **capture of neutrons by light seed nuclei**, such as iron, in a dense neutron-rich environment, in which the time scale for neutron capture is shorter than the lifetimes for  $\beta$ -decay.
- **Opacities of r-process elements:** Barnes and Kasen (2013) showed that more realistic opacities of the *r*-process material may have a dramatic effect upon the predicted **light curves of a kilonovae**. In these simulations, they applied improved estimates of the radiative opacities of heavy elements as derived from *ab-initio* atomic-structure computations. The enhanced opacities of the lanthanides strongly affect the radio-active powered light curves from the ejecta of the neutron-star merger.
- **Production of heavy elements:** In all suggested scenarios, the r-process nuclei are produced within two steps. (i) An initial explosion burns at high temperatures until the electrons and ions freeze-out during expansion of the ejecta, although still with a high neutron-to-seed ratio. This initial expansion is followed by (ii) the rapid capture of neutrons by the seed nuclei, leading eventually to heavy nuclei.
- **Production of heavy elements:** Despite of intense research, little is known so far about the neutron-rich and in the *r*-process produced heavy elements. Indeed, the nuclei beyond the iron group elements (with mass numbers  $A \sim 90..100$ ) need to be formed via successive neutron capture, because all other nuclear reactions with charged particles exhibit a high Coulomb barrier.

- **Rapid neutron-capture:** The r-process always occurs along a nuclear path which resides quite far on the neutron-rich side of the valley of stable isotopes. Despite some seminal works on the r-process, however, the astrophysical environments, that are particularly suitable to this process, are not yet well understood. Indeed, a better understanding of the r-process environments is one of the great challenges in nuclear astrophysics.
- **r-process *versus* supernovae:** The rapid neutron capture or (so-called) r-process is considered to be responsible for about half of the elements heavier than iron, although this process was previously attributed also to core-collapse supernovae. However, recent studies of the r-process have disfavored supernovae because their conditions are not suitable to produce the heavy elements near to the *platinum peak* around  $A \propto 195$ . Instead, neutron-star mergers have received a lot of recent interest as a major r-process production site (Tanvir *et al.*, 2017).
- **Astrophysical environments for the r-process:** A question in contemporary astrophysics is whether the mergers of neutron stars gives rise to a robust r-process environment that lead to heavy neutron-rich isotopes with mass  $A \geq 130$ , and whether the generated proportions are similar to solar abundancies (Thielemann *et al.*, 2017). In the neutron-rich ejecta from neutron star (NS-NS) and BH-NS binaries, in particular, the r-process is expected to proceed rapidly, leading to many heavy elements like gold, platinum and many others.
- **Astrophysical environments for the r-process:** Various astrophysical sites have been suggested for the r-process of the nucleosynthesis. Apart from regular supernovas, the r-process has been associated especially with neutrino-induced processes in the outer shells of massive stars, the ejecta from compact binary mergers as well as from so-called magneto-hydrodynamic (MHD) jet supernovae which exhibit high magnetic fields and neutron-rich jet ejecta along the poles.
- **Astrophysical environments for the r-process:** In astrophysical environments, the theory of the r-process was worked out 60 years ago and made it clear that an enormous neutron flux is required in order to explain the observed abundances of the elements. Because of this enormous flux, the details and necessary conditions of the r-process is still under debate in astrophysics. New interest in this topic arose from the neutron-star mergers as a very probable r-process site, and the discovery of freshly synthesized r-process elements will stimulate this discussion.
- **Astrophysical environments for the r-process:** The observation of the solar abundance of elements suggest just two (rather extreme) environments for neutron capture in nature: Either by the slow *s*-process production of  $\beta$ -stable isotopes or by the fast *r*-process for isotopes far from the stability (Freiburghaus *et al.*, 1999). Here, three interesting questions about the *r*-process refer to: (i) How frequently merge two neutron stars or a neutron star with a black hole ? (ii) How much mass is typically ejected per event ? (iii) How much of these ejected material contributes indeed to the *r*-process ?

## Kilonovae:

- **Simulation of kilonovae:** Although these simulations help explain some of the observed spectral features, they are still in their infancy and suffer from rather incomplete atomic data of the r-process elements. In particular, atomic data are available only for small number of r-process elements and with an expected accuracy  $\lesssim 30\%$ , although a more detailed comparison is difficult as well as because of insufficient measurements.
- **Modelling of kilonovae:** The recent progress with **opacity computations moved the predicted peak emission towards longer wavelengths**; the currently best estimates refer to the near-infrared band, and this shift needs to be taken into account in the modelling of kilonovae.
- **Kilonovae:** Kilonovae are day to week-long thermal, supernova-like transients which are powered by the radioactive decay of heavy, neutron-rich elements synthesized in the expanding ejecta of NS-NS or NS-BH mergers. The radioactive decay of such unstable neutron-rich nuclei powers a rapid evolution of a supernova-like transition of stellar matter that is **known as kilonova or macronova** in the literature. These kilonovae can be understood also as **roughly isotropic electromagnetic counterpart to the GW signal** and, thus, provide a unique and direct probe of such r-process sites (Metzger 2017).
- **Kilonovae** refer to optical transients that are powered by the radioactive decay of material ejected in the neutron-star merger. Simulations suggest an ejected mass of  $10^{-4} \dots 10^{-1} M_{\odot}$  due to a tidal stripping during the merger process itself or by a subsequent disk wind in course of the evolution of a post-merger remnant.
- **Kilonovae versus  $\gamma$ -ray burst:** Kilonovae are powered by the radioactive decay of excited nuclear matter. These kilonovae will emit more isotropically (when compared to the accretion disk of the merger event) and will peak later than short-GRB afterglows. Kilonovae are the best candidates for the electromagnetic counterparts of the GW detection.
- **Photon emission from kilonovae:** A detailed understanding of the photon emission from kilonovae requires (detailed) information and simulations on the composition, velocity structure and the opacity of the ejecta as well as on the transport of radiation through the ejecta. The kilonova emission from NS mergers is centered around the optical/IR bands since this is the first spectral window through which the expanding ejecta from NS-NS mergers becomes transparent.
- **Key observables of kilonovae:** Three main ingredients need to be understood in order to quantify the **key observables of a kilonovae, namely its peak time scale, the luminosity and the effective temperature**. In more details, these ingredients are: (i) The mass and velocity of the ejecta from NS-NS or BH-NS mergers; (ii) the opacity  $\kappa$  of the expanding neutron-rich matter; and (iii) the variety of sources which contribute to the heat of the ejecta  $Q(t)$ . These ingredients are important especially on the time scale of  $t^{(\text{peak})}$ , when the ejecta is first becoming transparent.

- **Kilonovae:** This term refers to an optical/infrared transient that has been observed a few days after the merger of two neutron stars. These transient spectra may allow to observe spectral signatures of newly created neutron-capture elements. For example, Watson *et al.* (2019) reported the identification of the neutron-capture element strontium from a detailed re-analysis of the observed transient spectra. The identification may prove that neutron stars are made of neutron-rich matter, although the discussion by Watson *et al.* seem not so stringent.

### Source of $\gamma$ -ray emissions:

- **Multi-photon Compton scattering:** Multi-photon Compton scattering has been studied experimentally at the Stanford Linear Accelerator Center (SLAC) (Bula *et al.*, 1996) as a possible source of gamma rays that are emitted from various astrophysical objects. From classical electrodynamics, it is well known that accelerated, charged particles emit em radiation which, in turn, affects their own dynamics through recoil. In astrophysical models, the particle dynamics and emitted radiation must be coupled self-consistently to each other. This coupling is also called **radiation reaction** and is typically neglected in all nonrelativistic plasmas. This coupling is very closely related also to the electron self-interaction problem in both, the classical and quantum electrodynamics (ED). In classical ED, the Dirac-Lorentz equation (Dirac 1938) describes the covariant dynamics of a point charge including the radiative corrections due to the recoil momentum of the photon field. This radiative correction can be interpreted also as **reaction force due to the self-ineraction of a charged particle with its own em field**.



### 8.5.e. Absorption and emission spectra of distinct astrophysical objects

#### Infra-red emission spectra from astrophysical missions:

- **Astrophysical observation of infra-red spectra:** Various astrophysical missions and spectrographs, such as GIANO, CRIRES or SOFIA have moved the observations into the infra-red region. These observations made visible a large number of new objects because of the higher transmission of infra-red radiation through dust clouds. In the infra-red spectra, many of the observed lines hereby arise from either forbidden transitions within the ground-state configuration or from Rydberg series of rather highly-excited atoms and ions.

#### EUV emission spectra from astrophysical missions:

- **High-quality EUV spectra:** The Solar EUV Rocket Telescope and Spectrograph (SERTS, 1992) and the Extreme Ultraviolet Explorer (EUVE, 1990) spectrometers provided high-quality EUV spectra and helped improve the diagnostics of high-temperature plasmas in astrophysical objects.
- **High-quality EUV spectra:** The ability to resolve a large number of individual emission lines and to measure the accurate intensities over a wide wavelength range have enabled one to analyze the temperatures, densities and abundances of elements in a variety of astrophysical sources (Brickhouse *et al.*, 1995).
- **High-quality EUV spectra:** The fine structure of (line) multiplets nowadays allow to solve the full rate equations for several atoms in the plasma, including collisions among all levels and cascades. This enables one to calculate also the **emissivities of weak lines that were previously omitted from the investigation.**
- **SERTS catalog:** The SERTS catalog provides for an average solar active region about 270 emission lines between 170 to 450 Å from which about 90 lines from Fe IX to Fe XVII are identified. These lines cover a temperature range between  $4 \cdot 10^5$  to  $6 \cdot 10^6$  K. Indeed, these observations combine an excellent spectral and spatial resolution with a good calibration of most lines between 235 ... 450 Å. In these spectra, each charge state of iron contains at least four lines, making it possible to determine the relative line intensities for each model atom.

#### x-ray emission spectra from astrophysical missions:

- **X-ray emission from astrophysical objects:** From the analysis of line intensities in exotic dense-plasma environments, several key properties of astrophysical objects may be derived that are not attainable through other observational windows.



- **x-ray spectra from Chandra and XMM-Newton:** In x-ray astronomy, the satellites Chandra and XMM-Newton provided (x-ray) spectra from many different astronomical objects, including  $K$ -shell transitions of carbon, nitrogen, oxygen, neon, silicon and sulphur as well as  $K$ -shell transitions from the iron-group elements with wavelength between 5–45 Å. These spectra help understand extreme astrophysical environments in active galactic nuclei, x-ray binary systems, Wolf-Rayet Stars as well as from interstellar media (ISM; Sant’Anna *et al.*, 2011). A detailed analysis of spectra from XMM-Newton enables one to characterize the ISM if the absorption cross sections near to  $K$ -edge are known.
- **High-resolution x-ray observations from XMM-NEWTON:** Sako *et al.* (2001) present first results from high-resolution x-ray observation of IRAS 13349+2438 with the XMM-NEWTON observatory. The observed spectrum was obtained with the Reflection Grating Spectrometer (RGS) and shows a wealth of discrete spectral features, including the (first) astrophysical detection of an unresolved transition array (UTA) due to the  $2p - 3d$  inner-shell excitations of  $M$ -shell iron ions. These spectral features could have been easily misidentified, for instance, as an O VII edge, when observed with only moderate resolution spectrometers.
- **High-resolution x-ray observations from XMM-NEWTON:** Other prominent features in the spectra of Sako *et al.* (2001) were the  $K$ -shell absorption lines of hydrogen- and helium-like carbon, nitrogen, oxygen and neon as well as the  $L$ -shell lines of Fe XVII-XX.
- **Diffusion approximation for the radiative flux in a plasma:** In optically thick layers, the diffusion approximation is justified in which the variation of the radiation flux  $\mathbf{F}$  in the plasma is related to the (radiative) luminosity  $L_r$  by

$$\delta \operatorname{div} \mathbf{F} = \frac{1}{4\pi r^2} \frac{d\delta L_r}{dL_r}, \quad \frac{d\delta L_r}{dL_r} = \frac{dr}{d \ln T} - \frac{d\kappa^{(\text{Rosseland})}}{\kappa^{(\text{Rosseland})}} + A \left( \frac{\delta T}{T} + \frac{\delta r}{r} \right)$$

In this expression, the first term describes the **radiative dissipation that stabilizes the star**. Moreover, the term  $\delta T/T$  is also known as  $\gamma$  mechanism and describes the direct influence of the temperature variation on the luminosity (this is typically small),  $\kappa^{(\text{Rosseland})}$  is the Rosseland mean opacity,  $A$  a constant and the last term contributes to the instability because the radiating area is reduced in case of the compression.

## Emission spectra from the solar photo- and chromosphere & comets:

- **x-ray emission from comets:** The discovery of x-ray emission from the **comet Hyakutake** was initially found surprising since comets are known to be quite cold (Cravens, 2002). First observations of such x-ray emissions were made with the x-ray satellite ROSAT; they clearly indicated that x-rays are produced by almost all comets due to charge-exchange collisions of highly-charged ions from the solar wind with neutral atoms from the comets. Meanwhile, x-rays were observed from several 10 comets with emphasis upon their total luminosity, spatial

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morphology, temporal variation as well as their energy spectrum. Since these spectra include multiple emission lines, they are related to various electron capture processes and to  $K_\alpha$  emissions.

- **Composition of the solar wind:** Apart from (mainly) protons and electrons, the solar wind also contains minor fractions of  $O^{7+}$ ,  $O^{6+}$ ,  $C^{6+}$ ,  $C^{5+}$ ,  $N^{6+}$ ,  $Ne^{8+}$ ,  $Si^{9+}$  and  $Fe^{12+}$  ions. In collision with (nearly-) neutral atoms and molecules, these ions will capture electrons into some excited shell and emit x-rays.
- **x-ray emission from comets:** In collision with comets, the ions from the solar wind will mainly recombine. A better understanding of the underlying charge-transfer processes require a suitable magnetic & hydrodynamic model, a better knowledge about the solar wind as well as reliable charge-transfer cross sections from either laboratory measurements and/or atomic theory. The energy of the x-ray emission from comets is therefore stored as potential energy in the multiply-charged ions and arise directly from the sun.

### Generation of synthetic spectra:

- **Synthetic stellar spectra:** The generation and comparison with synthetic spectra is a primary instrument in order to understand the atmospheres of stars. Different elements in the stellar plasma occur in millions of spectral lines, and from which the the plasma decomposition and properties need to be derived. Apart from using a local-thermodynamical equilibrium (LTE), non-LTE (NLTE) approaches have become relevant to gain a better understanding. However, these NLTE approaches are computationally (much) more demanding. In a NLTE plasma, the population of energy levels and the intensity of the radiation affect each other and need to be solved *simultaneously*, for instance by using radiative transfer equation (Tagirov *et al.*, 2017).
- **Plasma parameters and ion abundances:** Different theoretical (spectral) models are needed in astro and plasma physics in order to determine the electron temperature, (electron) density distribution as well as the abundances of ions and elements in different environments. In astrophysics, simulation codes usually differ in the number of (astrophysically relevant) elements as well as in the number (and quality) of the emission lines. A comparison of different simulations shows that the use of (most) recent atomic data and a proper treatment of the continuum processes is very crucial.

### 8.5.f. Radiation transport in astrophysical and hydrodynamical environments

#### Energy transport in plasma:

- **Role of radiation and neutrino transport:** Radiation transport plays a key role for the dynamics of many astrophysical processes; for instance, the radiation feedback from stars and black holes plays an essential role for the rate of gas accretion in the formation of stars within galaxies. The **star formation rate determines the observable properties from galaxies**, such as stellar luminosity, color, and age.
- **Energy transport in plasma:** Energy transport simulations in plasma is a very complex or even formidable task for various reasons:
  - (1) There occurs a large number of processes at the atomic scale, including, e.g., emission, absorption, scattering;
  - (2) the vast majority of astrophysical scenarios are intrinsically three-dimensional (Reed *et al.*, 2018).
- **Energy transport in plasma:** In many astrophysical environments, the energy transport by radiation or relativistic particles is ubiquitous and need to be modelled by hydrodynamical simulations. Examples of such environments range from the formation of planets to the evolution of cosmic structures, and up to core collapse supernova or gamma-ray bursts.
- **Energy transport in plasma:** Often, the energy transport simulations in plasma are limited by the (approximate) treatment of the radiation transport and the relativistic particles. These limitations also hinder our understanding of the complex astrophysical Universe as well as the star and galaxy formation. Many requirements for an improved understanding arise similarly at short time scales and for large astrophysical environments.
- **Radiation and neutrino transport (RT/NT) codes:** Most of the presently available codes apply very approximate algorithms and can be utilized only for a limited range of parameters and conditions, e.g. a single radiative source with an optically thin diffuse gas. This limitation is quite in contrast to the typically large dynamical structures in astrophysics and, hence, to the large effective range of the optical depth that occur in such environments.
- **DIAPHANE library:** This library provides various radiation and neutrino transport (RT/NT) routines for a wide range of astrophysics simulations (Reed *et al.*, 2018). These routines can be utilized directly in simulations, although it remains rather unclear from this write-up which hierarchy of models apply and how they need to be adapted for certain physical environments. In this library, the mean opacity  $\kappa(\rho, T)$  is simply interpolated from a table of Rosseland mean opacities.

### 8.5.g. Plasma light sources for nanolithography

#### EUV light sources:

- **EUV light sources at 13.5-nm wavelength:** In order to generate extreme ultraviolet (EUV) light at 13.5-nm wavelength by laser-produced plasmas, the emission of multiply-charged tin ions have been found promising for nanolithographic applications. For these ions, the EUV light is generated by thousands of transitions that form so-called unresolved transition arrays (UTA), and with rather little dependence on the particular charge state of the tin ions (Winderberger *et al.*, 2016).
- **EUV light sources from multiply-charged tin ions:** For multiply charged tin ions with a  $[\text{Kr}] 4d^m$ ,  $m = 6 \dots 0$  configuration, the upper configurations for an EUV emission are  $[\text{Kr}] (4p^6 4d^{m-1} 4f + 4p^6 4d^{m-1} 5p + 4p^5 4d^{m+1})$  (Winderberger *et al.*, 2016).

### 8.5.h. Laser-induced fluorescence spectroscopy (LIFS) in flames

#### Laser-induced fluorescence & applications:

- **Laser-induced fluorescence** describes the spontaneous emission from atoms or molecules following the prior excitation by laser irradiation. In multi-level atoms or molecules, the laser is usually tuned to one of the absorbing transitions. From the so-excited level, the atoms then decay either to some lower lying state or are re-populated by collisions to adjacent states. In LIFS, therefore, a fluorescence spectrum is observed that contains individual transition of the excited level as well as from levels nearby (Daily 1997).
- **Laser-induced fluorescence signal:** The laser-induced fluorescence signal after laser excitation can be exploited in various ways: (i) The observed spectrum provides a measure for the population of the initially excited states; (ii) it allows to extract the total number density of different species in the probe, if a clear relationship can be established between the number density of all involved quantum states; (iii) the observed spectrum (may) help deduce the ground-state distribution function and, hence, the temperature of the probe. Moreover, (iv) the pressure, temperature and velocity may be deduced from the observed line shapes under suitable circumstances.
- **Application of LIFS:** LIFS has been utilized for studying combustion processes, to measure species concentration, temperature, pressure and velocity in flames. Indeed, LIFS contributes today significantly to many experimental combustion studies.

### Combustion processes:

- **Combustion:** Combustion is the primary propulsion technology and is very frequently applied for the generation of electricity, the heating of buildings and at many places elsewhere. Combustion is applied also for the synthesis of new materials and for chemical processing (Daily 1997). In nature, combustion is a frequent source when natural areas are changed by fire.
- **Combustion systems:** Flames and combustion systems vary widely in their size, fuel type and purpose. They range from small mm-to-cm systems, such as furnace and stove pilot flames, gas stove burners or small laboratory burners to medium-size motors and heating systems, and up to pulverized coal fire boilers, marine diesels and forest fires, each with length scales on the order of several meters (Daily 1997).
- **Performance evaluation of combustion processes:** Combustion processes are often analyzed with regard to their energy conversion efficiency, material synthesis yield, material purity and/or pollutant emissions. This analysis is often made by measuring the exhaust and without that the combustion zone is affected directly.

### 8.5.i. Synthetic spectra for laser-induced breakdown spectroscopy (LIBS)

#### Laser-induced breakdown spectroscopy:

- **Laser-induced breakdown spectroscopy (LIBS)** has been found a versatile analytical tool with various applications. In this technique, a high-power laser beam is typically focused upon the surface of a sample that need to be analyzed. If the laser power exceeds a certain threshold, an optical breakdown occurs due to the formation of a laser-induced plasma. In practice, **the breakdown threshold depends on the wavelength and duration of the laser pulses as well as on the analyzed media.**
- **LIBS for nanosecond laser ablation:** For a nanosecond laser ablation, for example, the threshold varies from  $1.9 \cdot 10^8 \text{ W cm}^{-2}$  for copper up to  $10^{10} \dots 10^{11} \text{ W cm}^{-2}$  for aqueous solutions (Yaroshchyk *et al.* 2006).

#### Simulation of LIBS spectra:

- **Synthesized LIBS spectra:** Ciucci *et al.* (1999) first estimated theoretically with limited accuracy the composition of a laser-induced plasma by using computational tools instead of the (standard) calibration. Their computation were based on the assumption that the plasma and sample compositions are the same and that the plasma is optically thin and in local thermal equilibrium (LTE) during the observation.
- **Synthesized LIBS spectra:** Yaroshchyk *et al.* (2006) describe some software for synthesizing laser-induced breakdown spectroscopy emission spectra and to predict sample compositions by using a proposed **calibration-free algorithm**. This code applies a database of atomic emission lines in order to create a theoretical emission spectrum for selected elements using defined plasma parameters.
- **Synthesized LIBS spectra:** The code by Yaroshchyk *et al.* (2006) is also based on the assumption of a LTE and a well-defined plasma temperature and electron density; it takes a number of characteristics atomic emission lines as input to create a synthesized theoretical emission spectrum of selected elements which are compared to the spectra of four separate compact spectrometers covering the spectral region 185–950 nm.
- **Synthesized LIBS spectra:** Until the present, all heavy elements are typically represented in LIBS plasmas only by their neutral atoms as well as their singly- and doubly-charged ions, that emit radiation at characteristic wavelengths. From the intensity of the individual wavelength, the composition of the samples are then estimated both, qualitatively and quantitatively.

### 8.5.j. Laser-produced plasma

## Remarks and properties of laser-produced plasma (LPP):

- **Laser-produced plasmas (LPP)** have attracted recent interest because of their use in developing laboratory ion sources and pulsed light sources at short wavelengths.
- In LPP, hot electrons can subsequently ionize the much cooler atoms, **forming an x-ray-emitting, high-temperature plasma spark** at the surface of the solid (Murnane *et al.*, 1991).
- The emitted **x-rays from LPP** are generally incoherent but have a high brightness because of the small size, short lifetime and the high temperature of the radiating plasma.
- The deposition of laser energy at high densities is crucial for the production of short x-ray pulses. If the LPP is produced by short pulses, the **electron heating and the rise time of the emitted x-ray pulse will be comparable to the duration of the laser pulse**.
- **Properties of LPP:** To determine the properties of LPP, such as temperature, density or its radiation emission, one needs a proper model for the coupling of the laser light with the heavy element (solid-state) target.
- **Scaling laws for LPP:** Scaling laws predict that brighter and more efficient x-ray sources will be obtained if (more) intense laser pulses are employed. These sources can then be used for time-resolved x-ray scattering studies and for the development of x-ray lasers.
- **Scaling laws for LPP:** Simple arguments can be used to derive scaling laws predict the response of the LPP if the laser parameters are varied. If any hydrodynamic expansion is neglected during the interaction with the laser pulse, we can equate the incident heating flux to the cooling flux that occurs due to classical thermal conduction.

## Applications of LPP:

- **EUV lithography:** LPP will find applications in extreme ultraviolet (EUV) lithography, EUV metrology as well as in the modification of surfaces.
- **Water window:** LPP sources have been developed for x-rays in the water window, though with limited conversion efficiency and/or brightness so far. These plasmas can be used for novel microscope designs as well as for cell tomography.
- **Source of x-rays and multiply-charged ions:** LPP have been proposed as source of both, x-rays and multiply-charged ions. Whereas x-ray sources aim for a high radiation loss from the plasma due to the generation of highly stripped atoms, high charge states of ions are mainly produced by a high plasma temperature and a low radiation level (loss).

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- **Time-resolved x-ray scattering:** Fast x-ray sources from LPP can be applied to investigate the time-resolved x-ray scattering from rapidly evolving materials (for example, the diffraction from materials with rapid phase transitions), time-resolved photoemission, or the flash-lamp pumping of x-ray lasers.

### Ultrafast x-ray pulses from LPP:

- A high-temperature plasma is created when an intense laser pulse is focused onto the surface of a solid (Murnane *et al.*, 1991). From such a plasma, an **ultrafast pulse of x-ray radiation is emitted when the laser pulse duration is less than about a picosecond.**
- X-ray pulses with a duration of a picosecond or less have been observed, more than an order of magnitude shorter than those produced by any other x-ray source.
- A direct comparison of fast x-ray pulses from LPP with other x-ray sources is difficult; in general, however, LPP yield x-rays with much higher peak power but lower average power than synchrotrons and other high-average power sources such as rotating anode tubes.
- Short x-ray pulses are expected if the plasma can cool rapidly. Deposition of laser energy at solid density allows such a rapid cooling because (i) the associated high thermal gradient allows rapid conduction of electron energy into the bulk of the solid beyond the optical skin depth; (ii) the associated high pressure gradient allows rapid cooling by expansion into the vacuum in front of the surface; and (iii) nonequilibrium conditions in the underionized plasma allow hot electrons to cool rapidly by inelastic collisions with atoms and ions (Murnane *et al.*, 1991).

### Ionization models for LPP:

- **Collisional-radiative (CR) ionization model:** A CR model can be applied to LPP with temperatures above a few tens of eV. At these temperatures, the average ionization stage  $A^{q+}$  of a given element is dominated by the electron plasma temperature due to electron and photon-impact excitation and ionization processes.
- **Collisional *versus* radiative processes:** Indeed, **two main types of excitation and ionization processes occur in LPP:** collisional and radiative processes, and where the corresponding de-excitation and recombination simply refer to the time-reversed processes. The ionization-recombination equations for both processes are:





- **Ionization-recombination equations:** In the set of ionization-recombination equations, one often only considers collisions with (free) electrons since these collisions are much more efficient than those with heavier particles. Obviously, however, these equations neglect autoionization and its (inverse) dielectronic recombination.
- **Local thermodynamic equilibrium (LTE):** For many laboratory plasmas, a local thermodynamic equilibrium (LTE) can be assumed, in which the collisional excitation and ionization processes are just balanced by their inverse processes, namely the collisional decay and recombination. These plasma are very different from **corona (models) for which no detailed balance applies since the collisional excitation and ionization lead predominantly to spontaneous line emission and radiation loss.**

### Deflagration models for LPP:

- **Deflagratio** refers to an explosion, in which the speed of burning is lower than the speed of sound in the surroundings. In other words, a deflagration is a fire in which a flame travels rapidly through a gas, but at subsonic speed.
- **Radiative deflagration model:** T model describes the rapid interaction of the incident laser radiation with a very thin layer near to the target surface. In this layer, the electron density reaches a cut-off density  $n^{(\text{cut-off})} = 10^{21} / \lambda^2 [\mu\text{m}]$ . This rapid interaction also leads to a (very) **hot plasma that expands into the vacuum** and which, *vice versa*, results in a shock wave into the solid owing to momentum conservation.
- **Hot plasma:** The properties of the hot plasma in the (thin) interaction layer can be determined mainly from the power density in the focal zone and the wavelength of the incident radiation.

### Laser-produced plasmas for laboratory astrophysics:

- **Laser-produced plasma:** Laser-produced plasmas have been successfully generated to simulate astrophysical plasmas in the laboratory for more than a decade. Indeed, researchers can nowadays create, control and characterize plasmas in the laboratory that replicate important features of different astrophysical objects. At present, high-intensity, femtosecond laser systems are available with peak powers between terawatt to petawatt. Often, they are used together with synchronized and laser-accelerated electron bunches with subpicosecond duration and terahertz bandwidths; cf. 8.5.k.
- **Application of laser-produced plasma:** These plasmas can be utilized to explore selected phenomena from supernovae, stellar evolutions, the solar corona, cosmic rays, planetary and celestial matter, or interstellar plasmas (Hartemann *et al.*, 2000). Together with a proper scaling, moreover, these plasmas can model a wide range of temperatures and densities that arise in astrophysical environments. Laboratory-based experiments help interpret astrophysical data by focusing up on the most relevant (physical) processes, and often without the need to reproduce the exact conditions.

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- **Laser-electron interactions in intense light beams:** The laser-electron interaction changes the (relativistic) intensity of a laser pulse drastically when it passes through matter. This can be understood already from the high transverse momenta of the electrons in the generated plasma wave. In some more details, three laser-electron interaction processes are particularly relevant: (1) a relativistic ponderomotive scattering for the collinear propagation of the laser and electrons; (2) the intense Compton backscattering in head-on collisions; and (3) the nonlinear Kapitza-Dirac scattering in standing laser waves.

### 8.5.k. Laser wake-field acceleration (LWFA) of particles

#### Laser wake-field acceleration (LWFA):

- **Laser-wakefield acceleration (LWFA) of electrons:** In a laser-produced plasma, a wakefield acceleration of electrons can be used to generate stable, tunable and nearly monoenergetic electron bunches at the MeV-GeV energy scale and with some (tens of) pC charge. These bunches have a quite short duration ( $\sim$  fs), small transverse bunch size ( $\sim \mu\text{m}$ ) and low divergence ( $\sim$  mrad); they are comparable with bunches at conventional state-of-the-art linear accelerators (Khrennikov *et al.*, 2015).
- **Application of LWFA bunches of electrons:** The unique properties of such laser-accelerated electron bunches makes them very promising for developing cheap and compact x-ray sources with high peak brilliance. Indeed, these sources might fill the gap in price and performance between standard laboratory x-ray tubes and large-scale synchrotrons, with an high (inherent) synchronization to both, the laser and electron beam. These novel x-ray sources can be applied also in other research areas, such a clinical imaging, material research, few-fs time-resolved x-ray emission spectroscopy and ultrafast pump-probe studies of structural dynamics (Khrennikov *et al.*, 2015).
- **Laser-wakefield acceleration (LWFA) of electrons:** When an intense laser pulse ( $a_o > 1$ ) passes through an underdense plasma, it generates a plasma wave by first repelling electrons from the region of high intensity due to the ponderomotive force of the light field. The phase of this plasma wave is hereby equal to the group velocity of the laser field, and both close to the (vacuum) speed of light. The plasma wave then results in a fast-moving longitudinal electric field that accelerates the electrons that remain (trapped) in the high-intensity region. The energy spread of the accelerated electrons can be further reduced, if a shock-front injection of electrons is employed (Khrennikov *et al.*, 2015). Such a shock-front can be created by placing some proper nozzle into the plasma-forming gas stream.

### 8.5.l. Fusion research

#### Hot fusion plasma:

- **Tungsten as key element for fusion research:** Tungsten (W,  $Z = 74$ ) has found much attention for building magnetic fusion devices, such as ITER (Cadarache, France) or WendelsteinX (Greifswald, Germany), and elsewhere. It is often considered as primary facing material within the vacuum vessel due to its low sputtering rate, high-temperature characteristics and low tritium absorption. Apart from this ability to withstand intense energy loads, however, tungsten is a high- $Z$  element that may contaminate the plasma and may then lead to large radiative power loss. Many theoretical case studies have therefore been performed to understand, predict and control the behaviour of tungsten in quite many charge states. Owing to the ionization dynamics of multiply-charged ions, only a few charged states typically dominate the overall ion dynamics.

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- **Spectroscopy of tungsten:** In most spectroscopic studies of tungsten plasma, the dominant line emissions arise from ions with either a closed-shell structure (for instance, Pd-like) or from configurations with a single electron outside a closed (sub-) shell (for instance, Ag-like). These line spectra are quite *sparse* and do not suffer from a spread over a large (huge) number of fine-structure transitions.

### 8.5.m. Mass attenuation coefficients

#### Attenuation coefficients:

- **photon mass-attenuation coefficient  $\mu/\rho$ :** The photon mass-attenuation coefficient is calculated from the density  $\rho$  of the target material and the thickness  $d$  of the material in the direction of the incident photons as

$$\frac{\mu}{\rho} = -\frac{1}{\rho d} \ln \left( \frac{N}{N_o} \right),$$

and where  $N_o$ ,  $N$  are the numbers of incident and transversing photons, respectively.

### 8.5.n. X-ray absorption of solid-state materials

#### Near-edge spectroscopy of solid-state samples:

- **Chemical sensitivity:** In the near-edge region of materials and samples, one is very sensitive to the surroundings of the absorbing atom. This makes absorption spectroscopies a very useful tool to investigate the geometric and electronic structure of the samples.
- **X-ray near-edge absorption (XANES):** XANES as well as other related spectroscopies, such as the resonant x-ray scattering spectroscopy (RXS) and x-ray magnetic circular dichroism (XMCD), are powerful spectroscopic techniques for probing the electronic structure around the absorbing atom in a fluid or solid-state probe sequences (Bunau and Joly, 2009).
- **X-ray absorption spectroscopy (XAS):** This technique is widely used at synchrotron radiation facilities for determining the local geometric and/or electronic structure of matter, such as gases, solutions, or solids.
- **X-ray absorption spectroscopy (XAS):** The absorption of x-ray photons result in a core-excited initial state with a well-defined symmetry, and which determines due to selection rules also the final states in the continuum following the relaxation of the core holes. While the

most intense features arise of course from electric-dipole allowed transitions, mixtures of multipole components may also occur. The most intense features at a  $K$ -edge are typically due to the  $1s \rightarrow np$  core excitations, and at the  $L_3$ -edge those due to  $2p \rightarrow nd$  excitations.

- In x-ray absorption spectroscopy, codes are needed and greatly appreciated that help reproduce the near-edge structure within a reasonable calculation time.
- Classification of codes for x-ray absorption spectroscopy: These codes can be classified into two major categories:
  - i) multi-electronic but monoatomic codes which are based on some multiplet theory and which give rise to a proper parametrized description of the localized electronic state. In these codes, however, the delocalized states are often not described correctly.
  - ii) multi-atomic but mono-electronic codes which provide correct description of the extended states but fail to account for the highly correlated state that interact with the core hole. This applies, for example, for the calculation of the L2 and L3 edges of the  $3d$  elements.
- Multi-atomic and multi-electronic absorption calculations: There have been various attempts in the literature to perform multi-atomic and multi-electronic x-ray absorption calculations based on either the time-dependent density functional theory, the Bethe-Salpeter equation or on other multi-channel methods. However, most of these approaches are still in their early phase and will require much further work.

### Nonlinear optical properties of mesoscopic composite materials:

- Free atoms *versus* bulk materials: Apparently, the optical and spectral properties of bulk material, such as of metals or semiconductors, are usually quite different from those of the constituent atoms. Indeed, most of these properties are determined by the extended (non-localized) electronic states and must then be characterized by the electron mean free path, the electron/hole Bohr radii, or the de-Broglie wavelength of the electrons in the bulk. Non-linear interaction processes of materials with light can drastically modify the behaviour of materials, for instance, by opening additional optical channels and quantum interferences. Different non-linear interaction mechanisms can be analyzed by means of saturation spectroscopy, two-photon spectroscopy, photon echo and other techniques (Flytzanis, 2005).

### 8.5.o. Coherent x-ray scattering at high intensities

#### Novel x-ray radiation sources:

- **Linac Coherent Light Source (LCLS):** In 2009, the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory was the first x-ray FEL in operation with photon energies up to 8.3 keV, up to  $2 \times 10^{12}$  photons per pulse, and with a pulse length of just a few femtoseconds.
- **Current x-ray FEL:** Nowadays, further x-ray FEL include the SPring-8 Compact SASE Source (SCSS, Japan) and the European x-ray FEL (XFEL) at DESY. The XFEL can deliver photon energy up to 14 keV and has a 50–500 times higher average brightness than the (early) LCLS.

#### Single-shot imaging:

- **Single-shot imaging:** One central goal and application of the European XFEL is **single-shot imaging of individual macromolecules by means of coherent x-ray scattering**. Such an imaging should help determine the atomically resolved structure of non-crystallized nanoparticles and biomolecules. Single-shot imaging might become possible for a sufficiently high-fluence and well-focused FEL pulse that generate a large-enough number of scattered photons from each (single-molecule) sample.
- **Radiation damage:** One of the key problems in single-shot imaging is the radiation damage in course of the irradiation of the sample. Typically, a much higher flux is required than the **conventional radiation damage limit of about 200 photons/Å<sup>2</sup>** (for bio- and nano-materials), and this may seriously degrade the scattering pattern and the possibility of determining the atomic positions within the target molecule (Son *et al.*, 2011). Single-shot imaging will therefore require a sufficiently short duration of the intense x-ray pulse of less than 10 fs in order to keep the atomic position effectively frozen during the irradiation by the pulse.
- **Single-shot imaging:** Even if the atomic positions are nearly frozen, the single-shot imaging will be affected also by dynamical changes in the electron density of the target. This makes it necessary to understand the detailed ionization and relaxation dynamics in individual parts of the molecules under ultrashort and ultraintense x-ray pulses (Son *et al.*, 2011). This electron-density dynamics can be simulated by means of time-dependent rate equations in order to explore the formation and relaxation of the inner-shell vacancies.

### Ionization dynamics in short light pulses:

- **Rate equations for configuration-averaged population dynamics:** The transitions among all possible electronic configurations  $c$  of a given atom are described by a set of coupled rate equations of the form,

$$\frac{dP_c(t)}{dt} = \sum_{c' \neq c} (A_{c' \rightarrow c} P_{c'}(t) - A_{c \rightarrow c'} P_c(t))$$

where  $P_c$  is the (relative) population of the  $c$ -th configuration,  $\Gamma_{c' \rightarrow c}$  is the rate for generating the configuration  $c$  from  $c'$  and  $A_{c \rightarrow c'}$  the rate for all decay transitions from configuration  $c$  to other configurations  $c'$ . In a simplified dynamical model,  $A$  can be either a (configuration-averaged) time-independent Auger or fluorescence rate, or a time-dependent photoionization rate. For the photon flux  $J(t)$  of the x-ray pulse at some given time  $t$ , the photoionization rate is given by  $\sigma_p J(t)$  with .

- **Anlge-differential cross section for coherent x-ray scattering:** For unpolarized and linearly-polarized x-rays, the anlge-differential cross section for coherent scattering is given by (Son *et al.*, 2011)

$$\frac{d\sigma^{(\text{unpolarized})}}{d\Omega} = \alpha^4 |f^{(0)}(Q)|^2 \frac{1 + \cos^2 \vartheta}{2}, \quad \frac{d\sigma^{(\text{lin-polarized})}}{d\Omega} = \alpha^4 |f^{(0)}(Q)|^2 (1 - \cos^2 \varphi \sin^2 \vartheta),$$

where  $\varphi$  is the azimuthal angle of the scattered photon momentum with respect to the polarization axes in the plane perpendicular to the x-ray propagation. This angle-differential cross section gives well-defined distributions of the scattered x-ray emission if one restricts the model to fixed electronic configurations. From measurement of the x-ray distribution, *vice versa*, one can retrieve information about the electronic density.

- **Configuration-averaged anlge-differential cross section for coherent x-ray scattering:** If an atomic cloud is exposed to an ultraintense x-ray pulse, the atomic electron density is dynamically modified. This may require to introduce a suitably averaged, time-dependent differential scattering cross section,

$$\frac{d\sigma^{(\text{averaged})}}{d\Omega}(t) = \sum_c^{\text{all configs}} P_c(t) \frac{d\sigma^{(c)}}{d\Omega}$$

where  $P_c(t)$  is the population of the  $c$ -th configuration as obtained from the rate equations above. The differential scattering cross section for the  $c$ -th configuration is evaluated from the form factor for the charge density  $\rho(r)$  of the  $c$ -configuration.

### 8.5.p. X-ray quantum optics

#### Phenomena in x-ray quantum optics:

- **X-ray quantum optics** has rapidly evolved during the last years owing to the development of novel x-ray light sources and x-ray optics. In particular, the resonant interaction of x-ray photons with nuclear transitions has attracted recent interest.
- **Phenomena from quantum optics:** A few important phenomena from x-ray quantum optics include: i) x-ray parametric down conversion; ii) nuclear  $\gamma$ -ray superradiance, and several others. Indeed, various concepts from conventional (visible or nearly-visible) quantum optics have been suggested also at higher photon energies. These concepts include photon correlations and entanglement, squeezing, and others.
- **Optical *versus* x-ray quantum optics:** There are important differences between the interaction of x-rays and optical photons due to the inner-shell atomic excitations, the occurrence of nuclear resonances, or quite large energy shifts in Compton scattering when the photon energies approach the electron rest mass.
- **Advantages of x-ray photons:** Hard x-ray photons with an energy of  $\sim 10$  keV are easy to detect, can be focused to small spot sizes and can penetrate quite deeply into materials. They may also lead to fast information processing owing to their higher frequencies.

### 8.5.q. Gamma-factory project

#### Gamma-factory:

- **Forthcoming CERN research program:** The long-term planning at CERN requires to discuss also applications outside of the original high-energy community. A multipurpose Gamma Factory has therefore been suggested as a novel (Compton backscattered) light source, based on existing accelerator infrastructures.
- **Design parameters of the planned Gamma factory:** For sufficiently strong lasers and ions beams, the gamma factory might push the intensity limit several orders of magnitude with a estimated photon flux of  $10^{17}$  photons/s at the gamma-ray photon energies  $1 < E^{(\text{photon})} < 400$  MeV. These photon energies are out of reach for the FEL-based light sources. The energy-tuned, quasi-monochromatic gamma beams, together with the gamma-beam-driven, high intensity secondary beams of polarized positrons, polarized muons, neutrons and radioactive ions would constitute the basic research tools of the proposed Gamma Factory.
- **Compton backscattered light from ions:** Head-on collisions of light with fast ions leads predominantly to the Compton (back-) scattering of photon that are *twice* Doppler-shifted (in the absorption and re-emission process) and which are concentrated in a quite narrow cone



around the propagation direction of the ions

$$\omega'' = \gamma \omega' (1 + \cos \vartheta') = \frac{4\gamma^2 \omega}{1 + (\gamma \vartheta_o)^2}.$$

Here  $\vartheta_o$  is the observation angle for recording the photons with regard to the ion beam axis. These backscattered photon energies can therefore take values up to 10 MeV for initially optical light and the  $\gamma \lesssim 2000$  parameters from above. When compared with synchrotrons, the generated laser frequency  $\omega''$  can hereby be tuned by either the incident laser frequency *or* the  $\gamma$ -factor of the ion beam.

### 8.5.r. Spin-waves and spin-wave engineering (magnonics)

#### Magnons:

- **Magnons** generally refer to quantized (magnetic) excitations in an ordered ensemble of magnetic moments; these magnetic excitations are closely related to the **spin waves** in a classical ensemble of magnetic moments. For example, (metastable) magnons have been studied in geometrically frustrated magnets where they occur as persistent magnetic excitations even at very low temperatures.
- **Spectra of magnons:** High-resolution spectroscopic techniques are typically required in order to measure the spectrum of such magnons, for instance, by the scattering of light. In the optical regime, Brillouin light scattering enables one to probe magnons with high energy resolution, while a high spatial resolution can be obtained by resonant inelastic x-ray or neutron scattering (Roehlsberger, 2014). In particular, inelastic neutron scattering on magnons has been applied for several decades, while the x-ray scattering on single magnons as been achieved only recently. In all these measurements, however, the energy resolution of such magnon spectra was limited by the energy resolution of the incident particles and/or the analyzers.
- **Spin waves:** Spin waves describe the classically-collective motion of a large number of (atomic) magnetic moments in a given sample; they are usually represented by a (local) magnetization vector  $\mathbf{m} = \mathbf{m}(t)$  that precesses with some angular frequency  $\Omega$  around the direction of the *effective* magnetic field  $\mathbf{B}^{(\text{eff})}$ , forming the surface of cone.

### 8.5.s. Decay of medical radioactive isotopes

#### Radioactive isotopes used in clinical therapy:

- **Linear energy transfer (LET):** Most radioactive isotopes, that are used in clinical therapy, emit  $\beta$  particles as ionizing radiation. The biological effect of this radiation is often characterized by the so-called linear energy transfer (LET) and measured in units of  $[\text{keV}/\mu\text{m}]$  for the deposited energy along the particle track.
- **LET versus kinetic energies:** The electrons and positrons emitted in the nuclear  $\beta$  decay or in internal conversion processes often have kinetic energies from tens of keV to several MeV, while their  $\text{LET} \sim 0.2 [\text{keV}/\mu\text{m}]$  is much lower than for  $\alpha$  emitters.
- **$\alpha$ -emitters:** A new class of radioactive nuclides refer to the  $\alpha$  emitters  $^{149}\text{Tb}$ ,  $^{213}\text{Bi}$ ,  $^{211}\text{Po}$ ,  $^{211}\text{A}$ ,  $^{223}\text{Ra}$ ,  $^{225}\text{Ac}$ ,  $^{227}\text{Ac}$ ,  $^{226}\text{Th}$  and  $^{230}\text{U}$ , which have been considered for therapy.
- **$\alpha$ -emitters:** The LET for most therapeutic  $\alpha$  emitters ranges from 25 to 230  $[\text{keV}/\mu\text{m}]$ .
- **LET of Auger electrons:** Auger electrons with relatively low energies can have a much higher LET due to their short range (nm to  $\mu\text{m}$ ). For electron energies below 1 keV, for example, the LET peaks at around 26  $[\text{keV}/\mu\text{m}]$ . Auger electrons have a much shorter range in materials, when compared to the emission of  $\alpha$  and  $\beta$  particles, and this makes them ideal tools for targeted radiation therapy.

### 8.5.t. Universal shape function for charged-particle impact ionization

#### Universal shape functions:

- **Universal shape function for charged-particle impact ionization cross sections:** A universal shape function can be formulated for the cross sections of single and multiple impact ionization by charged particles. If we refer to the position and the height of the cross section maximum by  $E_M$  and  $\sigma_M$ , and if  $E$  refers to the *excess* energy of the particle impact, this parametrization is given by (Pattard, 2002)

$$\sigma(E) = \sigma_M x^\alpha \left( \frac{\alpha + 1}{\alpha x + 1} \right)^{\alpha + 1}, \quad x = E/E_M.$$

Here,  $\alpha$  is the **Wannier exponent that is characteristic for the given process**, and which follows from Wannier theory. Note that the *excess* energy  $E$  is not the projectile (kinetic) energy but the energy that is left to all collision partners after ionization.

- **Universal shape function for charged-particle impact ionization cross sections:** The parametrization above describes indeed the particle-impact ionization cross sections quite well **as long as no excitation-autoionization processes occur at these impact energies**. Apart from the position and height of the *cross section maximum*, the formula is free of further parameters and can be readily applied for fittings (Pattard, 2002).
- **Universal shape function for charged-particle impact ionization cross sections:** The reason that the impact ionization by different particles, such as electrons, positrons, protons or even antiprotons, all follow the same parametrization is given by the **inclusion of the correct power law behaviour** (which is of course different for the different projectiles) near to the ionization threshold. The derivation and use of such threshold laws has been found useful also for parametrizing few-body Coulomb break-up processes.
- **Universal shape function for single-photon multiple-ionization cross sections:** The shape function by Pattard (2002) provides an excellent parametrization of photoionization cross sections if *all* electrons are ionized simultaneously, e.g. for helium. It help parametrize multiple-ionization cross sections whose *ab-initio* calculations is highly non-trivial, especially if three or more electrons are involved. — For photon impact, a universal shape function can only be derived for multiple, at least double, (photo-) ionization.
- **Universal shape function for single-photon multiple-ionization cross sections:** For single-photon multiple-ionization, Pattard (2002) suggest the parametrization

$$\sigma(E) = \sigma_M x^\alpha \left( \frac{\alpha + 7/2}{\alpha x + 7/2} \right)^{\alpha + 7/2}, \quad x = E/E_M,$$

and which obeys the correct limits at low and high photon energies. This is in contrast to the parametrization for charged-particle impact, for which the  $\ln E/E$  was neglected for the sake of simplicity.

- **Cross sections at high energies:** From hydrogenic atoms, it is known that photoionization cross sections are proportional to  $e^{-7/2}$ , while particle-impact cross sections typically follow a  $E^{-1}$  or  $\ln E/E$  behaviour.

### 8.5.u. Configuration-averaged energies and cross sections

#### Configuration averages:

- **Configuration-averaged energies:** For various applications, it is desirable to use and readily access configuration-averaged energies, rates and cross sections.
- **Configuration-averaged energies:** Cowan (1981) provides a non-relativistic expression for the configuration-averaged energy as it often occurs in the computation of radiative and collisional rates (Peyrusse, 1999)

$$E_c = \sum_a N_a \langle a \rangle + \sum_{ab} N_a (N_b - \delta_{ab}) \langle a, b \rangle$$

$$\langle a \rangle = \varepsilon_a + \left\langle a \left| -V^{(\text{SCF})}(r) - \frac{2Z}{r} \right| a \right\rangle, \quad \langle a, b \rangle = \frac{1}{2} \frac{g_a}{g_a - \delta_{ab}} \left[ R^{(0)}(ab, ab) - \frac{1}{2} \sum_k \begin{pmatrix} \ell_a & k & \ell_b \\ 0 & 0 & 0 \end{pmatrix}^2 R^{(k)}(ab, ba) \right].$$

Here,  $g_a = 2(2\ell_a + 1)$  is the degeneracy of subshell  $a$ ,  $V^{(\text{SCF})}(r)$  is the self-consistent atomic potential and  $R^{(k)}(ab, cd)$  is the non-relativistic Slater integral.

## 9. Atomic cascades

### Glossary:

- **Absorption cross sections:** The absorption cross section of an atomic cloud is (mainly) determined by the contributions from photoionization and the photoexcitation with subsequent autoionization. In JAC, the absorption cross sections are therefore obtained from a cascade simulation that includes data from an `PhotonIonizationScheme` and `PhotonExcitationScheme` for the photon energies of interest.
- **Cascade approach:** Since atomic cascades may require a large or even huge computational effort, different *approaches* of increasing complexity are distinguished in order to establish a hierarchy of approximations. These approaches differ by the generation and use of the required orbitals, the use of configuration-averaged energies as well as the treatment of electronic correlations (configuration mixing) in the representation of the ASF. In JAC, the (abstract data) `struct Cascade.AbstractCascadeApproach` has been introduced to distinguish and deal with the different approaches.
- **Cascade block:** A group of electron configurations that is described by a common SCF field and Hamiltonian matrix and, hence, accounts for all configuration mixing within this group of levels.
- **Cascade:** A cascade typically includes ions of an element in three or more charge states that are connected to each other by different atomic processes, such as photoionization, Auger emission or radiative transitions. A quantum modelling of a cascade requires to follow all possible *pathways* that the ions leads eventually into some stable ground state. In JAC, we distinguish between different *cascade scheme* (photoionization cascades, decay cascades) and *cascade approaches* to account for different computational models in dealing with the pathways.
- **Cascade computation:** Formally, each cascade computation is splitted into several steps which are treated independently: (i) A list of electron configurations is generated as they may occur during the (photo-) excitation, ionization or decay of levels from one or several initial configurations. (ii) From these configurations, a list of *cascade blocks* (groups of configurations) is then formed and a common SCF field and Hamiltonian matrix calculated for each of these blocks. (iii) For each pair of such cascade blocks, all fine-structure transitions are calculated for all the selected excitation or decay processes. (iv) A (common) list of radiative lines, Auger lines, etc. is compiled and (usually) written to disk; this *line lists* later form the basis for all subsequent cascade simulations to be considered for the atoms.

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- **Cascade scheme:** Since the ‘physics’ of an atomic cascade can be very different as well, a number of cascade *schemes* are distinguished internally by introducing the (abstract data) struct `Cascade.AbstractCascadeScheme`. At present, JAC supports the computation of decay cascades (`StepwiseDecayScheme`), photoionizing cascades (`PhotonIonizationScheme`) and photoexciting cascades (`PhotonExcitationScheme`), respectively.
- **Cascade simulation:** A cascade simulation makes use of a pre-calculated list of (many-electron) amplitudes, rates and/or cross sections in order to derive different ion, photon and/or electron distributions and spectra, and which can be compared directly to experiment. In JAC, cascade computations and cascade simulations are always handled independently.
- **Distribution:** Experimentally, different ion distributions or photon and electron spectra are measured and need to be compared with simulated data. JAC attempts to model such distributions following the prior excitation or ionization of atoms.
- **Electron configuration:** Describes the occupation of shells within the atomic shell model, for instance,  $1s^2 2s^2 2p^6 3s^2$ . In JAC, closed-shell configurations can be abbreviated by using the noble gases or selected closed-shell atoms with a closed ground-state configuration.
- **Graphical representation of a cascade:** The level energies of the different ionization stages of an atom can be arranged as *columns* of either a table or graph; for large cascades, the total table/graph can then be readily ‘reduced’ to a selected energy interval and/or a range of ionization stages. Typically, such a list/graph can provide the user with a very first overview about the cascade. It also enables one to ‘zoom’ into details of the cascade or may form the basis for more sophisticated graphs which, for instance, allow access to lifetimes or *transition data* for pairs of fine-structure levels.
- **Line:** A (transition) line refers to an atomic transition that is characterized in terms of a well-defined initial and final level; these lines frequently occur in the computation of atomic properties, such as cross sections or rates, angular distribution parameters. Typically, a line contains various channels (sublines), for instance, due to occurrence of multipoles or of partial waves in the decomposition of the many-electron levels and/or matrix elements.
- **Pathway:** In contrast to an (atomic) line, that is characterized by an initial- and a final-level (from the corresponding multiplets), a pathway describes a sequence of three or more levels, and which are often connected via different atomic processes. These levels are usually referred to as initial, (one or several) intermediate as well as the final level of the pathway. Pathways occur naturally in dielectronic recombination of ions, in various excitation-ionization or excitation-autoionization processes and in photoionization and decay cascades.
- **Shake configuration:** An electron-configuration that does directly occur in an atomic cascade due to photon or electron emission but which may appear by taking *one* or *two* additional (de-) excitations of electrons into account. These shake configurations can often be considered also as configurations that occur due to (auto- or photo-) *ionization-with-excitation* processes.

## 9.1. Cascade computations and cascade simulations

Atomic cascades often require an enormous computational effort in order to generate, simulate and interpret all data as required for a given experiment. It is therefore both, necessary and desirable, to distinguish between a number of cascade schemes to deal with the underlying physics as well as cascade approaches to handle a hierarchy of different computational models (approximation). Here, we shall briefly summarize those features that currently supported by the JAC toolbox and by providing a few technical details.

### Cascade schemes:

- **Abstract type:** The abstract type `Cascade.AbstractCascadeScheme` defines internally an abstract (data) type to distinguish different excitation, ionization and decay schemes of an atomic cascade. Currently (partly) supported sub-types are `StepwiseDecayScheme`, `PhotonIonizationScheme`, `ElectronExcitationScheme`.
- **Decay cascade:** Such a cascade starts from either a few excited (electron) configurations or a given set of initial levels. These (inner-shell) excited levels can then decay by different user-selected atomic processes, such as autoionization, photon emission and others, until a given number of electrons is released and/or the ions cannot further decay to lower levels.
- **Photoionization cascade:** A photoionization cascade just models the first (photo-) ionizing part of a cascade. It usually starts from the ground configuration of the atom and automatically includes all those configurations with one electron less that can be reached for the given photon energy. These computation return a (line) list of photoionization amplitudes which, in a cascade simulation, can be combined with data from a subsequent decay cascade.

### Cascade approaches (computations):

- **Abstract type:** The abstract type `Cascade.AbstractCascadeApproach` defines internally an abstract (singleton data) type to distinguish between various computational approaches/models that can applied to generate and evaluate a cascade. Currently (partly) supported sub-types are `AverageSCA`, `SCA`.
- Here, we briefly summarize these (pre-defined) approaches which can be further controlled by choosing proper parameters for the given cascade computation.
  - i) **Average singe-configuration approach (AverageSCA):** In this approach, just one common set of orbitals from the initial set of levels is applied for all subsequent stages of ionization stages. Moreover, all electron configurations in the cascade are treated as a set of single-CSF levels, i.e. without any configuration mixing. Further restrictions of this approach include: Only E1 dipole transitions are applied in all

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radiative decay steps; for each decay step, a (single) set of continuum orbitals is used with energy as obtained from the configuration-average from the initial- and final-state levels of the corresponding configuration blocks.

- The AverageSCA approach is perhaps the simplest way to describe a decay cascade as a sequence of atomic (fine-structure) levels that contribute to the (de-) excitation of inner-shell excited atoms. This simple approach should be realistic in practice for (almost) all atoms and ions from the periodic table. However, much further work is needed to understand how well this approach describes the underlying physics of autoionization cascades.
- ii) **Single-configuration approach (SCA):** This approach applies a **common set of orbitals for each individual electron configuration (cascade block)** in the given cascade. This includes the configuration mixing among all levels from the same configuration. Some further restrictions of this approach include: Again, only E1 dipole transitions are applied in all radiative decay steps; all continuum orbitals are generated without *exchange* with the bound electrons but for the correct fine-structure transition energies in this approach.
- iii) **Multiple-configuration approach (UserMCA):** In this approach, we intent to support further configuration mixing (electron-electron correlations) between user-selected (and close-in-energy lying) configurations. Here, the user need to *group* different configurations together due to physical insight into the cascade process. Some further restrictions of this approach include: ....
- For each of these (cascade) approaches above, the mean computational effort is expected to increase by (at least) one order of magnitude, perhaps also by several orders.
- Although the overall computational effort is quite difficult to estimate and formalize in advance for general atomic systems, **the different cascade approaches of the JAC toolbox should be clearly discernible from each other, and the 'cost' of any simpler approach (than some currently selected cascade approach) should be typically negligible.** In general, however, by far not all of these envisaged approaches will be feasible for some requested (desired) cascade computation.

### Implementation of cascade computations:

- **List of electron configurations:** An automatically generated list of electron configurations forms the basic *framework* of all the (implemented) cascade approaches; such a list is the starting point in order to *group* configurations into the cascade blocks.
- **List of electron configurations:** It is quite **easily possible to remove electron configurations from the automatically generated list of configurations, either 'by hand' in order to reduce the size of a given cascade computation by physical insight and/or by practical needs;** here, further information about the actual size of a given computation should always be made available *before* this 'removal' is made explicit.
- **Line list:** A cascade computation always returns one (or a few) line lists which comprises all lines of the same type, such as `PhotoEmission.Line`, `AutoIonization.Line`, etc. These lines may occur in any order with regard to their transition energies, level



specification, or even the charge state of the ions. These line lists are the expensive parts of any cascade computation and, hence, are stored on disk; they form the input for all subsequent cascade simulations.

- Since, we always have a quite simple access to a list of all levels of the cascade (with more or less full physical specification of each level with regard to its coupling and quantum numbers), it would/should not be difficult to 'add' (or 'replace' some further) rates or transition amplitudes. Such an explicit setting would enable one to incorporate additional 'decay steps' into the cascade, such as double Auger, two-photon decay, etc., and even if the corresponding decay processes are not (yet) supported by the standard scheme of JAC.
- **Initial levels:** A short table is printed for all initial levels, and to which all configurations/levels from the subsequent steps of the cascades are closely related.
- **Cascade blocks:** To enable the user to analyze and 'reconstruct' the computations, the program prints the list of generated cascade blocks as well as their size, i.e. the number of CSF, as well as the range of fine-structure energies of each block.
- **Cascade steps:** The requested atomic processes, such as photo or Auger emission, is considered for all pairs of cascades blocks; these pairs then define the (so-called) *cascade steps*. Since these steps may consider large fine-structure array for both, the initial- and final-state arrays of the given block, the particular output generally depend on the complexity of the computation. For each of these steps, moreover, JAC reports the number of `lines` that are appended to some *line list* as well as the total number of such line in the list.
- **Cascade data:** In JAC, the output of different cascade computations is distinguished by the (abstract data) `struct Cascade.AbstractCacadeDat` with the presently supported sub-types: `DecayData`, `PhotoIonData`; cf. below for further details.
- **File storage on disk:** The obtained *line list* are printed to disk eventually by means of the JLD package (and format). JAC tells the user the filename of the given computation, and which are needed for all subsequent cascade simulations.

## Cascade simulations:

- **Cascade computations *versus* cascade simulations:** While a cascade computation just generates all the necessary and expensive (many-electron) transition amplitudes and rates, a cascade computation applies the results from one or several such computations to obtain all ion, photon or electron distributions. These cascade simulations are typically much faster than the computation, and the existing features can be readily extended due to the needs of the users. However, it remains the task of the user to make sure that all physical-relevant transition data were generated by some prior cascade computation and that they can be uniquely distinguished by the subsequent cascade simulation. Because of the complexity of (most) cascades, special care has to be taken by the user to ensure *consistency* of all generated data. For this consistency, JAC can provide only limited help.

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- **Simulation methods:** Various methods can be applied to *simulate* the propagation of the (quantum) probability distribution through an atomic cascade. In JAC, these methods are distinguished by means of the (abstract singleton data) `struct Cascade.AbstractSimulationMethod` which, at present, supports the sub-types `ProbPropagation` in order to stepwise propagate the (occupation) probabilities of the atomic levels until no further changes *do* occur. Other possible methods refer to Monte-Carlo methods (`MonteCarlo`) to simulate large cascades by the random selection and analysis of pathways or by means of rate equations (`RateEquations`). However, the latter two methods are not (yet) supported at present.
- **Simulation properties:** In JAC, different properties (distributions) of a cascade can be simulated; they are internally distinguished by means of the (abstract data) `struct Cascade.AbstractSimulationProperty` with the presently supported sub-types: `IonDistribution`, `FinalLevelDistribution`, `DecayPathes`, `ElectronIntensities`, `PhotonIntensities`; cf. below for further details.
- **Ion distribution:** Determine the distribution of the ionic charge states after the (decay) cascade of some initially excited atomic levels; cf. `Cascade.IonDistribution`.
- **Final-level distribution:** Determine the final-level distribution of one or several ionic charge states after the (decay) cascade of some initially excited atomic levels; cf. `Cascade.FinalLevelDistribution`.
- **Photon spectra:** Determine the photon (-line) intensities of a cascade as function of energy; cf. `Cascade.PhotonIntensities`.
- **Electron spectra:** Determine the electron (-line) intensities of a cascade as function of energy; cf. `Cascade.ElectronIntensities`.
- **Absorption cross sections:** Determine the total absorption cross section of atoms or ions in a given ground-state configuration as function of photon energy; cf. `Cascade.AbsorptionCrossSection`.

## 9.2. In JAC implemented cascade schemes

### 9.2.a. Decay cascades

#### Remarks on implementation:

- **Decay cascade:** Such a cascade starts from either a few excited (electron) configurations or a given set of initial levels. These (inner-shell) excited levels can then decay by different user-selected atomic processes, such as autoionization, photon emission and others, until a given number of electrons is released and/or the ions cannot further decay to lower levels.

- Using JAC: Perform an `Cascade.Computation(..., approach=Cascade.AverageSCA(), scheme=Cascade.StepwiseDecayScheme([Auger, ...], ...), initialConfigs=[Configuration(".."), ...] )` .
- In JAC, a step-wise decay cascade is specified by `scheme=Cascade.StepwiseDecayScheme([process1, process2, ...], nmax, nshake, ...)`, where process<sub>i</sub> refers to one of the allowed decay processes of JAC, n<sub>max</sub> is the (maximum) number of electrons in which the initial- and final-state configurations can differ from each other and n<sub>shake</sub> the maximum number of electron displacements due to shake-up or shake-down processes in any individual step of cascade (not yet supported).
- **Output data:** The final results of a decay-cascade computation is provided by an instance of the (data) `Cascade.DecayData <: Cascade.AbstractData` that defines a container for a lists of radiative and Auger lines.

### 9.2.b. Photoionization & decay cascades

#### Remarks on implementation:

- **Photoionization cascade:** A photoionization cascade just models the first (photo-) ionizing part of a cascade. It usually starts from the ground configuration of the atom and automatically includes all those configurations with one electron less that can be reached for the given photon energy. These computation return a (line) list of photoionization amplitudes which, in a cascade simulation, can be combined with data from a subsequent decay cascade.
- Using JAC: Perform an `Cascade.Computation(..., approach=Cascade.AverageSCA(), scheme=Cascade.PhotonIonizationScheme([Photo], ...), initialConfigs=[Configuration(".."), ...] )` .
- In JAC, a photo-ionizing cascade is specified by `scheme=Cascade.PhotonIonizationScheme([Photo], nmax, [e1, e2])`, where Photo refers to the photoionization process, n<sub>max</sub> is the (maximum) number of photoelectrons, i.e. the number of electrons in which the initial- and final-state configurations can differ from each other and e<sub>i</sub> refers to a list of incident photon energies. At present, only single photoionization (n<sub>max</sub>=1) is supported by JAC.
- If, as usual, the photoionization leads to a subsequent photon or Auger electron emission, a *decay-cascade* computation has to be performed independently, and the data (from these two or more cascade computations) later combined in the cascade simulations.
- **Output data:** The final results of a decay-cascade computation is provided by an instance of the (data) `Cascade.PhotoIonData <: Cascade.AbstractData` that defines a container for a lists of photon energies and associated photoionization lines.

### 9.2.c. Photoexcitation & decay cascades

#### Remarks on implementation:

- **Photoexcitation cascade:** A photoexcitation cascade just models the first (photo-) exciting part of a cascade. It usually starts from the ground configuration of the atom and automatically includes all those excited configurations that can be reached for the given photon energies. These computation return a (line) list of photoexcitation amplitudes which, in a cascade simulation, can be combined with data from a subsequent decay cascade.
- Using JAC: Perform an `Cascade.Computation(.., approach=Cascade.AverageSCA(), scheme=Cascade.PhotonExcitationScheme([PhotoExc()], ...), initialConfigs=[Configuration(".."), ...] )` .
- In JAC, a photo-exciting cascade is specified by `scheme=Cascade.PhotonExcitationScheme([PhotoExc()], minPhotonEnergy, maxPhotonEnergy, NoExcitation, ...)`, where `minPhotonEnergy`, `maxPhotonEnergy` determines the range of photon energies, and hence excited configurations, that need to be considered. `NoExcitations` refer to the (maximum) number of electron replacements with regard to the initial configurations/multiplets.
- If, as usual, the photoionization leads to a subsequent photon or Auger electron emission, a *decay-cascade* computation has to be performed independently, and the data (from these two or more cascade computations) later combined in the cascade simulations.
- **Output data:** The final results of a decay-cascade computation is provided by an instance of the (data) `Cascade.PhotoIonData <: Cascade.AbstractData` that defines a container for a lists of photon energies and associated photoionization lines.

### 9.2.d. Ion impact & decay cascades

#### Remarks on implementation:

- **Electron-impact excitation cascade:** It is planned to extend JAC towards electron-impact processes, and which would allow to implement some similar procedure as for photoionization cascades. However, this has not yet been done.

## 9.3. In JAC implemented cascade approaches

### 9.3.a. Average single-configuration approach (AverageSCA), based on a common set of orbitals (Cascade)

#### Cascade, notations & application:

- **AverageSCA approach:** This approach simply applies a **common set of orbitals (from the initial ground- or hole-state configuration of the atom or ion) also for all subsequent steps of the cascade**. Moreover, each single configuration, that occurs in the decay of the initially excited levels, forms an independent multiplet (cascade block), and each CSF of this configuration also an approximate atomic state; i.e. all further configuration interactions are omitted in this simple approach. This **single-CSF representation of all atomic levels** is assumed to be rather equivalent to using *configuration-averaged rates and cross sections*, although this equivalence is far from being obvious for complex configurations.
- **General restrictions:** (a) Only electric-dipole (E1) transitions are included for all radiative decays; (b) continuum orbitals are always generated at an configuration-averaged transition energy and only for partial waves with  $|\kappa| \leq 4$ .

#### Computational steps of the AverageSCA and SCA approaches:

- The following steps are carried out separately in both of these two approaches:
  - 1) **Determination of all cascade blocks:** Determine all single configurations that may energetically occur due to photoemission and autoionization processes from the initially chosen configurations/levels, and until a given maximum number of electrons are released from the atom or ion. These electron configurations then form a list of (so-called) **cascade blocks** from which the decay cascade is built by just calculating all possible decay lines of the user-selected atomic processes for each pair of blocks.
  - 2) **Radial orbitals:** Bound radial orbitals are calculated only for the first (and uppermost) block in the cascade, i.e. the initial hole configuration with the energetically highest-lying energy levels. These bound orbitals are utilized to make the **basis::Basis** of all other blocks explicit together with the geometric specification of all CSF.
  - 3) **Level representation:** An individual level multiplet is calculated for each single non-relativistic electron configuration (cascade block) but without any CI, i.e. without all configuration mixing. Therefore, the levels in all cascade blocks are given by a single CSF, and no explicit diagonalization of the Hamiltonian matrix is required in this approach; the energies of these levels just coincide with the diagonal matrix elements  $\langle \gamma \mathbb{J} || \mathbb{H}^{(\text{Dirac-Coulomb})} || \gamma \mathbb{J} \rangle$ .

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- 4) **Decay processes & cascade steps:** The user-requested radiative and non-radiative decay processes are considered for all pairs of cascade blocks (configurations). For each of these pairs, standard atomic computations are performed by using the submodules `AutoIonization`, `PhotoEmission`, etc. For a user-selected atomic – excitation or decay – process, this step gives rise to a list of `lines`, if this process can connect this pair of cascade blocks. However, by far not all details of these line computations are printed to screen.
- 5) **Decay lines:** All these decay line data are comprised into a few common lists `linesR` (radiative lines), `linesA` (Auger lines, `linesP`) (photoionization lines), ... and which are finally returned by an instance of `Cascade.Data`.

### 9.3.b. Single-configuration approach (SCA) with individual sets of orbitals (Cascade)

#### Cascade, notations & application:

- **SCA approach:** This approach applies an **individual set of orbitals for all blocks of the cascade**, while each electron configuration in the decay tree still forms an independent cascade block, i.e. level multiplet. For each of these blocks, an independent SCF is generated and the configuration mixing included by diagonalizing the Hamiltonian matrix of this configuration. **The single-configuration approach (SCA) is expected to already provide a quite reasonable description of all strong decay pathes.**
- **General restrictions:** (a) Multipoles of the radiative transitions can be defined by the given `Settings` of the cascade computation; (b) continuum orbitals are generated in a slightly simplified Dirac-Fock-Slater potential of the corresponding (final-level) configuration but for energies that are specific to the individual fine-structure transitions; (c) no orbital relaxation is incorporated into the amplitudes apart from those due to the separate orbital representation (SCF) of the initial and final levels.
- See subsection 9.3.a for the individual steps of the cascade computation.

## 9.4. In JAC partly-implemented cascade approaches

### 9.4.a. User-grouped multi-configuration approach (UserMCA; Cascade)

#### Cascade, notations & application:

- **UserMCA approach:** This approach also applies an individual set of orbitals for each block of the cascade which, in addition, can be compiled by the user. To facilitate the compilation of these cascade blocks, the program first provides a list of (electron) configurations that can be either combined interactively or by some explicitly provided (code). For each of these user-specified cascade blocks, an independent SCF is generated and the full configuration mixing included by diagonalizing the corresponding Hamiltonian matrix. In comparison to the SCA above, the UserMCA enables one to include further physical insight about strong configuration mixing into the computation of the cascade.
- **General restrictions:** (a) Multipoles of the radiative transitions can be defined by the given **Settings** of the cascade computation; (b) continuum orbitals are generated in a slightly simplified Dirac-Fock-Slater potential of the corresponding (final-level) configuration but for energies that are specific to the individual fine-structure transitions; (c) no orbital relaxation is incorporated into the amplitudes apart from those due to the separate orbital representation (SCF) of the initial and final levels.
- In this approach, the user can *group* various (electron) configurations together in order to better account for electron-electron correlations (configuration mixing). The set-up of these groups will be supported in JAC by an automatically generated list of electron configurations and by simple tools to compile them together into **cascade blocks** using some list indices.
- For each stage of ionization, the arrangement of electron configurations into a *group* is typically based on either the mean energy, a maximum size (No. of CSF) of individual groups, or on prior knowledge about strongly-interacting configurations. This UserMCA approach often requires manual work and, thus, is also prone for making errors.
- A full (average-level) MCDF approach of all atomic levels can be considered as well within this approximation, if all configurations of each ionization stage are simply grouped together; in practice, however, such a computation is likely unfeasible and of little practical interest.
- Analogue to the SCA approaches, the energies, amplitudes, etc. are calculated for all pairs of levels within a given cascade block (configuration group) or from two such blocks. As before, all line data are comprised into a few line lists and are returned by a **CascadeData** structure, and before these data can be utilized in simulations of the cascade.

### 9.4.b. Multi-configuration approach with shake transitions (ShakedMCA; Cascade)

#### Cascade, notations & application:

- **ShakedMCA approach:** This approach also applies an **individual set of orbitals for each block of the cascade**. However, these cascade blocks do include not only those electron configurations that obviously occur in the cascade due to the emission of photons and electrons but also configurations with a *replacement of additional electrons*, and which corresponding to shake-up or shake-down transition. The generation of these additional configurations are done via a *maximal number of electron replacements* that are considered in addition to the standard decay configurations.
- **General restrictions:** (a) Multipoles of the radiative transitions can be defined by the given **Settings** of the cascade computation; (b) continuum orbitals are generated in a slightly simplified Dirac-Fock-Slater potential of the corresponding (final-level) configuration but for energies that are specific to the individual fine-structure transitions; (c) no orbital relaxation is incorporated into the amplitudes apart from those due to the separate orbital representation (SCF) of the initial and final levels.
- These **shake configurations** can be treated as individual groups of configurations or can be grouped together with other configurations of the decay cascade.
- Analogue to the UserMCA, the program first provides a list of automatically generated (electron) configurations that can be either combined interactively or by some explicitly provided code. For each of these user-specified cascade blocks, again, an independent SCF is generated and all configuration mixing included by diagonalizing the corresponding Hamiltonian matrix.
- Although the UserMCA and ShakedMCA are quite similar in spirit, the incorporation of shake-up or shake-down configurations typically enlarges the effort enormously and need to be handled with great care. **The ShakedMCA enables one to include further physical insight about strong shake processes and configuration mixing into the computation of the cascade.**



## 9.5. In JAC implemented cascade simulations

### Concept and control of cascade simulations:

- **Concept:** While the ‘physics’ of cascade is often dominated by a few atomic processes, such as (spontaneous) photon emission or autoionization, the experimentally observed spectra and distribution depend on the particular set-up and geometry of detectors, spectrographs, etc. Here, the **cascades simulation** may help to flexibly adapt JAC to the particular need to experiment. Only a few *standard* simulations (properties) are pre-defined and can be further controlled by some proper settings.
- **Simulation properties:** In JAC, different properties (distributions) of a cascade can be simulated; they are internally distinguished by means of the (abstract data) `struct Cascade.AbstractSimulationProperty` with the presently supported sub-types: `IonDistribution`, `FinalLevelDistribution`, `DecayPathes`, `ElectronIntensities`, `PhotonIntensities`; cf. below for further details.
- **Settings (`Cascade.SimulationSettings`):** All cascade simulation can be further controlled by the setting which allow to specify:
  - `minElectronEnergy :: Float64 ...` Minimum electron energy for the simulation of electron spectra.
  - `maxElectronEnergy :: Float64 ...` Maximum electron energy for the simulation of electron spectra.
  - `minPhotonEnergy :: Float64 ...` Minimum photon energy for the simulation of electron spectra.
  - `maxPhotonEnergy :: Float64 ...` Maximum photon energy for the simulation of electron spectra.
  - `initialPhotonEnergy :: Float64 ...` Photon energy for which photoionization data are considered.
  - `initialOccupations :: Array{Tuple{Int64,Float64},1} ...` List of one or several (tuples of) levels in the overall cascade tree together with their relative population.
- **Simulation data:** All simulations are based on data from prior cascade computations, and which are provided by a list of dictionaries, `computationData :: Array{Dict{String,Any},1}`.

### 9.5.a. Ion distributions (Cascade)

#### Remarks on implementation:

- **Ion distribution:** Determine the distribution of the ionic charge states after the (decay) cascade of some initially excited atomic levels; cf. `Cascade.IonDistribution`.

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- Using JAC: Perform an `Cascade.Simulation(.., properties=Cascade.AbstractSimulationProperty[Cascade.IonDistribution()], settings=Cascade.SimulationSettings(..), computationData=data`.

### 9.5.b. Final-level distributions (Cascade)

#### Remarks on implementation:

- **Final-level distribution:** Determine the final-level distribution of one or several ionic charge states after the (decay) cascade of some initially excited atomic levels; cf. `Cascade.FinalLevelDistribution`.
- Using JAC: Perform an `Cascade.Simulation(.., properties=Cascade.AbstractSimulationProperty[Cascade.FinalLevelDistribution()], settings=Cascade.SimulationSettings(..), computationData=data`.

### 9.5.c. Photon intensity spectra (Cascade)

#### Remarks on implementation:

- **Photon spectra:** Determine the photon (-line) intensities of a cascade as function of energy; cf. `Cascade.PhotonIntensities`.
- Using JAC: Perform an `Cascade.Simulation(.., properties=Cascade.AbstractSimulationProperty[Cascade.PhotonIntensities()], settings=Cascade.SimulationSettings(..), computationData=data`.

## 9.6. In JAC partly-implemented cascade simulations

### 9.6.a. Electron intensity spectra (Cascade)

#### Remarks on implementation:

- **Electron spectra:** Determine the electron (-line) intensities of a cascade as function of energy; cf. `Cascade.ElectronIntensities`.
- Using JAC: Perform an `Cascade.Simulation(.., properties=Cascade.AbstractSimulationProperty[Cascade.ElectronIntensities()], settings=Cascade.SimulationSettings(..), computationData=data`.



# 10. Collision- and field-induced atomic responses

## 10.1. Interaction with external particles and fields. Notations

### 10.1.a. Atoms interacting with external particles

#### Ion-atom collisions:

- **Coupled-channel calculations:** In particular, coupled-channel calculations within an independent-electron model has been found capable to predict the single-electron capture in slow collisions with helium.
- **Application of ion-atom collision data:** A detailed understanding of the ionization and charge-exchange phenomena in ion-atom collisions is essential for different fields of physics, such a astrophysics, plasma physics or hadron therapy
- **First Born approximation (FBA):** This approximation has often been applied to high-energy ion-atom collisions for which the coupling between different excitation or ionization channels is expected to be negligible. There exist several versions of the FBA approximation to calculate, for instance, electron-capture cross sections in the p-He collisions. For example, a FBA with corrected boundary conditions were developed and utilized at intermediate-to-high energies collision energies, usually based in some independent-particle model. However, the FBA and other perturbative approaches become unreliable whenever the speed of the projectiles is comparable or smaller than the velocity of the target (valence) electrons. For such collisions, a **semi-classical close-coupling approach** is a useful alternative, although these approaches are expensive and often appear quite sensitive to the choice of basis functions as well as to a proper *completeness* of the basis.

### 10.1.b. Atoms in time-harmonic (Floquet) fields

#### Floquet formalism:

- **Floquet formalism:** Many physical systems are time-periodic to a good approximation. For these systems, the (time) evolution can be solved either directly by numerical integration of the (time-dependent) SE or by making use of the **Floquet ansatz** to separate out parts of the (time-dependent) Hamiltonian.
- **Floquet formalism:** For a periodic evolution, any time-dependent problem can be transformed also quite easily into a time-independent problem by applying the Floquet formalism. Such a transformation may simplify the solution considerably since time-independent problems can often be solved more efficiently.

### 10.1.c. Atoms in intense radiation fields

#### Few-cycle intense laser pulses:

- **Intense laser pulses:** Nowadays, few-cycle femtosecond laser pulses can be routinely produced **both, in the visible as well as mid-infrared regimes**. If these few-cycle pulses are focused properly, **ultra-intense electric fields can be generated with peak-field strengths which are comparable to the (static field) in the atom**.
- **Carrier-envelope phase (CEP):** Light pulses with a well-defined absolute or **carrier-envelope phase (CEP)** are crucial for extracting information about the electron dynamics in strong-field physics. A good control of the CEP is particularly important if the HH are generated by pulses with just one or a few optical cycles, since the CEP phase then directly determines the relevant electron trajectories and whether a single or multiple attosecond bursts of radiation is emitted.

#### Electron dynamics & processes in intense radiation fields:

- **Simple man's model:** This **three-step model for the electron dynamics in intense radiation fields** provides an intuitive basis for both, the (analytical) strong-field approximation (SFA) as well as for interpretations of the (numerical) solutions of the time-dependent Schrödinger equation. In particular, this model helps explain different strong-field phenomena, such as high-harmonic generation (HHG), above-threshold ionization (ATI), the non-sequential multi-electron ionization (NSMI), and several others.

- **Keldysh parameter  $\gamma$** : The ionization regimes of strong-field processes are often classified by means of the Keldysh parameter

$$\gamma = \sqrt{\frac{I_p}{2U_p}} = \frac{\omega \sqrt{2I_p}}{\mathcal{E}_o} \approx \frac{\omega}{\mathcal{E}_o}, \quad U_p = \frac{e^2 \mathcal{E}_o^2}{4m_e \omega_o^2} = \frac{I_o^2 e^2 \lambda_o^2}{8\pi^2 m_e \epsilon_o c^3} = 9.337 \cdot 10^{-20} I_o \lambda_o^2 \frac{\text{eV}}{\text{W cm}^{-2} \text{ nm}^2}.$$

Here,  $\mathcal{E}_o$  is the electric-field amplitude,  $m_e$  the mass of the electron, and  $\omega_o$ ,  $\lambda_o$ ,  $I_o$  refer to the central frequency, wavelength and, respectively, the intensity of the incident laser radiation. As usual, moreover,  $\epsilon_o$  is the vacuum permittivity and  $c$  the speed of light.

- **Ionization regimes**: Different operational conditions for strong-field ionization processes are often distinguished in the literature due to the photon energy  $\omega$ , ionization potential  $I_p$  of the atomic targets as well as the ponderomotive energy of the laser field  $U_p$ . This table has been adapted from Amini *et al.* (2019).

Ionization regime	Conditions
Single-photon ionization (SPI)	$\hbar\omega > I_p \gg U_p$
Multi-photon ionization (MPI)	$I_p > \hbar\omega \gg U_p$
Above-threshold ionization (ATI)	$I_p > U_p > \hbar\omega$
Tunnel ionization (TI)	$U_p > I_p > \hbar\omega$

- **Above-threshold ionization (ATI)** is a natural extension of multi-photon ionization but where one or several photons *more* are absorbed of which are needed in order to surpass the ionization potential  $I_p$  of the atom. In general, ATI processes are often governed by the coexistence of perturbative and non-perturbative distortions of the electron dynamics.
- **High-order ATI (HATI)**: In the high-energy region of the photoelectron spectrum at  $2U_p \leq \varepsilon_p \leq 10U_p$ , the electron dynamics is strongly governed by recollisions and the interplay between elastic and inelastic scattering processes.
- **Frustrated tunnel ionization**: Frustrated tunnel ionization is one of the dominant channels in strong-field ionization that results in the excitation of atoms. Theory predicts that the excitation efficiency increases with the pulse duration and decreases when going to a few-cycle regime.

### Strong-field spectroscopy:

- **Laser-induced electron diffraction (LIED)** refers to a spectroscopic technique in which structural information about the atomic target is derived by measuring the doubly-differential elastic scattering cross-sections in the re-collision of electrons with the target atoms. Obviously,

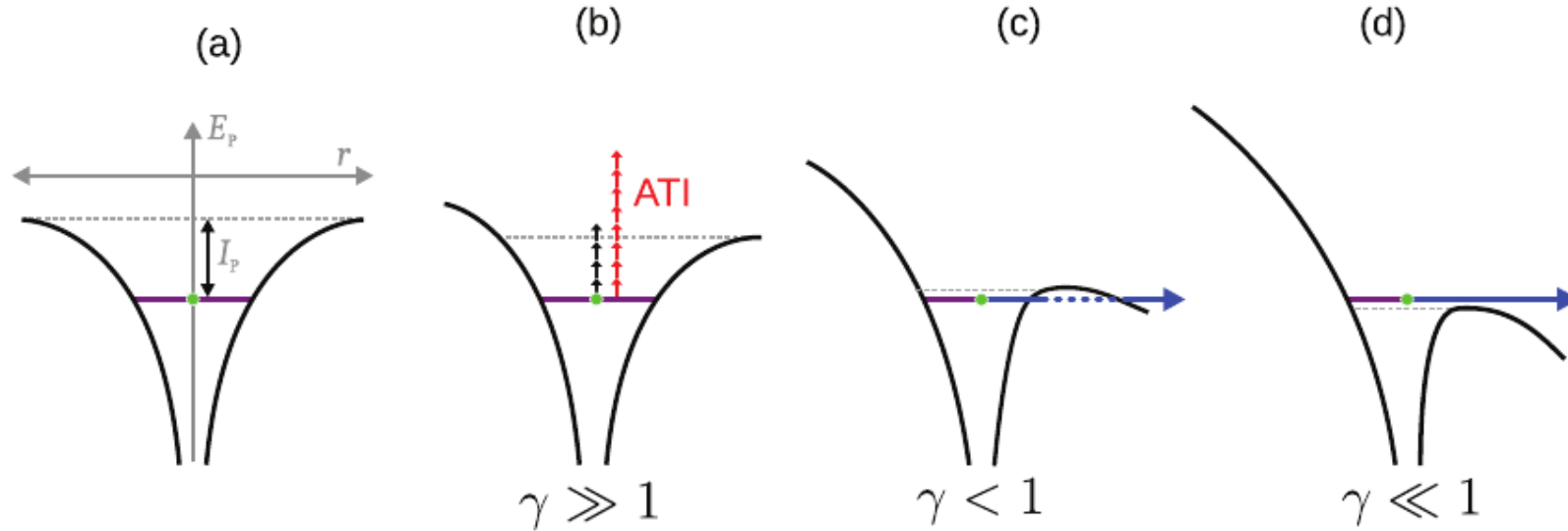


Figure 10.1.: Atomic potential in the presence of an intense laser field: (a) without the laser; (b) ATI absorbs more photons than required for the release of an electron; (c) tunnel ionization, and (d) over-the-barrier ionization. Taken from Amini *et al.* (2019, Fig. 1).

however, a very detailed theoretical understanding of the ATI and HHG processes is hereby needed in order to extract useful information from (time-resolved) LIED and HHG spectrum. In the simple man's model, contributions to the LIED spectrum arise especially from highly-energetic returning electrons with  $2U_p \leq \varepsilon_p \leq 10U_p$  that collide elastically with their parent ion and that lead to a very characteristic momentum transfer and momentum distributions of the released electrons.

- **Above-threshold ionization (ATI) spectroscopy:** Since both, the bound-free and the rescattering continuum-continuum transitions are CEP sensitive, the ATI photoelectron distribution can be utilized also in order to extract information about the electronic structure of the target atoms.
- **Subcycle tracing of ionization enabled by infrared (STIER) pulses:** STIER pulses refers to a streak camera that temporally resolves strong-field ionization caused by a linearly-polarized few-cycle pulse. STIER provides insight into the sub-cycle dynamics of strong-field ionization. STIER samples the photoelectrons produced by a few-cycle laser pulse in the near-visible spectral range, for example at 735 nm (Kübel *et al.*, 2017).
- **STIER:** This method enables one to separate the electron wave packets generated at different half-cycle maxima of the visible pulse. The



best separation occurs, when the visible pulse is centered around a field maximum of the IR pulse, i.e. when the signal in the STIER trace is centered around  $p_z = 0$ . In this case, the observed momentum distribution directly reflects the ionization dynamics during a single half-cycle.

### Atto-second pulse trains:

- **Attosecond pulse trains:** The high-harmonic process can be applied to **generate attosecond pulses with excellent coherence in the extreme ultraviolet or even in the soft x-ray regime**; here, an unprecedented time structure of these trains can arise quite readily since the ionization of the electrons occurs just close to the maxima of the electric field and, hence, the electrons always return *in time*, namely, when the laser field is just *zero*.
- **Attosecond pulse trains:** Such pulse trains are generated by means of multi-cycle femto-second laser pulse, while a single broadband attosecond pulse can be produced from a single-cycle continuous broadband spectrum.
- **Circularly-polarized attosecond pulse trains (APT):** Because of the spatial separation of the left- and right-circularly polarized harmonics at the detector, **twisted APT with well-defined circular polarization can be generated**. For example, one obtains a right-circularly polarized APT for low angles of divergence  $\beta \approx 1$  mrad, and right-circularly polarized APT for  $\beta \approx 2$  mrad.
- **Attosecond pulses:** The generation of structured high-frequency pulses with well-defined torus-knot angular momentum also results in bright xuv radiation with customized polarization and OAM. These pulses may enable one to explore the spin-orbit coupling at the nanoscale or to study subtle changes in the photoionization dynamics of single atoms or molecules.
- **Attosecond pulse measurements:** Attosecond pulses help resolve the electronic motion in atoms, molecules and solid-state matter and have lead to number of novel spectroscopic techniques, such a attosecond streaking or ...
- **Photoelectron momentum distributions in attosecond pulses:** In any (attosecond) light pulse, the asymptotic momentum of the photoelectron depends of course on the em fields (vector potential) of the streaking pulse and how the electron propagates in the continuum. A particular **streaking trace** can be obtained by detecting the asymptotic momentum (for a given direction in the PMD) as a function of the time delay between the ionizing and streaking pulses. A (so-called) **temporal shift (streaking time delay)** can be assigned to each streaking trace when compared to the oscillation of the incident vector potential. This streaking time delay is often expressed as sum of the Wigner-Smith time delay and a laser-Coulomb (coupling) delay (Goldsmith *et al.*, 2017)

$$\Delta t^{(\text{streaking})} = \Delta t^{(\text{Wigner-Smith})} + \Delta t^{(\text{laser-Coulomb delay})} .$$

## *10. Collision- and field-induced atomic responses*

While the Wigner-Smith time delay is related to the short-range potential of the residual photoion, the laser-Coulomb (coupling) delay follows from the long-range part of the Coulomb potential. Predictions for this time delay have been performed both, numerically and analytically.

### **10.1.d. Atoms forming local plasma**

None.

## 10.2. In JAC considered ion-atom collisional responses

### 10.2.a. Semi-classical ion-atom collisions [theoretical background]

#### Semi-classical approximation for ion-atom collisions:

- **Semi-classical approximation (SCA) for ion-atom collisions:** In the semi-classical approximation, the target is often assumed to be fixed (for instance, at the origin of the coordinates), while the projectile moves with constant speed  $v_p$  along a straight line with impact parameter  $b$ :  $\mathbf{R}(t) = (b, 0, v_p t)$ .
- **Goals of the SCA:** The goal is to solve an **effective single-electron TDSE** for initially occupied target electrons; in general, the *key* in using the SCA is to find a proper potential to be included into the single-electron TDSE.

$$i \frac{\partial \phi_k(\mathbf{r}, t)}{\partial t} = h(t) \phi_k(\mathbf{r}, t), \quad k = 1, \dots, N.$$

- **Charge-exchange in ion-atom collisions:** The charge-exchange or (charge-) transfer between bare projectiles and multi-electron atoms has mainly been studied experimentally during the past decades. In most early measurements, however, the capture into specific shells of the target could not be resolved and only estimates of the total capture cross sections could be made. For low collision energies, the charge transfer is dominated by the capture of electrons from the outermost target shells, while at higher collision energies more and more inner-shell electrons get involved. At the intermediate and practically most interesting collision energies, therefore, the interplay (interferences) due to the capture of both, inner-and outer-shell electrons, need to be taken into account and may considerably change the curvature of the total cross sections. This is in contrast to ion-hydrogen collisions for which the charge-transfer cross section usually vary monotonically at all energies (Belkic, 1988)).

#### Applications of ion-atom collisions:

- **Proton-atom collisions & ionization:** Chuluunbaatar *et al.* (2019) presents fully differential single-ionization cross sections for the impact of 1 MeV protons on helium. Both, ultra-high resolved experimental and theoretical cross sections in Born approximation are provided and agree reasonably well within the *kinematic* regime close to the (so-called) Bethe ridge. Further away from this region, however, the binary peak is clearly shifted with regard to the observations.

## 10. Collision- and field-induced atomic responses

- **Measurement of ion-atom collision cross sections:** The cold-target recoil ion momentum spectroscopy (COLTRIMS) has been found a versatile tool for measuring and analyzing ion-atom ionization processes since it help determine the three-dimensional angular distribution of electrons at given values of energy and momentum transfer. Moreover, COLTRIMS has reached an unprecedented precision.
- **Application of ion-atom collisions:** Studies of ion-impact ionization processes are of fundamental and applied interest in order to understand, for instance, the penetration of swift ions through matter. Moreover, ion-atom collisions find their application in radiation material science and ion therapy.
- **Measurement of ion-atom collision cross sectionss:** In COLTRIMS measurement, the following fully-differential cross sections (FDCS) have been recorded for proton-helium collisions with regard to the energy  $E_e$  and solid angle  $\Omega_e$  of the electron as well as the solid angles of the scattered proton  $\Omega_p$ :

$$\text{FDCS} := \frac{d^5 \sigma}{dE_e d\Omega_e d\Omega_p} = \frac{k_e m_p^2}{(2\pi)^5} |T_{if}|^2, \quad \text{FDCS} := \frac{d^5 \sigma}{dE_e d\vartheta_e d\varphi_e dq d\varphi_q} = |\sin \vartheta_e| \frac{k_e q}{(2\pi)^5 v_p^2} |T_{fi}|^2,$$

and where  $(\vartheta_e, \varphi_e)$  are the angles of the emitted electrons with regard to the axis of the incident proton beam and  $\varphi_q$  the azimuthal angle of the momentum transfer.

- **Fully-differential cross sections:** The upper form of the FDCS is used especially for studying the binary and recoil peaks in the electron angular distribution and how these peaks are shifted with regard to those from a simple Born approximation. In contrast, the second form can hardly be compared with experiment but has been applied in order to analyze various kinks in the cross sections as well as the asymmetry of the FDCS in forward and backward directions.
- **Kinematic region for ion-atom collisions:** For proton-helium collisions, most previous computations were done so far for the kinematic regime of small momentum transfer (0.75 a.u.) and low ejected-electron energy (6 eV).

### Single-electron capture and subsequent x-ray emission in ion-atom collisions:

- Leung *et al.* (2015) studied the x-ray spectra following the single-electron capture in collisions of 4.54 keV/amu bare Ne<sup>10+</sup> ions with helium, neon and argon gas targets. In this work, the single-particle capture probabilities were calculated by using the two-center basis generator method, based on independent electrons. Moreover, the response of the target on the capture cross sections and x-ray spectra was modeled by means of an time-dependent screening potential.
- Using COLTRIMS techniques, a triple-coincidence measurement on 4.54 keV/amu Ne<sup>10+</sup> ion collisions with helium, neon and argon gas targets were carried out by Ali *et al.* (2010) who obtained (relative) shell-selective capture cross sections and x-ray spectra. In these

measurements, the x-ray spectra from single-electron capture were separated from those from a multiple-electron capture due to coincidences with hydrogenic  $\text{Ne}^{9+}$  ions.

- Several groups have studied charge-exchange collisions in the laboratory in order to measure capture cross sections and the subsequent x-ray emission. For example, the Lyman-*alpha* emission was recorded for  $\text{C}^{6+}$ -Kr and  $\text{O}^{8+}$ -Kr collisions at low and intermediate collision energies. In these studies, emphasis was placed especially to estimate reliable single-electron capture cross sections.
- **Classical overbarrier model (OBM):** This model suggests that hydrogen and krypton should have (very) similar shell-selective capture cross sections because of the similar ionization potentials of 13.6 eV and 14.0 eV, respectively. However, a comparison of experimental data shows a rather different subshell selectivity, i.e. with regard to the electron capture rate into  $(n\ell)$  subshells.
- To model the single-electron capture cross sections from a krypton target, an effective ground-state potential was obtained from the optimized-potential method by Talman and coworkers which includes the electron-nucleus interaction as well as terms due to screening and exchange (Leung *et al.*, 2018)).

## 10.3. In JAC considered high harmonic (HH) responses

### 10.3.a. High-harmonic generation HHG [phenomenology]

#### Basics of HHG:

- **HHG:** High-order harmonic generation is a non-linear (optical) up-conversion process for which the conservation of energy, linear momentum as well as spin and orbital angular momentum of individual harmonics can often be expressed by means of simple selection rules. This non-linear process is **mediated by a laser-driven recollision mechanism of electrons**, and which may lead to high harmonics with photon energies hundreds or even thousands times larger than the driving laser frequency.
- **High-harmonic generation:** When an *intense* laser ( $I \sim 10^{14} \text{ W cm}^{-2}$ ) irradiates an (atomic) gas target, coherent radiation at multiples of the fundamental laser frequency is emitted. This process is called **high-harmonic generation (HHG)**.
- **HHG versus multi-photon emission:** In comparison to HHG, most multi-photon emission and ionization processes have a rather limited complexity and can be described perturbatively.
- **Maximum harmonic order:** In a classical model, the electron can gain in a field with ponderomotive potential  $U_p = I/4\omega^2 = \mathcal{E}_o^2/4\omega^2$  a maximum of  $3.17 U_p$  kinetic energy and, hence, the (so-called) **cut-off energy for the harmonics is  $3.17 U_p + I_p$** . In the saddle-point approximation, in contrast, one finds solutions where the electron returns with a kinetic energy  $\gtrsim 4 U_p$  and which correspond to orbits with no *classical* counterpart.
- **Plateau auf HH:** If the high harmonics arise from the excitation with low-frequency lasers, the (HH) spectrum exhibits a characteristic behaviour, namely, a rapid decrease of the yield for the first few harmonics, and which is followed then by a **plateau and a rather abrupt cut-off**.
- **HHG** is known as a unique source of coherent and collimated xuv femto- and attosecond pulses. However, the efficiency of HHG is notoriously low, although it might be (moderately) enhanced if the resonances of the atomic or molecular targets are properly exploited. Indeed, the *free* one-dimensional motion of the electrons in the laser field is very essential for HHG as seen from the rapid decrease of the harmonic yield for an incident elliptical laser.
- **Efficiency of HHG:** Great efforts have been undertaken in order to increase the efficiency and photon flux in HHG. This efficiency is strongly influenced also by collective effects, such as the propagation and phase matching of the HH emitted from individual atomic targets, and where the maximum efficiency is affected by the absorption of the harmonics in the surrounding gas.

- **Gas-phase HH generation:** Gas-phase HH are generated when a (gas-jet) of atoms or molecules are irradiated by strong laser pulses. The emitted harmonics from such a jet are *coherent* and may easily reach the soft x-ray regime. HHG is now frequently applied in various ultrafast-science experiments. HHG can be utilized to generate single attosecond pulses and attosecond pulse train, and which open the door to time-resolved studies of the electron dynamics at the attosecond scale.
- **Absorption-limited conversion efficiency of HHG:** Constant *et al.* (1999) found that the maximum conversion efficiency of HHG is ultimately limited by reabsorption of the generated HH photons within the (generating atomic) medium itself. In particular, this so-called **absorption-limited conversion efficiency** is proportional to the absorption cross section  $\sigma(q\omega)$  at the frequency  $q\omega$  of the  $q$ -th harmonic. Therefore, the efficiency can be enhanced only if the emission cross section can be enhanced independent of the absorption.
- **HHG:** High-order harmonics, i.e. highly-energetic photons at multiples of the (fundamental) laser frequency, can be produced by focusing either a high-frequency (excimer) laser or some low-frequency laser (Nd:glass, Ti:sapphire) into an atomic gas.
- **HH spectra:** The properties of high-harmonic spectra have been intensively explored with regard to the energy, linear momentum as well as the orbital and spin angular momenta of the individual harmonics.
- **Role of the atomic target for HHG:** For atoms, only the valence electrons (orbital) are considered to be relevant for HHG and, hence, a direct link between HHG and valence-shell photoionization might exist and might be observed in the spectra. For example, the HHG spectrum is known to show a lower intensity at the Cooper minimum in the photoionization cross section of argon atoms. Such a correspondence between the HHG and photoionization exist also for resonances in the photoionization cross sections and might help enhance the low efficiency of the HHG process. For the resonances in the photoionization cross sections, indeed, a large number of case studies exist in the literature and helped establish relations to the autoionization or to the shape and giant resonances of atoms.
- **HHG with linear *versus* circularly-polarized beams:** **All harmonics that are generated by means of linearly-polarized beams are generally also linearly polarized**, while HHG with (single) circularly-polarized beams is strongly suppressed, since the classical trajectories of the electrons will not come back so easily to the parent ion (Lorentz force) and since the (same) helicity of several photons *cannot* be add up to a well-defined helicity of the HH.
- **HHG with bicircularly-polarized beams:** HHG becomes possible for superposition of a circularly-polarized beam with its counter rotating second (or higher) harmonic. For such a superposition of two counter-rotating fields, the electric field of a bicircular field exhibits a Lissajous (-type) figure, and this obviously help return the electron back to the parent ion.
- **High-gain harmonic-generation at free-electron lasers:** Such a high-gain HHG@FEL has been demonstrated experimentally by means of laser-seeding in order to produce amplified, longitudinally coherent and Fourier transform-limited output at a certain harmonic of the seed laser. For example, a seed carbon dioxide laser with 10.6 micrometers help produce saturated and amplified second-harmonic wavelength

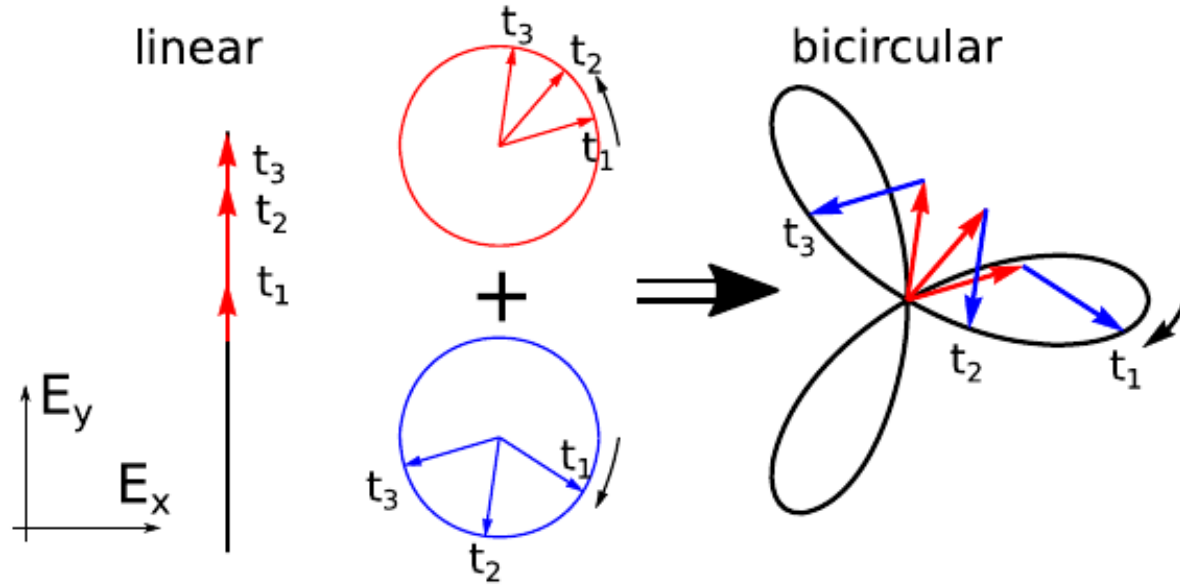


Figure 10.2.: Parametric plots of the electric field vectors at different times  $t_1, t_2, \dots$ . (Left) The electric field vector in a linearly-polarized beam just oscillates in one dimension. The red arrows indicate the electric field vectors at three different times. (Middle) Circularly-polarized field (red) and its counter-rotating second harmonic (blue). The arrows indicate the electric field vectors at the same times as for the linearly-polarized field. (Right) Bicircular field as a superposition of a circularly-polarized beam and its counter-rotating second harmonic, which gives rise to a Lissajous figure for the electric field. From Paufler *et al.* (2019, Fig. 5)

at 5.3 micrometers. These experiments helped verify the technique and paved the way for its application in the vacuum ultraviolet region of the spectrum, and perhaps to even provide intense and highly-coherent hard x-rays in the future.

- **High-gain harmonic-generation at free-electron laser:** Single-pass FEL bunches provide the intensity and spatial coherence of SASE but with high temporal coherence. In the HHG@FEL, a seed laser imposes a small energy modulation of the electron beam while passing through a short undulator (the modulator). This energy modulation is then converted into a coherent spatial density modulation as the electron beam traverses a dispersion magnet (a three-dipole chicane). If a second undulator (the radiator) is tuned to a higher harmonic of the seed frequency  $\omega$ , a microbunched electron beam emits coherent radiation at the harmonic frequency  $n\omega$ . These HH have a single phase that is determined by the seed laser and spectral bandwidth that is limited by the Fourier transform. **The HHG@FEL may result in a high degree of stability and control of the central wavelength, bandwidth, energy, and duration of the output pulse.**



- **FERMI FEL:** FERMI is located at the Elettra laboratory in Trieste; it covers the VUV to soft x-ray photon energy range with two FEL that are both based on High-Gain Harmonic Generation (HGHG) seeded mode.
- **Rates for HHG:** Explicit formulas for the HHG rate within the three-step model are provided, for instance, by the Lewenstein model and include a *factor* from the field-free photorecombination cross section (third step). While the derivation of these formulas are made in the single active-electron approximation, the proportionality of the HHG rate to the field-free photorecombination cross section already indicates quite **strong multi-electron effects upon the HHG rate for most atoms, since the photorecombination cross section are known to be sensitive to the description of the many-electron wave functions**. Although the role of such electron correlations upon the HHG spectra has been discussed *qualitatively* in the literature, not many detailed computations have been carried out so far.
- **Resonant electron capture in HHG:** If the relative phase of different capture processes is neglected, the dielectronic resonance strength  $S(i \rightarrow d \rightarrow f) \propto \frac{2\pi^2 \hbar}{k_i^2} A_r$  determines entirely the behaviour of the resonance. For low- and medium-Z elements, therefore, no significant enhancement in the HHG spectrum is expected even if the capture (Auger) rate for the formation of the doubly-excited states is quite large.
- **Microscopic and macroscopic view of HHG:** Any theoretical modelling of HH spectra in a gaseous medium must combine a microscopic *and* macroscopic analysis of the generation and superposition of the emerging high-frequency radiation field. In the microscopic model, the harmonic spectrum of the individual atoms is obtained from the (approximate) solution of the Schrödinger equation, and these single-atom spectra need then to be superposed from a macroscopic viewpoint due to the target and intensity distribution within the focus area of the laser. Of course, this superposition generally leads to a loss of coherence and to a broadening of the HH.
- **Harmonic emission rates of single-active electron atoms:** If the laser field is not too strong, the harmonic emission rates can be estimated from perturbation theory. For a strong laser pulse, in contrast, one needs either to resort to the direct numerical solution of the time-dependent Schrödinger equation (TDSE) or to the strong-field approximation (SFA). While a direct solution of the TDSE is often possible only for some (1D or 3D) *model atom*, the SFA combines a rigorous theoretical treatment (of parts of the electronic motion in the TDSE) with various semi-empirical arguments about the generation and the potentials, as seen by the *free* electrons. Such a quantum-mechanical description of harmonic generation was originally formulated by Lewenstein *et al.* (1994). Both approaches give rise to very similar results for the (so-called) *cut-off* frequency  $\omega^{(\text{cut-off})} \approx I_p + 3.2 U_p$  of the harmonic spectrum in terms of the ionization potential  $I_p$  and the ponderomotive energy  $U_p = \mathcal{E}_0^2/(4\omega^2)$ , i.e. the mean kinetic energy of an electron in the laser field.
- **Blueshift and reduction of the laser intensity in HHG:** In experiments with increasing laser intensities or gas densities (or length), the driving laser field can be remarkably re-shaped during its propagation through the atomic cloud, and this then leads to a **blueshift and an intensity reduction of the laser pulse**. For similar reasons also, the recorded high-order harmonic spectra crucially depends on the frequencies and phase matching that may or may not arise during the propagation of the pulse.

## Phase matching of HHG spectra:

- **Phase matching of HHG:** Usually, rather dense atomic targets of  $\sim 10^{17}$  atoms/cm<sup>-3</sup> are needed in order to generate high-order harmonics. Apart from the microscopic interaction of individual atoms, however, one has also to consider also the macroscopic target distribution in order to analyze the superposition of all individual responses.
- **Phase matching in HHG:** Any theoretical treatment of HHG must incorporate both, the microscopic response of the atoms to the local em field as well as the macroscopic propagation of the field through the (extended) gas cloud. Such a complete treatment formally requires the self-consistent solution of Maxwells equations in three dimensions and coupled to the time-dependent Schrödinger equations (TDSE) for the atoms, a truly prohibitive task. In practice, even the solution of the TDSE for the response of the atoms is usually replaced by a separation of the electron excitation into the ionization (low-frequency part) and the high-harmonic radiation that is emitted during the oscillation of the electrons with regard to their parent ions (high-energy part). Moreover, this high-energy part is often treated semi-classically and by neglecting the potential of the ionic core upon the oscillations. Such a classical model then enables one to simulate experimental gas lengths and studies on control strategies, based on the trajectories of electrons after ionization (Berman *et al.*, 2018).
- **Phase matching of HHG:** A (phase matching) analysis of the HH spectrum may help improve the conversion efficiency and provides information about the cutoff of the harmonics. It also aims to find conditions so that the radiation from most atoms to a given harmonic add up constructively at the detector.
- **Size of atomic targets for HHG:** For the HHG with Gaussian beams, a sufficient intensity often occurs only within a thin cylinder of  $\simeq 7$  mm length and a radius of  $\simeq 730$   $\mu$ m, and with about 1000 atoms within this tiny volume. Even for such a rather small volume, however, the radiation emitted from different atoms is not in phase. **Phase-matching aims to find areas in the interaction regions, for which an intense signal with good phase is obtained at the detector.**
- **Phase of the emitted radiation:** For target atoms at different positions, two contributions crucially determine the phase of the  $q$ -th harmonic, namely, **(i) the dipole phase owing to the response of a single atom to the local intensity** of the beam as well as **(ii) the intrinsic beam phase** as it naturally arises from focusing the laser beam.
- **Phase matching on axis:** For Gaussian beams, this just refers to a simplified 1-dimensional model, and which can be adapted also to Laguerre-Gaussian beams.

### High-harmonic generation (HHG) with twisted light beams:

- **High harmonics with well-defined OAM:** Circularly-polarized HH with well-defined OAM can be generated with bicircular LG beams. Moreover, these HH may form also **circularly-polarized (twisted) attosecond pulse trains** if the intensity ratio of the bicircular driving fields has been tailored properly.

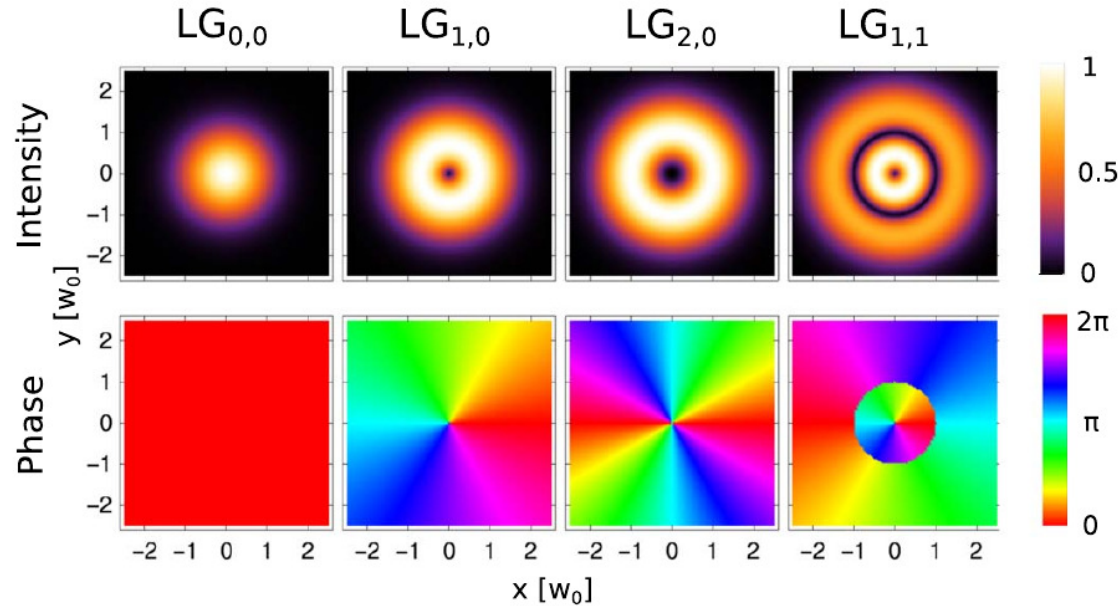


Figure 10.3.: Intensity (upper panel) and phase profiles (lower panel) of different LG beams at the focal plane ( $z = 0$ ). Left column: A Gaussian beam has its intensity maximum at the beam axis and a constant phase profile because of its *zero* OAM. Middle columns:  $LG_{\ell,p}$  beams with angular momentum  $\ell$ , in contrast, have zero intensity at the beam axis and a  $2\pi\ell$  phase change in going once around the beam axis. Right column:  $LG_{\ell,p}$  beams with  $p > 0$  exhibit  $p + 1$  rings in the intensity profile and a corresponding phase profile with a  $p$ -dependent phase and a phase change  $2\pi\ell$ . From Paufler *et al.* (2019, Fig. 1).

- **Microscopic & macroscopic interplay of HHG with twisted beams:** For driving beams with helical phase fronts, in particular, both the (microscopic) interaction of the individual target atoms as well as the (macroscopic) superposition of the emitted radiation in the far-field

plays a crucial role for the generation and detection of HH. The interplay of these two components to the recorded spectra determines eventually the OAM as well as divergence of the emitted high harmonics.

- **HHG with OAM:** The OAM of the HH can be controlled, or even explicitly *selected*, by tuning the polarization, intensity (ratio) and OAM of the driving laser fields.
- **Selection rules for the  $q$ -th harmonic:** For an (incident) linearly-polarized twisted light beam with frequency  $\omega$  and orbital angular momentum  $\ell$ , the  $q$ -th harmonic obeys the selections rules:

$$\text{HHG @ LG}_{\ell,p}^{\omega \leftrightarrow} \longrightarrow \begin{cases} \omega_q = q \cdot \omega \\ \ell_q = q \cdot \ell \\ \text{linearly - polarized} \end{cases} .$$

- **Selection rules for the  $q$ -th harmonic:** For (a co-linear superposition of) two bicircular light beam with frequencies  $(\omega, 2\omega)$  and orbital angular momenta  $(\ell_1, \ell_2)$ , both the SAM and OAM are conserved simultaneously, and the  $q$ -th harmonic obeys the selections rules:

$$\text{HHG @ LG}_{\ell_1,0}^{\omega \odot} \oplus \text{LG}_{\ell_2,0}^{2\omega \odot} \longrightarrow \begin{cases} \omega_q = q\omega = m\omega + n2\omega \\ \ell_q = m\ell_1 + n\ell_2 \\ m - n = \pm 1 \end{cases} .$$

For this particular HHG scheme with bicircular  $(\omega, 2\omega)$  beams, every *third* harmonic is suppressed, while the other two contributing harmonics exhibit alternating helicities due to  $m = n \pm 1$ . This can be seen also from the photon-coupling diagram for each harmonic and, hence, the OAM of the generated harmonics can be tailored explicitly for a proper combination  $\ell_1, \ell_2$  of the bicircular beam, cf. Fig. 10.3.a. In addition, it is possible that all generated harmonics carry the same modulus of OAM if the incident beams have the OAM  $\ell_1 = -\ell_2$ .

### High-harmonic generation (HHG) with linearly-polarized LG beams:

- **HHG with two (non-) colinear but linearly-polarized LG beams:** The OAM of the generated harmonics can be controlled by using superpositions (so-called mode mixing) of two or more twisted beams; cf. Figure 10.3.b.
- (1) For two co-linear and linearly-polarized LG beams with the same frequency but different OAM, let us simply write

$$\text{HHG @ LG}_{1,0}^{\omega \leftrightarrow} \oplus \text{LG}_{2,0}^{\omega \leftrightarrow} \Rightarrow .$$

For such mixed beams, different photon paths contribute to the  $q$ -th harmonic; cf. the photocoupling diagrams in Fig. 10.3.b. Obviously, however, if the electron absorbs  $n$  photons from the first beam, it must emit  $q - n$  from the second beam (and where  $n > q$  is also possible, though much less likely). Quite generally, the HHG probability decreases with the (total) number of photons that are involved in the process, and with a rather sharp cut-off criterion.

- (2) For two non-colinear but linearly-polarized LG beams with the same frequency and different OAM, we write instead

$$\text{HHG} @ \text{LG}_{0,0}^{\omega \leftrightarrow} \oplus \text{LG}_{1,0}^{\omega \leftrightarrow}, \angle.$$

For such a superposition, the high harmonics will not have a well-defined OAM here but their wave vectors still need to fulfil  $\mathbf{k}_q = n_1 \mathbf{k}_1 + n_2 \mathbf{k}_2$ ,  $n_1 + n_2 = q$ . Therefore, the harmonics generated by different pairs of photon numbers  $(n_1, n_2)$  will eventually be spatially separated at the detector.

- (3) For two non-colinear but linearly-polarized LG beams with different frequencies and different OAM, we write

$$\text{HHG} @ \text{LG}_{0,0}^{\omega \leftrightarrow} \oplus \text{LG}_{1,0}^{2\omega \leftrightarrow}, \angle.$$

### 10.3.b. High-harmonic generation in the strong-field approximation [theoretical background]

#### High-harmonic theory:

- **Lewenstein's model for HHG:** This model describes the interaction of a single (-electron) atom with a plane-wave laser within the **dipole approximation** (homogeneous electric field). In this approximation, the time-dependent SE can be solved analytically if the following three assumptions are made: (i) only the ground state and the continuum states of the electron contribute to the overall time-evolution of the state of the atom; (ii) the electron always moves as *free* particle within the continuum, independent of the remaining potential  $V(r)$  of the parent ion; and (iii) the time evolution of the electronic state does not lead to a depletion of the ground state.
- **Lewenstein's model for HHG with twisted beams:** This model, and especially the dipole approximation, is still justified to describe the HHG with twisted light beams, if the **azimuthal phase dependence due to the OAM  $\ell$  is properly taken into account**. In particular, the dipole approximation remains valid here in the optical and infra-red regions since the released electron in the HHG process typically just travels 1-2 nm away from its target atom and, hence, does not feel (much of) the spatial structure of the twisted light field.

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- **Lewenstein's model of HHG** is therefore expected to be valid for low-frequency and rather intense lasers, i.e. the basic assumptions of SFA. The long-wavelength limit for  $\lambda_o$  (when compared with the Bohr radius  $a_o = 5.29 \cdot 10^{-11}$  m) ensures a spatially homogeneous electric field over the extent of the atom (**dipole approximation**),

$$\mathbf{E}(t) = \mathcal{E}_o f(t) \sin(\omega_o t + \phi_o) \mathbf{e}_z.$$

- **HHG power spectrum:** From the time-dependent dipole amplitude  $d(t)$ , the HHG power spectrum is obtained as the time-integrated Fourier transform

$$d(\omega, \omega^{(\text{laser})}) = \frac{i}{\omega T} \int_{-T}^T dt e^{-i\omega t} d(t), \quad \mathcal{P}(\omega, \omega^{(\text{laser})}) = |d(\omega, \omega^{(\text{laser})})|^2.$$

### High-harmonic amplitudes in the near- and far-field:

- **Far-field HH spectra from twisted beams:** To predict (and explain) the HH spectra in the far-field at the detector, one needs to sum over all the single-atom responses due to the interaction of these atomic centers with the twisted beam. Obviously, this summation affects the overall phase and intensity profile as well as the OAM of the observed HH radiation in the far-field.
- **Fraunhofer diffraction formula:** This formula can be applied in order to calculate the phase and intensity profile of the far-field for the different orders of the HH. To make use of this formula, the contributions of the individual target atoms to the HH amplitude need to be model properly, for instance by assuming a thin layer of (target) atoms, and which might be displaced with regard to the focus plane.
- **Complex amplitude of  $q$ -th harmonic:** Using Fraunhofer's diffraction formula, the spatically-dependent (complex) light field, averaged over time, can be written in terms of the wavelength  $\lambda_q = \lambda/q$  and the (complex) near-field amplitude  $A_q^{(\text{near-field})}(\rho', \varphi', z')$  of the  $q$ -th harmonic

$$A_q^{(\text{far-field})}(\beta, \varphi) = \int_0^\infty d\rho' \rho' \int_0^{2\pi} d\varphi A_q^{(\text{near-field})}(\rho', \varphi', z') \exp\left(-\frac{2\pi i}{\lambda_q} q' \tan \beta \cos(\varphi - \varphi')\right),$$

and where  $\beta$  refers to the polar angle (angle of divergence) with regard to the incident beam.

- **Near-field amplitude of the  $q$ -th harmonic & for an incident twisted beam:** In Lewenstein's model, the near-field amplitude of the  $q$ -th harmonic can be expressed as  $A_q^{(\text{near-field})}(\rho', \varphi') = f(\rho') e^{i\ell_q \varphi'}$ , and where  $f(\rho')$  includes all the radial dependence.

- **Complex amplitude of  $q$ -th harmonic:** For this simple expression of the near-field amplitude from Lewenstein's model, the integration over the azimuthal angle  $\varphi'$  in the complex far-field amplitude above can be carried out analytically

$$A_q^{(\text{far-field})}(\beta, \varphi) = 2\pi i^{\ell_q} e^{i\ell_q \varphi} \int_0^\infty d\rho' \rho' J_{\ell_q} \left( \frac{2\pi}{\lambda_q} \beta \rho' \right).$$

Here,  $J_k(x)$  refers to a Bessel function of the first kind. The polar angle  $\beta_{\max}$ , for which the (modulus of the) far-field amplitude reaches its maximum, is a simple measure for the divergence of each harmonic order. Apparently, this divergence increases with the OAM  $\ell_q \propto q \cdot \ell$  but decreases with the harmonic order  $q$ . Therefore, **all harmonics are emitted with quite similar divergence.**

### Phase of target atoms to the far-field amplitude:

- **Effective dipole phase:** Different terms contribute to the effective dipole phase of an atomic target atom:
- (i) The **focal phase** arises from the phase-front ratio  $R(z) = z(1 + z_r^2/z^2)$  due to the non-zero Rayleigh range  $z_r = k W_o^2/2$  and the finite beam waist  $W_o$ . For LG beams, the focal phase is  $k r^2/2 R(z)$  and, hence, independent of the OAM of the beam.
  - (ii) The **intrinsic phase** owing to the Gouy phase as well as the OAM of the beam.
- **Coherence length of HHG:** This length characterizes the (changes in the) total phase of the HH amplitude and is simply given by:

$$L_q^{(\text{coherence-length})}(r, z) = \frac{\pi}{|\nabla \phi_q(r, z)|}.$$

This expression shows immediately that a **zero phase-mismatch results in perfectly matched harmonics**  $L_q^{(\text{coherence-length})} \rightarrow \infty$ . In practice, a coherence length  $\sim 1$  mm already refers to quite good experimental conditions.

### Phase matching in HHG with twisted light:

- **Phase matching on maximum:** For an incident Gaussian beam, HH are dominantly emitted *along* the (beam) axis since these harmonics mainly arise near to the intensity maxima in the cross section perpendicular to the direction of the beam. In the phase-matching analysis, it is therefore often sufficient to consider the target distribution just *on axis*, a simplification known as **phase matching on axis**. A similar simplification can be made also for LG beams if this 'fictitious axis' is either shifted to the first intensity maximum of the beam or if one just considers the target distribution along the 'ring' as defined by the first intensity maximum. We here refer to this approximation as **phase matching on maximum**.

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- **Intensity maximum of LG beams:** For an LG<sub>ℓ,0</sub> beam, the first intensity maximum can be written is found in terms of the beam waist  $W_o$  and the Rayleigh length  $z_r$ ; it is given by the radius

$$r_{\ell}^{(\max)}(z) = \sqrt{\frac{|\ell|}{2}} W(z) = \sqrt{\frac{|\ell|}{2}} W_o \sqrt{1 + \frac{z^2}{z_r^2}}.$$

### 10.3.c. High harmonic spectra from localized target clouds [partly-implemented in Jac]

#### Use & notations:

- Using JAC: Perform an `HighHarmonic.Computation(.., observable=[UniColorSpectrum, BiColorSpectrum, ..], configs=[..], hhgSettings=HighHarmonics.Settings(..), ..)` or call directly functions from the module `HighHarmonic`.

### 10.3.d. Phase matching in high-harmonic generation from extended target clouds [partly-implemented]

#### Use & notations:

- Using JAC: Perform an `HighHarmonic.Computation(.., observable=[UniColorSpectrum, BiColorSpectrum, ..], configs=[..], hhgSettings=HighHarmonics.Settings(..), ..)` or call directly functions from the module `HighHarmonic`.

### 10.3.e. Far-field phase distributions [not yet implemented]

None.

### 10.3.f. Far-field intensity distributions [not yet implemented]

None.



## 10.4. In JAC considered above-threshold ionization (ATI) processes

### 10.4.a. ATI in the strong-field approximation [phenomenology]

#### Above-threshold ionization (ATI):

- Above-Threshold Ionization refers to the absorption by an atomic electron of more photons than are required for ionization. ATI was discovered in 1979 and is a rather universal phenomenon. This process occurs in light pulses that are short and strong enough to eliminate the influence of collisions.
- **ATI in strong fields:** In this multi-photon ionization regime (with Keldysh parameter  $\gamma > 1$ ), the atom absorbs more photons than required for the release of one of its bound electrons. This multi-photon absorption leads to the characteristic above-threshold ionization (ATI) peaks in the photoelectron spectra that are separated by the energy of the laser photons. Moreover, the overall spectrum is shifted by the ponderomotive potential with regard to a perturbative treatment of the binding and photon energies.

### 10.4.b. ATI in the strong-field approximation [theoretical background]

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## 10.5. In JAC considered non-sequential double ionization (NSDI) processes

### 10.5.a. NSDI in the strong-field approximation [phenomenology]

#### Non-sequential double ionization (NSDI):

- **Non-sequential double ionization (NSDI):** This (non-linear) strong-field process has been studied for more than 30 years but still attracts good attention for its sensitivity with regard to (a proper many-electron description of) the correlated motion of the two emitted electrons. The **observed (and characteristic) knee structure** provides clear evidence for NSDI since the double-ionization yield strongly increases at the 'knee' by one or several orders of magnitude. Indeed, this increase is much larger than predicted for a subsequent emission of two electrons from the same atom.
- **Rescattering picture of NSDI:** In the **rescattering picture of strong-field physics**, NSDI is simply attributed to the inelastic scattering of the returning electron in the (static) potential of the parent ion. Already this quite simplified picture requires however to take different ionization mechanisms into account: the recollision direct ionization (RDI) and the recollision excitation with subsequent ionization (RESI); cf. Chen *et al.* (2020).
- **NSDI:** This (non-linear) process depends crucially on the laser intensity as seen, for instance, from recoil-ion momentum measurements. In these measurements, a single peak in the momentum distribution becomes a double-hump structure as the intensity increases near to or beyond the threshold intensity. Moreover, the electron-electron (momentum) correlation function then displays a clear transition from an (angle-) correlated into an anti-correlated emission if the laser intensity decreases below the threshold intensity. In particular, prominent finger-like structures in the PEMD have been observed at the relatively low intensity of the laser field. These features show the correlated many-electron features of NSDI.

### 10.5.b. NSDI in the strong-field approximation [theoretical background]

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- **Theoretical models for NSDI:** The NSDI process has been explored by various models, including a semi-classical quasi-static model, the quantitative rescattering (QRS) model or the explicit solution of some (simplified) time-dependent Schrödinger equation. All these models confirmed, or at least indicate, that the finger-like structures in the PEMD at low laser intensity arise from the Coulomb interaction among the emitted electrons. However, different mechanisms are emphasized in most of these models, such as the *shake-off* of the second electron

by the nonadiabatic change of the atomic potential if the first electron is released, some  $(e, 2e)$  collision due to the ionized electron if driven back by the laser, or other mechanisms. Today, the role of laser-induced recollisional excitation and ionization model as the major mechanism is widely accepted, and the number of (sub-) mechanisms has been further refined for the NSDI (Chen *et al.*, 2020): (1) The interaction of the laser field with both electrons; (2) Coulomb interaction of the residual photoion and the two electrons; (3) the interaction among the electrons. Obviously, all these interactions can be easily read-off the (many-electron) Hamiltonian and should be treated on similar footings, if possible.

- **Quantitative rescattering (QRS) model for NSDI:** The QRS model was originally developed for high-order above-threshold ionization (HATI) as well as HHG but has been further improved over the years. This model nowadays incorporates different mechanisms, such as the lowering of the threshold potential due to the electric field at the time of recollision. This model is based on the S-matrix theory and strong-field approximation, and it has been applied to simulate the total double ionization yield, the cross section ratio for double-to-single ionization as well as correlated two-electron momentum distributions. In practice, the QRS model is conceptual much simpler than the explicit solution of the time-dependent Schrödinger equation or even the time-dependent Newton equations of the two electrons. The QRS model basically *factorizes* the electron dynamics of the two electrons into a returning wave packet for the initially ionized electron as well as the differential cross sections for its inelastic scattering with a second electron in the potential of the parent ion (Chen *et al.*, 2019).

## 10.6. In JAC considered collisional-radiative (CR) models

### 10.6.a. Simple CR models [phenomenology]

#### Role and applications of CR models:

- **Collisional-radiative (CR) models:** These zero-dimensional plasma models are typically applied in order to compute **atomic charge-state distributions for – (ionic) mixtures of – one or several elements**, and in particular as function of particle densities and temperatures.
- Different CR models have been found useful for the interpretation of experimental observations, for instance in order to derive the electron density and temperature in plasma. In addition, CR models can be applied to **determine effective ionization and recombination rates as well as the effective emissivity of plasma as function of its electron temperature and density**.
- **Atomic level population densities:** CR models help determine atomic level population densities of atoms in different plasma environments. Calculations are typically based on the CR recombination and ionization rate coefficients, radiative energy losses as well as on various individual rate coefficients.
- **Classification of CR models:** Different CR models can be distinguished due to the – analytical or numerical – treatment of the rate coefficients as well as due to the number and type of processes, for which such (effective) rate coefficients are taken into account.
- **Effectice rates:** CR models can be applied to calculate the effective emissivity or the effective ionization and recombination rates as function of electron temperature and density. In particular, these rates can later be utilized in **plasma transport model** in order to determine local ionization, recombination and radiation effects.

#### Frequent assumptions of CR models:

- Collisional radiative models are sometimes called also **zero-dimensional plasma models**. In these models, one often assumes that the radiative absorption and emission as well as electron-collision processes dominate the plasma and that all other (ion-atom, three-atom, ...) processes are negligible.
- In most CR models, the plasmas just consist out of a single atomic species but with various excited states in between the ground state of some charge state  $A^{q+}$  of the ion and the ground state of the next higher charge state  $A^{(q+1)+}$ . A further typical restriction of such models is that the density of the excited states is assumed to be small, when compared to the (two) ground state densities.

### 10.6.b. CR models [theoretical background]

#### Time-evolution of level densities:

- **Level densities  $n(p)$ :** CR models are typically built on the level densities  $n(p)$ ,  $p = p_1, p_2, \dots, p_N$  of a series of levels whose temporal and spatial distribution is related to each other by the diffusion equation

$$\left( \frac{\partial n(p)}{\partial t} \right)_{\text{CR}} = \frac{\partial n(p)}{\partial t} + \nabla \cdot (n(p) \omega(p)).$$

- **Dominance of radiative and collisional (de-) excitation processes:** If changes in the level density are dominated by radiative and collisional (de-) excitation processes, most CR models simply assume

$$\left( \frac{\partial n(p)}{\partial t} \right)_{\text{CR}} = 0 = P(p) - n(p) D(p)$$

and just solve a (single) matrix equation. Here,  $P(p)$  is the collisional and radiative production rate, and  $D(p)$  the (so-called) *destructive factor*. The two functions  $P(p)$ ,  $D(p)$  can be written in terms of different rate coefficients for electron-impact excitation, ionization as well as for radiative and three-body recombination.

## 10.7. Atomic responses not yet considered in JAC

### 10.7.a. Floquet theory [theoretical background]

#### Time-dependent SE and master equations:

- **Quasi-energy spectrum in a time-harmonic (ac) electric field:** For a monochromatic (time-harmonic) external field, the Schrödinger equation is formally solved by the **Floquet's theorem on linear homogenous differential equations with periodic coefficients**:

$$\psi(\mathbf{r}, t) = \exp(-i E_o t) \phi(\mathbf{r}, t), \quad \phi(\mathbf{r}, t) = \phi\left(\mathbf{r}, t + \frac{2\pi}{\omega}\right)$$

$$\psi(\mathbf{r}, t) = \exp(-i E_o t) \sum_{k=-\infty}^{k=\infty} c_k(\mathbf{r}) \exp(-i k \omega t).$$

In an monochromatic external field, therefore, the total wave function  $\psi(\mathbf{r}, t)$  is a superposition of **stationary quasi-energy states with energies  $E_o \pm k \omega$** , and where  $E_o$  is referred to a quasi-energy. In physical settings, the number of quasi-energies is equal to the number of (unperturbed) level energies, while **the (sideband) energies  $E_o \pm k \omega$  are known also as spectrum of quasi-harmonics**. In atoms, the formation of a quasi-harmonic spectra (sidebands) can be observed especially, if the laser frequency is small but sufficiently intense, when compared to the (atomic) excitation energies to neighboured levels.

- **Time-dependent single-electron Schrödinger equation:** In quasi-harmonic light fields (and elsewhere), the single-electron SE can be written as

$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = H(\mathbf{r}, t) \Psi(\mathbf{r}, t) = \left( \frac{1}{2m} [-i \hbar \nabla + e \mathbf{A}(t)]^2 + V^{(\text{atom})} \right) \Psi(\mathbf{r}, t),$$

$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left( \frac{\hbar^2}{2m} \nabla^2 - \frac{i e \hbar}{m} \mathbf{A}(t) \cdot \nabla + V^{(\text{atom})} \right) \Psi(\mathbf{r}, t) \quad \dots \text{velocity gauge}$$

$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left( \frac{\hbar^2}{2m} \nabla^2 + e \mathbf{E}(t) \cdot \mathbf{r} + V^{(\text{atom})} \right) \Psi(\mathbf{r}, t) \quad \dots \text{length gauge ,}$$

and where the atomic potential  $V^{(\text{atom})}$  is often modeled by a Yukawa and a long-range Coulomic potential.

➤ Relation between the wave functions (solutions) in length and velocity gauge:

$$\exp \left[ -i \frac{e^2}{2m\hbar} \int dt \mathbf{A}^2(t) \right] \Psi^{(\text{velocity})}(\mathbf{r}, t) = \exp \left[ -i \frac{e}{\hbar} \mathbf{A}(t) \cdot \mathbf{r} \right] \Psi^{(\text{length})}(\mathbf{r}, t) \equiv \Psi(\mathbf{r}, t).$$

### Floquet ansatz:

- **Floquet ansatz:** With this ansatz, the time-dependent SE in a stationary incident field can be simplified to a **set of time-independent coupled differential equations**. This set of equations need to be solved by imposing (so-called) **Siegert boundary conditions** on the wave function and by expanding it, for instance, upon a complex basis set.
- **Generalized Floquet ansatz:** For the interaction with two laser fields with frequencies  $\omega_1, \omega_2$ , the Floquet ansatz can be written

$$\Psi^{(\text{velocity, length})}(\mathbf{r}, t) = e^{-iEt/\hbar} \sum_{N_1 N_2} e^{-i(N_1 \omega_1 + N_2 \omega_2)} F_{N_1 N_2}(\mathbf{r}).$$

In this ansatz, the Floquet components  $F_{N_1 N_2}(\mathbf{r}) \equiv F_{N_1 N_2}^{(\text{velocity, length})}$  and energies  $E \equiv E^{(\text{velocity, length})}$  satisfy a system of time-independent equations that are equivalent to the time-dependent Schrödinger equation, cf. Potvliege (1998).

➤ **Floquet ansatz for the wave function:**

$$\psi(t) = \exp(-iEt) \sum_{n=-\infty}^{\infty} \exp(-in\omega t) \psi_n, \quad E = \Re(E) - i\Gamma/2,$$

where the functions  $\psi_n$  are often called the **harmonic components**, while  $E$  is the complex quasi-energy of the **Siegert state**  $\psi(t)$  and  $\Gamma$  the total ionization rate of this state.

## Applications of Floquet theory to HHG:

- **Induced electric-dipole moment:** The induced electric-dipole moment from the theory of high harmonics can be expressed within the Floquet theory in the form (Gebarowski *et al.* 1997)

$$\mathbf{D}(t) = \exp(-\Gamma t) \left[ \mathbf{D}_o + 2 \sum_{q=1}^{\infty} \Re [\mathbf{D}_q \exp(-iq\omega t)] \right], \quad \mathbf{D}_q = \sum_{n=-\infty}^{\infty} -\langle \psi_{n-q} | \mathbf{R}_N | \psi_n \rangle.$$

- **Emission rate for photons with frequency  $\omega_q = q\omega$  and polarization  $\boldsymbol{\lambda}$ :** The rate for emission of photons into a given solid angle  $d\Omega$  is then obtained by summing over all polarizations of the emitted radiation

$$\frac{dR(\omega_H, \boldsymbol{\lambda})}{d\Omega} = \frac{\omega_H^3}{2\pi c^3} |\boldsymbol{\lambda}^* \cdot \mathbf{d}_q|^2,$$

and the total emission rate by an integrating over all directions.

### 10.7.b. Two-color sideband formation in atomic photoionization [theoretical background]

#### Processes & notations:

- **Photoionization by a long twisted pulse and a long NIR pulse:**

$$\hbar\omega^{(\text{long, twist})} + A + \hbar\omega^{(\text{String NIR})} \longrightarrow A^+ + e_p^- (E_p, \text{sidebands})$$

- In this strong-field ionization process, the photoelectron moves after its ionization in a Volkov state with the NIR field, and this gives rise to well-defined sidebands in the photoionization probability  $W(E_p; m, \Lambda_X, \Lambda_L)$ .



### 10.7.c. Phase control of atomic photoionization in multi-color fields [theoretical background]

#### Processes & notations:

- **Coherent-control schemes:** While various quantum coherent-control schemes have been developed and utilized already within the optical and IR regions, their use at high frequencies has been hampered by the lack of sufficient coherent xuv sources. An important step ahead was made by seeded FEL beams, for instance at FERMI, which provide high longitudinal coherence. This coherence of the light beams enables one to observe interference of two- and one-photon pathways in the photoelectron angular distributions following the xuv irradiation.
- **Application of phase control:** The phase control of photoprocesses has attracted much recent interest and has found promising applications, such as the control of chemical reactions, the study of biological changes, ultrafast and nonlinear optics as well as four-dimensional (4D) ultrafast electron microscopy.
- **Differential ionization probability:** In second-order perturbation theory, the angle-differential ionization probability for the emission of a photoelectron and for a transition  $i \rightarrow f$  of the photoion can be expressed as

$$\frac{dW}{d\Omega} = \frac{1}{2J_i + 1} \sum_{M_i, M_f \mu} \left| \eta U_{M_i, M_f \mu}^{(1, 2\omega)} + U_{M_i, M_f \mu}^{(2, \omega)} \right|^2$$

where  $U_{M_i, M_f \mu}^{(1, 2\omega)}$  is the first-order amplitude for ionization by the second harmonic and  $U_{M_i, M_f \mu}^{(2, \omega)}$  the second-order amplitude for two-photon ionization by the fundamental frequency. Here, the magnetic quantum numbers refer to the initial atomic state  $|\mathbb{J}_i M_i\rangle$ , the residual ion  $|\mathbb{J}_i M_i\rangle$  as well as the photoelectron  $|\mathbf{p} \mu\rangle$ .

- **Electric dipole approximation:**

$$U_{M_i, M_f \mu}^{(1, 2\omega)} = -i \langle \alpha_f \mathbb{J}_f M_f, \mathbf{p} \mu^{(-)} | e \mathbb{D} | \alpha_i \mathbb{J}_i M_i \rangle T^{(1)}$$

$$U_{M_i, M_f \mu}^{(2, \omega)} = \sum_{\nu} \int \langle \alpha_f \mathbb{J}_f M_f, \mathbf{p} \mu^{(-)} | e \mathbb{D} | \alpha_{\nu} \mathbb{J}_{\nu} M_{\nu} \rangle \langle \alpha_{\nu} \mathbb{J}_{\nu} M_{\nu} | e \mathbb{D} | \alpha_i \mathbb{J}_i M_i \rangle T_{E_{\nu}}^{(2)}.$$

Here  $\alpha_{\nu}$  specifies the quantum numbers of the intermediate states  $\nu$ , while  $\sum_{\nu} \int$  denotes the infinite summation over all discrete and continuum states. The minus sign in the outgoing electron wave indicates the proper asymptotic form of the continuum wave function,  $E_{\nu}$  is the energy of the intermediate virtual atomic state. The time-dependent  $T^{(1)}$  and  $T_{E_{\nu}}^{(2)}$  were described elsewhere in the literature (Gryzlova *et al.*, 2018).

### 10.7.d. Amplified spontaneous emission (ASE) & superfluorescence (SF)

#### Motivation:

- **Nonlinear optical light-matter interactions:** In the optical regime, the two nonlinear phenomena **Amplified spontaneous emission (ASE)** and **superfluorescence (SF)** have been studied, both experimentally and theoretically. In these processes, a short and intense light pulse partly creates a population inversion of some excited level(s), and which may then decay either by fluorescence or stimulated emission. In an ASE spectrum, the number of emitted photons increases exponentially with the density of the excited-state(s), while the duration of light emitted also increases. In superfluorescence spectra, in contrast, the number of emitted photons just depends linearly on the density of the excited-state(s), and the emitted fluorescence occurs slightly delayed with regard to the incident light and *reduced* in duration.
- **Nonlinear optical light-matter interactions:** In optical experiments, both phenomena (ASE and SF) have been explored and distinguished by counting the total photon yield and/or by measuring the time-dependence of the emitted radiation as function of the intensity of the incident pulse. Theoretically, most computations are based on (so-called) time-dependent Maxwell-Bloch equations, in which the spontaneous emission is described by some stochastic noise. In practice, this model is not able to obtain the exponential increase of the emission intensity in ASE but just gives rise to a delayed peak in the temporal profile of the emitted field, and with regard to the incident field.

## 10.8. Theoretical background to atomic responses considered above

### Theoretical methods:

- **Time-dependent CI singles (TDCIS):** This one-electron formulation for describing strong-field ionization is guided mainly by the first step in all strong-field processes, in which an electron is pulled away from the parent ion by the laser field. The use of the single-active electron (SAE) approximation has been shown to be sufficient to predict the single-ionization production, the cutoff in the HHG spectrum as well as the ATI photoelectron spectra in different atoms.
- **TDCIS:** This is an approximate one-electron approach that goes beyond the SAE treatment. In this *ab-initio* electronic-structure method, the time-dependent wave function is restricted to spin-singlets which conserve single-particle excitations from the ground-state determinant.

### 10.8.a. Strong-field approximation (SFA) [background]

#### Elements of SFA:

- **Strong-field approximation (SFA):** This approximation assumes a Keldysh parameter  $\gamma < 1$  and, hence, is expected to be **valied especially for intense, low-frequency laser fields**. For such fields, the electron dynamics of the electron in the continuum is distorted only weakly by the (Coulomb) field of the residual ion, and this influence of the atom is then described perturbatively. With these assumptions in mind, the *standard* SFA can be summarized as follows (Amini *et al.*, 2019):
  1. The strong laser field couples only to the atom in its ground state or to one (active) electron in the continuum, and only this *active* electron has a spatial structure and is included into the dynamics.
  2. An approximate time-dependent amplitude  $a(t)$  of the active electron in the ground-state of the atom is considered to be known.
  3. The *continuum* is formed by all solutions of the Scjrödinger equation (with the atomic single-electron Hamiltonian  $H^{(\text{atom})}$ ) with well-defined (kinetic) momentum  $\mathbf{p}$  :  $H^{(\text{atom})} |\mathbf{p}\rangle = \frac{\mathbf{p}^2}{2m} |\mathbf{p}\rangle$ . In the evaluation of the continuum-continuum matrix elements, however, the interaction with the atomic potential is treated only perturbatively.
- **Representation of the time-dependent wave function:** In the SFA, the wave function of the active electron is given by

$$|\psi(t)\rangle = e^{iI_p t/\hbar} \left( a(t) |0\rangle + \int d^3\mathbf{p} b(\mathbf{p}, t) |\mathbf{p}\rangle \right)$$

where  $|0\rangle$  is the ground (product) state of the active electron in the atomic potential, and  $I_p$  its binding energy. While the amplitude  $a(t)$  is assumed to be known, the quantum (transition) amplitude  $b(\mathbf{p}, t)$  of (quasi-) free electrons with well-defined  $\mathbf{p}$  need to be determined as solution of the (single-electron) TDSE. This quantum amplitude depend not only on the *kinetic* momentum  $\mathbf{p}$  of the outgoing electron but also on the laser pulse and, parametrically, on the potential of the residual ion.

- **Approximate time-dependent amplitude  $a(t)$  of the active electron in the atomic ground level:** There are various methods to find an approximate time-dependent amplitude  $a(t)$  for an atom in the light field, either from the single-electron TDSE or by using some cheaper method, such as phase-space averaging or the truncated Wigner approximation (Berman *et al.*, 2018). Moreover, for very short pulses *or* long-but-weak pulses, one may simply assume  $a(t) \simeq 1$ , i.e. that the depletion of the ground level is negligible.
- **Electric-dipole matrix elements in the SFA:** To evaluate the interaction of the active electron with the laser field, one needs to know the dipole-interaction matrix elements between the continuum states  $\langle \mathbf{p} | \mathbf{d} | \mathbf{p}' \rangle$  and from the atomic ground state to the continuum  $\langle \mathbf{p} | \mathbf{d} | 0 \rangle$ , respectively. In the nonrelativistic theory, these matrix elements can be written as (Amini *et al.*, 2019)

$$\langle \mathbf{p} | \mathbf{d} | \mathbf{p}' \rangle = e \langle \mathbf{p} | \mathbf{r} | \mathbf{p}' \rangle = i e \nabla_{\mathbf{p}} \delta(\mathbf{p} - \mathbf{p}') + \hbar \mathbf{g}(\mathbf{p}, \mathbf{p}'), \quad \langle \mathbf{p} | \mathbf{d} | 0 \rangle = e \langle \mathbf{p} | \mathbf{r} | 0 \rangle = \mathbf{d}(\mathbf{p}).$$

Note that, if  $\mathbf{g}(\mathbf{p}, \mathbf{p}')$  is neglected, the dipole matrix elements  $\langle \mathbf{p} | \mathbf{r} | \mathbf{p}' \rangle = i e \nabla_{\mathbf{p}} \delta(\mathbf{p} - \mathbf{p}')$  are here the same as for plane-waves (*free* electrons without the atomic potential) or Volkov states (electrons in a plane-wave laser field).

- **Solution of the SFA equations:** Using the SFA ansatz of the time-dependent wave function in the (time-dependent) Schrödinger equation and by using the length gauge for the coupling of the laser field, the time-derivatives of the quantum amplitudes are given by (Amini *et al.*, 2019)

$$\begin{aligned} \dot{a}(t) &= \frac{i}{\hbar} \int d^3 \mathbf{p} \mathbf{E}(t) \cdot \mathbf{d}^*(\mathbf{p}) b(\mathbf{p}, t) \\ \dot{b}(\mathbf{p}, t) &= -\frac{i}{\hbar} \left( \frac{\mathbf{p}^2}{2m} + I_p \right) b(\mathbf{p}, t) + \frac{i}{\hbar} \mathbf{E}(t) \cdot \mathbf{d}(\mathbf{p}) a(t) - e \mathbf{E}(t) \cdot \nabla_{\mathbf{p}} b(\mathbf{p}, t) + i \mathbf{E}(t) \cdot \int d^3 \mathbf{p}' b(\mathbf{p}', t) \mathbf{g}(\mathbf{p}, \mathbf{p}'). \end{aligned}$$

For  $\dot{b}(\mathbf{p}, t)$ , the first term on the rhs represents the time-evolution of a (*quasi-*) *free* electron in the potential of the residual ion and without the oscillating laser field. Moreover, the second term describes the coupling due to the laser field of these (quasi-) free electrons to the ground state, the third term its coupling due to the laser to other (quasi-) free-electron states, while the last term the modification in the continuum-continuum coupling due to the re-scattering of the electron by the atomic potential. Obviously, the time-derivative  $\dot{b}(\mathbf{p}, t)$  is

described by an integro-differential equation that need to be solved iteratively. This iterative procedure gives rise to the – usual separation of – a **direct-ionization amplitude**  $b_0(\mathbf{p}, t)$  and a **re-scattering amplitude**  $b_1(\mathbf{p}, t)$ .

- **Direct-ionization amplitude**  $b_0(\mathbf{p}, t)$ : This amplitude is obtained by simply omitting the 4-th term for  $\dot{b}(\mathbf{p}, t)$ , and which is then the solution of a first-order inhomogeneous differential equation. This equation can be formally integrated (Amini *et al.*, 2019)

$$\dot{b}_0(\mathbf{p}, t) = -\frac{i}{\hbar} \left( \frac{\mathbf{p}^2}{2m} + I_p \right) b_0(\mathbf{p}, t) + \frac{i}{\hbar} \mathbf{E}(t) \cdot \mathbf{d}(\mathbf{p}) a(t) - e \mathbf{E}(t) \cdot \nabla_{\mathbf{p}} b_0(\mathbf{p}, t)$$

$$b_0(\mathbf{p}, t) = \frac{i}{\hbar} \int_0^t d\tau \mathbf{E}(\tau) \cdot \mathbf{d}(\mathbf{p} + e \mathbf{A}(t) - e \mathbf{A}(\tau)) \exp \left( -\frac{i}{\hbar} \int_{\tau}^t d\tau' \left[ \frac{(\mathbf{p} + e \mathbf{A}(t) - e \mathbf{A}(\tau'))^2}{2m} + I_p \right] \right) a(\tau)$$

This formal solution is written for the case that the electron appears in the continuum at time  $\tau$  with kinetic momentum  $\mathbf{p}(\tau) = \mathbf{p} + e \mathbf{A}(t) - e \mathbf{A}(\tau)$ , and where  $\mathbf{p}$  is the final kinetic momentum at the detector and  $\mathbf{A}(t) = \int^t d\tau \mathbf{E}(\tau)$  the vector potential of the electro-magnetic field.

- **Applications of SFA**: This theory help explain multi-photon ionization (MPI), above-threshold ionization (ATI), tunnel ionization (TI) as well as over-the-barrier (OTB) ionization. In the strong-field regime, the forces of the laser field are comparable to those of the Coulomb force between the nucleus and electrons so that neither one can be described (only) perturbatively. Such a distortion of the Coulomb potential often also leads to a lowering of the ionization barrier.
- **Angular-dependent PEMD**: The angular-dependent PEMD of an electron with asymptotic momentum is

$$\frac{d^3 \mathcal{P}^{(SFA)}}{dp_x dp_y dp_z} = |\{^{(SFA)}(\mathbf{p})\}|^2.$$

For a linearly- or circularly-polarized laser field, the angular-dependent PEMD has cylindrical symmetry and, hence, a 2-dimensional PEMD can be defined by

$$\frac{d^2 \mathcal{P}^{(SFA)}}{dp_{\perp} dp_z} = 2\pi p \sin \vartheta_p |\{^{(SFA)}(\mathbf{p})\}|^2, \quad p_{\perp} = \sqrt{p_x^2 + p_y^2},$$

and where  $\vartheta_p$  is the angle between the polarization axis  $\boldsymbol{\mathcal{E}} \parallel \mathbf{e}_z$  and the direction of the emitted photoelectron (linear polarization) or the polar angle between the photoelectron and the propagation axis of the laser  $\mathbf{k} \parallel \mathbf{e}_z$  (circular polarization), respectively. In both cases, the integration over the azimuthal angle  $\varphi_p$  can be carried out explicitly.

➤ **Energy-dependent PEMD:** The energy-dependent distribution is obtained from the SFA amplitude by

$$\frac{d \mathcal{P}^{(\text{SFA})}}{d E} = 2\pi \sqrt{2 E} \int_{-1}^1 d(\cos \vartheta_p) |\{^{(\text{SFA})}(\mathbf{p})|^2.$$

### Transition amplitudes in SFA:

➤ **Probability to detect electrons with asymptotic momentum  $\mathbf{p}$ :** In the SFA, the probability to detect a photoelectron with (asymptotic) energy  $\varepsilon_p$  is given in terms of the transition amplitude  $\mathcal{T}^{(\text{SFA})}(\mathbf{p})$  and momentum  $\mathbf{p} = (p, \vartheta_p, \varphi_p) = (\sqrt{2\varepsilon_p}, \vartheta_p, \varphi_p)$  by

$$\mathcal{P}^{(\text{SFA})}(\mathbf{p}) = \frac{d^3 \mathcal{P}^{(\text{SFA: density})}(\mathbf{p})}{d\Omega_{\mathbf{p}} d\varepsilon_p} = p |\mathcal{T}^{(\text{SFA})}(\mathbf{p})|^2.$$

This simple relation follows from the **transformation of the (triple-) differential probability density** for the emission of an electron in momentum space to a differentially-mixed representation in energy and the angular variables in momentum space; this transformation is then readily obtained by using  $d^3 \mathbf{p} = p^2 d\Omega_{\mathbf{p}}$  and the non-relativistic energy-momentum relation ( $d\varepsilon_p = p dp$ ):

$$\mathcal{P}^{(\text{total SFA})} = \int d^3 \mathbf{p} |\mathcal{T}^{(\text{SFA})}(\mathbf{p})|^2 = \int d\Omega_{\mathbf{p}} d\varepsilon_p |\mathcal{T}^{(\text{SFA})}(\mathbf{p})|^2 \frac{d^3 \mathbf{p}}{d\Omega_{\mathbf{p}} d\varepsilon_p} = \int d\Omega_{\mathbf{p}} d\varepsilon_p p |\mathcal{T}^{(\text{SFA})}(\mathbf{p})|^2.$$

➤ **Transition amplitude  $\mathcal{T}^{(\text{SFA})}(\mathbf{p})$ :** In the SFA, the interaction of the photoelectron with the residual ion is assumed to be weak and, hence, treated perturbatively. With this assumption in mind, the total transition amplitude  $\mathcal{T}^{(\text{SFA})}(\mathbf{p})$  can be expressed approximately as sum of a (so-called) **direct** and — one or several — **rescattering amplitudes** as

$$\mathcal{T}^{(\text{SFA})}(\mathbf{p}) = \mathcal{T}^{(\text{SFA: direct})}(\mathbf{p}) + \mathcal{T}^{(\text{SFA: rescattering})}(\mathbf{p}) + \dots$$

$$\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p}) = -i \int_{-\infty}^{\infty} d\tau \langle \chi_{\mathbf{p}}^{(\text{Volkov})}(\tau) | \mathbb{H}^{(\text{laser})}(\tau) | \Psi_i(\tau) \rangle$$

$$\mathcal{T}^{(\text{SFA: rescattering})}(\mathbf{p}) = (-i)^2 \int_{-\infty}^{\infty} d\tau \int_{\tau}^{\infty} d\tau' \langle \chi_{\mathbf{p}}^{(\text{Volkov})}(\tau') | \mathbb{V}^{(\text{atom})} \mathbb{U}^{(\text{laser})}(\tau', \tau) \mathbb{H}^{(\text{laser})}(\tau) | \Psi_i(\tau) \rangle.$$

Here  $\Psi_i(t)$  refers to the (time-dependent) atomic ground state and  $|\chi_{\mathbf{p}}^{(\text{Volkov})}(t)\rangle$  to a Volkov state of the 'atom + photoelectron', in which the outgoing electron moves in the field of the laser (and, perhaps, in the potential of the ionic core). Moreover,  $\mathbb{V}^{(\text{atom})}$  is the atomic potential of the ionic core,  $\mathbb{U}^{(\text{laser})}(t', t) \equiv \mathbb{U}^{(\text{electron-field interaction})}(t', t)$  the time evolution operator of the atom due to the interaction with the (intense) laser field and  $\mathbb{H}^{(\text{laser})} \equiv \mathbb{H}^{(\text{electron-field interaction})}$  the associated interaction Hamiltonian of the (atomic) electrons with the laser field. In the first line, the dots indicate that second- and higher-order (in the atomic potential  $\mathbb{V}^{(\text{atom})}$ ) re-scattering terms will generally also contribute to the total transition amplitude, although such higher-order terms have rarely been considered in the literature.

- **Initial atomic state:** For a many-electron atom, the initial (ground) state is simply given by a state (level) with well-defined angular momentum:

$$|\Psi_i(t)\rangle = e^{-i E_i t} |\psi_i\rangle = e^{-i E_i t} |\alpha_i J_i M_i\rangle .$$

- **Initial (non-relativistic) hydrogenic state:**

$$|\Psi_i(t)\rangle = e^{-i \varepsilon_i t} |n \ell m\rangle = e^{-i \varepsilon_i t} \frac{P_{n\ell}(r)}{r} Y_{\ell m}(\vartheta, \varphi) \quad \Longrightarrow \quad |\Psi_i(t)\rangle = e^{-i \varepsilon_i t} \sum_{m_\ell, m_s} |n \ell j m\rangle \langle j m | \ell m_\ell, 1/2 m_s\rangle .$$

The expression on the rhs here indicates that most atomic bound states are most readily classified as above by their total angular momentum  $J_i$ ,  $M_i$  and parity  $P_i$ :  $|\alpha_i J_i M_i\rangle \equiv |\alpha_i J_i^{P_i} M_i\rangle$ , and where  $\alpha_i$  refers to all additional quantum numbers that are needed for a unique specification of the state.

- **Electron-field interaction Hamiltonian  $\mathbb{H}^{(\text{laser})}$  in Coulomb gauge:** The interaction operator for a single or many-electron atom reads (with  $\mathbf{d} = -e \mathbf{r}$ ) as

$$\mathbb{H}^{(\text{laser})} = \begin{cases} -\mathbf{d} \cdot \boldsymbol{\mathcal{E}}(\mathbf{r}) & \Longrightarrow & -\mathbb{D} \cdot \boldsymbol{\mathcal{E}}(\mathbf{r}) & \text{length gauge} \\ \mathbf{A}(t) \cdot \mathbf{p} + \frac{\mathbf{A}^2}{2} & \Longrightarrow & \mathbf{A}(t) \cdot \left( \sum_j^N \mathbf{p}_j \right) + \frac{\mathbf{A}^2}{2} & \text{velocity gauge.} \end{cases}$$

In the treatment of the electron-field interaction, the Coulomb gauge  $\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0$  is usually adopted for the vector potential  $\mathbf{A}(\mathbf{r}, t)$ ; this is trivial for a purely time-dependent field  $\mathbf{A}(t)$  but crucial for a general  $\mathbf{A}(\mathbf{r}, t)$  to get rid of a term  $\mathbf{p} \cdot \mathbf{A}(\mathbf{r}, t)$  in  $\mathbb{H}^{(\text{laser})}$ .

- **Volkov state:** A Volkov state generally describes a **scattering state of '(one quasi-) free photoelectron, in which the free electron moves in the laser field and, perhaps, some ionic potential**. However, since these solutions to the Schrödinger equation are not known for general

## 10. Collision- and field-induced atomic responses

atomic (ionic) potentials, *approximate* solutions for a (quasi-) free electron in an intense field are typically applied in order to evaluate the SFA transition amplitudes above. In our notation, the Volkov states are therefore formally defined as solutions of the (full singleton) Hamiltonian but for some — more or less approximate — atomic potential:

$$\mathbb{H} = \frac{\mathbf{p}^2}{2} + \mathbb{V}^{(\text{atom})} + \mathbb{H}^{(\text{laser})}.$$

Obviously, these **approximate (quasi-free) Volkov solutions** also depend on the vector potential  $\mathbf{A}(t)$  and, hence, the gauge for the coupling of the radiation field to the electronic motion.

- **Spherical-Volkov states:** If one assumes that the quasi-free electron only feels the laser field, the Volkov state of the photoelectron with kinetic (asymptotic) momentum  $\mathbf{p}$  can be written as

$$|\chi_{\mathbf{p}}^{(\text{Volkov})}(t; \mathbf{A})\rangle = \begin{cases} \frac{1}{(2\pi)^{3/2}} e^{-i S^{(\text{Volkov})}(t)} e^{i(\mathbf{p} + \mathbf{A}(t)) \cdot \mathbf{r}} & \text{length gauge} \\ \frac{1}{(2\pi)^{3/2}} e^{-i S^{(\text{Volkov})}(t)} e^{i \mathbf{p} \cdot \mathbf{r}} & \text{velocity gauge} \end{cases}$$

$$S^{(\text{Volkov})}(t; \mathbf{A}) \equiv S^{(\text{Volkov})}(t) = \frac{1}{2} \int^t d\tau (\mathbf{p} + \mathbf{A}(\tau))^2.$$

In velocity gauge, in particular, the (spherical) partial-wave expansion of the plane-wave  $e^{i \mathbf{p} \cdot \mathbf{r}}$  or some related (quasi-) free-electron wave can be used quite easily. For the partial-wave expansion of the plane-wave  $e^{i \mathbf{p} \cdot \mathbf{r}}$ , we shall below denote the corresponding Volkov state sometimes also by  $|\chi_{\mathbf{p}}^{(\text{Volkov})}(t; \mathbf{A})\rangle^{(\text{spherical, V} \equiv 0)}$  for the sake of simple comparison.

- **Coulomb-Volkov states:** If one assumes that the electron feels the laser *and* a Coulomb field from the residual ion, the Volkov state of a photoelectron with (asymptotic) kinetic momentum  $\mathbf{p}$  can be written in terms of outgoing Coulomb waves  $|\phi_{\mathbf{p}}\rangle$  as

$$|\chi_{\mathbf{p}}^{(\text{Coulomb-Volkov})}(t; \mathbf{A})\rangle = e^{-i S^{(\text{Volkov})}(t)} |\phi_{\mathbf{p}}\rangle = e^{-i S^{(\text{Volkov})}(t)} \frac{1}{(2\pi)^{3/2}} e^{\pi \eta_p/2} \Gamma(1 + i \eta_p) e^{i \mathbf{p} \cdot \mathbf{r}} {}_1F_1(-i \eta_p; 1; -i(p r + \mathbf{p} \cdot \mathbf{r}))$$

$$|\phi_{\mathbf{p}}\rangle = 4\pi \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} i^{\ell_p} \frac{w_{\ell_p}(\eta_p, p r)}{r} Y_{\ell_p, m_p}^*(\vartheta_p, \varphi_p) Y_{\ell_p, m_p}(\vartheta, \varphi)$$



with  $\eta_p = Z/p$ , the gamma function  $\Gamma(x)$  and the confluent hypergeometric function  ${}_1F_1(\dots)$ . Here, the second line represents the **partial-wave expansion of a (pure) Coulomb wave with well-defined asymptotic momentum  $\mathbf{p}$** .

- **Partial-wave expansions for a (quasi-) free electron with well-defined asymptotic momentum  $\mathbf{p}$** : A (quasi-) free-electron wave with well-defined (asymptotic, i.e. far away from the center of the potential) momentum propagates in its asymptotic region like a plane wave with given kinetic momentum  $|\mathbf{p}; r \rightarrow \infty\rangle \propto e^{i\mathbf{p}\cdot\mathbf{r}}$ . For any short-range central-field potential  $V = V(r)$  with Coulombic tail, and if normalized to one electron per *unit* volume, such a (distorted) free-electron wave can be expressed analogue to the well-known **partial-wave expansion of a plane-wave**

$$|\mathbf{p}\rangle^{(\text{spherical})} = \sqrt{\frac{2}{\pi}} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} Y_{\ell_p, m_p}^*(\vartheta_p, \varphi_p) |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical})}, \quad |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical})} = i^{\ell_p} j_{\ell_p}(pr) Y_{\ell_p, m_p}(\vartheta, \varphi)$$

$$|\mathbf{p}\rangle = \sqrt{\frac{2}{\pi}} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} Y_{\ell_p, m_p}^*(\vartheta_p, \varphi_p) |\varepsilon_p \ell_p m_p\rangle, \quad |\varepsilon_p \ell_p m_p\rangle = i^{\ell_p} \frac{P_{\varepsilon_p \ell_p}(r)}{r} Y_{\ell_p, m_p}(\vartheta, \varphi).$$

if the partial waves  $|\varepsilon_p \ell_p m_p\rangle$  just refer to solutions of the Schrödinger equation in the given potential:

$$|\varepsilon_p \ell_p m_p\rangle = |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical}, V \equiv 0)} \implies \begin{matrix} |\varepsilon_p \ell_p m_p\rangle^{(\text{Coulomb})} \\ |\varepsilon_p \ell_p m_p\rangle^{(\text{distorted})} \end{matrix}.$$

Here, *distorted* refers to any **distorted Coulomb potential**, i.e. a short-range central-field potential with a Coulombic tail. Of course, the same expansions still apply if we consider electron waves with given spin projections:

$$|\mathbf{p} m'_s\rangle \longrightarrow |\varepsilon_p \ell_p m_p\rangle |m'_s\rangle = |\varepsilon_p \ell_p m_p m'_s\rangle.$$

- **Partial-wave expansion for a free electron with well-defined asymptotic momentum  $\mathbf{p}$  in a coupled basis**: An analogue expansion can be written in terms of the coupled basis by using

$$|\mathbf{p} m'_s\rangle = \sqrt{\frac{2}{\pi}} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} \sum_{j_p} Y_{\ell_p, m_p}^*(\vartheta_p, \varphi_p) \langle \ell_p m_p, 1/2 m'_s | j_p, m_p + m'_s \rangle |\varepsilon_p \ell_p j_p, m_p + m'_s\rangle$$

- **Partial-wave expansion for free-electron Volkov states in velocity gauge**: In velocity gauge, the time-dependent Coulomb-Volkov and distorted-Volkov states can still be written analogue to the spherical-Volkov states from above, if the corresponding partial-wave expansions

are applied:

$$\begin{aligned}
 |\chi_{\mathbf{p}}^{(\text{spherical-Volkov})}(t; \mathbf{A})\rangle &= \sqrt{\frac{2}{\pi}} e^{-i S^{(\text{Volkov})}(t; \mathbf{A})} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} Y_{\ell_p, m_p}^*(\vartheta_p, \varphi_p) |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical})} \\
 |\chi_{\mathbf{p}}^{(\text{spherical-Volkov})}(t; \mathbf{A})\rangle &\Rightarrow \begin{cases} |\chi_{\mathbf{p}}^{(\text{Coulomb-Volkov})}(t; \mathbf{A})\rangle & \text{for } |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical})} \Rightarrow |\varepsilon_p \ell_p m_p\rangle^{(\text{Coulomb})} \\ |\chi_{\mathbf{p}}^{(\text{distorted-Volkov})}(t; \mathbf{A})\rangle & |\varepsilon_p \ell_p m_p\rangle^{(\text{spherical})} \Rightarrow |\varepsilon_p \ell_p m_p\rangle^{(\text{distorted})} \end{cases} .
 \end{aligned}$$

An analogue expansion also applies if the spherical Volkov states  $|\chi_{\mathbf{p}}^{(\text{spherical-Volkov})}(t, m'_s)\rangle$  include a well-defined spin-projection and, even if the rhs of the partial-wave expansion is written in a *coupled* basis of well-defined total angular momenta  $j$  :  $|\varepsilon_p \ell_p m_p m_s\rangle \rightarrow |\varepsilon_p \ell_p j_p m'_p\rangle$ .

To understand this rather straight generalization, we may argued here that the laser field gives rise to a time-dependent Volkov phase, while it does not affect the spatial structure of the outgoing plane-wave electron. Therefore, the *spherical Volkov states just become simple plane waves (and, analogue, for the Coulomb-Volkov and distorted-Volkov states, etc.) if the laser field is turned off ( $|\mathbf{A}(t)| \rightarrow 0$ )*. Following these arguments, the proper time dependence just arises by multiplying the (asymptotic) continuum states with the factor  $e^{-i S^{(\text{Volkov})}(t; \mathbf{A})}$ , and the same arguments still hold if the electron wave includes a well-defined spin-projection or is described within the *coupled* basis  $\{|\varepsilon_p \ell_p j_p m'_p\rangle\}$ . The same argument still holds for the many-electron atom if one assumes that the photoelectron moves in the (static) potential of the final ion.

- **Partial-wave expansion for (quasi-) free electron Volkov states in length gauge:** In length gauge, the Volkov states  $|\chi_{\mathbf{p}}^{(\text{Volkov})}(t; \mathbf{A})\rangle$  states cannot be so easily expanded since the kinetic momentum  $\mathbf{p}$  in the exponential has then to be replaced by the canonical momentum  $\mathbf{p} + \mathbf{A}(t)$ . *Until the present, therefore, we here restrict the further treatment to the SFA in velocity gauge.* However, the length gauge should be re-considered since this gauge often yields more reliable results for the photoelectron momentum distributions in the SFA, and this has been confirmed especially if the initial state is not spherical-symmetric. An expansion of the free-electron Volkov states in length gauge was performed by Milosevic and Becker (2019; appendix); in this treatment, a  $j_\ell(A(t)r)$ -term occurs from the expansion of  $e^{-i \mathbf{A}(t) \cdot \mathbf{r}}$ , although this need to be explored in further detail.
- **Spherical unit vectors:** To make use of the rotational symmetry of atoms and ions, all operators are typically expressed as *spherical tensors*, and by using a basis of (spherical) unit vectors. In this framework, one typically needs to distinguish between the *covariant spherical basis*

$\{\mathbf{e}_+, \mathbf{e}_-, \mathbf{e}_0\}$  and the contravariant spherical basis  $\{\mathbf{e}^+, \mathbf{e}^-, \mathbf{e}^0\}$ :

$$\mathbf{e}_\pm = \frac{1}{\sqrt{2}} (\mathbf{e}_x \pm i \mathbf{e}_y), \quad \mathbf{e}_0 = \mathbf{e}_z = \mathbf{e}^0, \quad \mathbf{e}^\pm = \frac{1}{\sqrt{2}} (\mathbf{e}_x \mp i \mathbf{e}_y).$$

This distinction between the covariant and contravariant spherical basis is necessary since only (unit) vectors from the co- and contravariant basis are still pairwise orthonormal,  $\mathbf{e}_q \cdot \mathbf{e}^s = \mathbf{e}^q \cdot \mathbf{e}_s = \delta_{qs}$  but, for instance,  $\mathbf{e}_+ \cdot \mathbf{e}_+ \neq 1$ .

➤ **Spherical decomposition of a vector in the covariant spherical basis:** A (cartesian) vector  $\mathbf{v} = (v_x, v_y, v_z) = v_x \mathbf{e}_x + v_y \mathbf{e}_y + v_z \mathbf{e}_z$  is usually expressed in the covariant spherical basis by:

$$\mathbf{v} = v_+ \mathbf{e}_+ + v_0 \mathbf{e}_0 + v_- \mathbf{e}_-, \quad v_+ = \mathbf{e}^+ \cdot \mathbf{v} = \frac{1}{\sqrt{2}} (v_x - i v_y), \quad v_- = \frac{1}{\sqrt{2}} (v_x + i v_y), \quad v_0 = v_z.$$

➤ **Polarized light in the spherical basis:** The (complex) polarization vector  $\mathbf{u}$  for circularly- and linearly-polarized light can of course be expressed also in the spherical basis. If we associate left-circularly polarized light with  $\lambda = +1$  (mathematical positive) and right-circularly polarized light with  $\lambda = -1$ , their (unit) polarization vectors are simply given by

$$\begin{aligned} \mathbf{u}^{(\text{circular})} &= \frac{1}{\sqrt{2}} (\mathbf{e}_x + i \lambda \mathbf{e}_y) = \sum_{q=\pm 1, 0} u_q \mathbf{e}_q \\ \mathbf{u}^{(\text{left-circular})} &= \frac{1}{\sqrt{2}} (\mathbf{e}_x + i \mathbf{e}_y) : \quad u_+ = 1, \quad u_- = u_0 = 0 \\ \mathbf{u}^{(\text{right-circular})} &= \frac{1}{\sqrt{2}} (\mathbf{e}_x - i \mathbf{e}_y) : \quad u_- = 1, \quad u_+ = u_0 = 0. \end{aligned}$$

For linearly-polarized light,  $\mathbf{u}^{(\text{linear})}$ , one similarly finds

$$\begin{aligned} \mathbf{u}^{(\text{linear})} &= \mathbf{e}_x : \quad u_+ = u_- = \frac{1}{\sqrt{2}} \quad u_0 = 0 \\ \mathbf{u}^{(\text{linear})} &= \mathbf{e}_y : \quad u_+ = -u_- = -\frac{i}{\sqrt{2}} \quad u_0 = 0. \end{aligned}$$

- **Relation between the complex- and real-valued vector potential:** In the framework of spherical tensors, a complex-valued vector potential is usually applied for a monochromatic wave with well-defined amplitude  $A_o$ , frequency  $\omega$ , carrier-envelope phase  $\phi^{(\text{cep})}$  and (unit) polarization vector  $\mathbf{u}$ ,  $\mathbf{A}_c(t) = A_o \mathbf{u} e^{-i(\omega t + \phi^{(\text{cep})})}$ . Of course, the electron-field interaction with the laser depends only on the real part of this complex potential

$$\mathbf{A}(t) = \Re\{\mathbf{A}_c(t)\} = \frac{1}{2} (\mathbf{A}_c(t) + \mathbf{A}_c^*(t)) .$$

Below, the – physical part of –  $\mathbf{A}(t)$  always occurs in the evaluation of the Volkov phases and related quantities, while the complex-valued form is required to make proper use of the spherical-tensor formalism.

- **Electron-field interaction Hamiltonian  $\mathbb{H}^{(\text{laser})}(t)$ :** With the simple relation above, the electron-field interaction Hamiltonian in (Coulomb +) velocity gauge can be re-written in terms of the complex-valued vector potential as

$$\begin{aligned} \mathbb{H}^{(\text{laser})}(t) &= \mathbf{A}(t) \cdot \mathbf{p} + \frac{1}{2} \mathbf{A}^2(t) = \frac{1}{2} \mathbf{A}_c(t) \cdot \mathbf{p} + \frac{1}{2} \mathbf{A}_c^*(t) \cdot \mathbf{p} + \frac{1}{8} (\mathbf{A}_c(t) + \mathbf{A}_c^*(t))^2 \\ &= -\frac{i}{2} \mathbf{A}_c(t) \cdot \nabla - \frac{i}{2} \mathbf{A}_c^*(t) \cdot \nabla + \frac{1}{8} (\mathbf{A}_c(t) + \mathbf{A}_c^*(t))^2 . \end{aligned}$$

- **Spherical decomposition of the electron-field interaction:** The interaction of an electron (with momentum  $\mathbf{p}$ ) with the complex-valued vector potential  $\mathbf{A}_c(t) = A_o \mathbf{u} e^{-i(\omega t + \phi^{(\text{cep})})}$  leads obviously to scalar products, such as  $\mathbf{u} \cdot \mathbf{p}$  and  $\mathbf{u}^* \cdot \mathbf{p}$ . These scalar products need to be expressed in a spherical basis ( $\mathbf{e}^q = \mathbf{e}_q^*$ ,  $\mathbf{e}_q^* \cdot \mathbf{e}_s = \mathbf{e}^q \cdot \mathbf{e}_s = \delta_{qs}$ )

$$\begin{aligned} \mathbf{u} \cdot \mathbf{p} &= \sum_{q,s=0,\pm 1} u_q p_s \mathbf{e}_q \cdot \mathbf{e}_s = \sum_{q,s=0,\pm 1} (-1)^q u_q p_s \mathbf{e}_{-q}^* \cdot \mathbf{e}_s = \sum_{q=0,\pm 1} (-1)^q u_q p_{-q} \\ \mathbf{u}^* \cdot \mathbf{p} &= \sum_{q,s=0,\pm 1} u_q^* p_s \mathbf{e}_q^* \cdot \mathbf{e}_s = \sum_{q=0,\pm 1} u_q^* p_q . \end{aligned}$$

These decompositions of the scalar products are necessary in order to make use of the Wigner-Eckardt theorem and to apply the (standard) **reduced matrix elements of the momentum operator** in the partial-wave decomposition of the electron waves and its interaction with the laser field.

- **Reduced matrix elements of the  $\mathbf{u} \cdot \mathbf{p}$  interaction with an external field in velocity gauge:** In the product basis of spin-orbitals  $\{|n\ell m_\ell m_s\rangle\}$ , the electron-field interaction can be traced back to the following matrix elements, and can be further *reduced by means of the Wigner-Eckardt theorem*:

$$\langle \varepsilon_p \ell_p m_p | \mathbf{u} \cdot \mathbf{p} | n\ell m \rangle = \sum_{q=0,\pm 1} (-1)^q u_q \langle \varepsilon_p \ell_p m_p | p_{-q} | n\ell m \rangle = \sum_{q=0,\pm 1} (-1)^q u_q \langle \ell m, 1(-q) | \ell_p m_p \rangle \langle \varepsilon_p \ell_p || \mathbf{p} || n\ell \rangle$$

$$\langle \varepsilon_p \ell_p m_p | \mathbf{u}^* \cdot \mathbf{p} | n\ell m \rangle = \sum_{q=0,\pm 1} u_q^* \langle \varepsilon_p \ell_p m_p | p_q | n\ell m \rangle = \sum_{q=0,\pm 1} u_q^* \langle \ell m, 1q | \ell_p m_p \rangle \langle \varepsilon_p \ell_p || \mathbf{p} || n\ell \rangle .$$

Rather analogue, these matrix elements read in the (coupled) basis of spin-orbital basis  $\{|n\ell jm\rangle\}$  as:

$$\langle \varepsilon_p \ell_p j_p m_p | \mathbf{u} \cdot \mathbf{p} | n\ell jm \rangle = \sum_{q=0,\pm 1} (-1)^q u_q \langle \varepsilon_p \ell_p j_p m_p | p_{-q} | n\ell jm \rangle = \sum_{q=0,\pm 1} (-1)^q u_q \langle jm, 1(-q) | j_p m_p \rangle \langle \varepsilon_p \ell_p j_p || \mathbf{p} || n\ell j \rangle$$

$$\langle \varepsilon_p \ell_p j_p m_p | \mathbf{u}^* \cdot \mathbf{p} | n\ell jm \rangle = \sum_{q=0,\pm 1} u_q^* \langle \varepsilon_p \ell_p j_p m_p | p_q | n\ell jm \rangle = \sum_{q=0,\pm 1} u_q^* \langle jm, 1q | j_p m_p \rangle \langle \varepsilon_p \ell_p j_p || \mathbf{p} || n\ell j \rangle$$

$$\langle \varepsilon_p \ell_p j_p || \mathbf{p} || n\ell j \rangle = \dots? \dots \langle \varepsilon_p \ell_p || \mathbf{p} || n\ell \rangle$$

- **Reduced matrix elements of the momentum operator  $\langle \varepsilon_p \ell_p || \mathbf{p} || n\ell \rangle$ :** The reduced matrix element of the momentum operator occurs at various places in atomic structure theory and can be written in terms of the reduced matrix elements of the  $\mathbf{C}^{(1)}$  tensors and some radial integrals as

$$\mathbf{p} = -i \nabla = -i \left[ \mathbf{C}^{(1)} \frac{\partial}{\partial r} - \frac{\sqrt{2}}{r} (\mathbf{C}^{(1)} \otimes \mathbf{L}^{(1)})^{(1)} \right]$$

$$\langle \ell_p || \mathbf{p} || \ell \rangle = -i \langle \ell_p || \mathbf{C}^{(1)} || \ell \rangle \left[ \frac{\partial}{\partial r} - \frac{(\ell_p - \ell)(\ell_p + \ell + 1) - 2}{2r} \right], \quad \langle \ell_p || \mathbf{C}^{(1)} || \ell \rangle = (-1)^{\ell_p} [\ell_p, \ell]^{1/2} \begin{pmatrix} \ell_p & 1 & \ell \\ 0 & 0 & 0 \end{pmatrix}$$

$$\begin{aligned}
 \langle \varepsilon_p \ell_p \parallel \mathbf{p} \parallel n\ell \rangle &= (-i)^{\ell_p} \int dr r^2 \frac{P_{\varepsilon_p \ell_p}(r)}{r} \langle \ell_p \parallel \mathbf{p} \parallel \ell \rangle \frac{P_{n\ell}(r)}{r} \\
 &= (-i)^{\ell_p+1} \langle \ell_p \parallel \mathbf{C}^{(1)} \parallel \ell \rangle \int dr r^2 \frac{P_{\varepsilon_p \ell_p}(r)}{r} \left[ \frac{\partial}{\partial r} - \frac{(\ell_p - \ell)(\ell_p + \ell + 1) - 2}{2r} \right] \frac{P_{n\ell}(r)}{r} \\
 &= (-i)^{\ell_p+1} \langle \ell_p \parallel \mathbf{C}^{(1)} \parallel \ell \rangle \int dr P_{\varepsilon_p \ell_p}(r) \left[ \frac{\partial P_{n\ell}}{\partial r} - \frac{(\ell_p - \ell)(\ell_p + \ell + 1)}{2r} P_{n\ell} \right].
 \end{aligned}$$

➤ Reduced matrix elements of the momentum operator  $\langle \varepsilon_p \ell_p j_p \parallel \mathbf{p} \parallel n\ell j \rangle$ :

$$\begin{aligned}
 \langle \varepsilon_p \ell_p j_p m_p \mid \mathbf{p} \mid n\ell j m \rangle &= \langle jm, 1q \mid j_p m_p \rangle \langle \varepsilon_p \ell_p j_p \parallel \mathbf{p} \parallel n\ell j \rangle \\
 &= \sum_{m_\ell m_s, m'_p m'_s} \langle \ell_p m'_p, 1/2m'_s \mid j_p m_p \rangle \langle \ell m_\ell, 1/2m_s \mid jm \rangle \langle \varepsilon_p \ell_p m'_p m'_s \parallel \mathbf{p} \parallel n\ell m_\ell m_s \rangle \\
 &= \sum_{m_\ell, m'_p m'_s} \langle \ell_p m'_p, 1/2m'_s \mid j_p m_p \rangle \langle \ell m_\ell, 1/2m'_s \mid jm \rangle \langle \ell m_\ell, 1q \mid \ell_p m'_p \rangle \langle \varepsilon_p \ell_p \parallel \mathbf{p} \parallel n\ell \rangle \\
 \langle \varepsilon_p \ell_p j_p \parallel \mathbf{p} \parallel n\ell j \rangle &=
 \end{aligned}$$

➤ Overlap integral  $\langle \varepsilon_p \ell_p m_p \mid n\ell m \rangle$ : If the radial orbitals  $P_{\varepsilon_p \ell_p}(r)$ ,  $P_{n\ell}(r)$  are taken to be *real*, the overlap integral becomes

$$\langle \varepsilon_p \ell_p m_p \mid n\ell m \rangle = \delta_{\ell_p \ell} \delta_{m_p m} (-i)^{\ell_p} \int dr P_{\varepsilon_p \ell_p}(r) P_{n\ell}(r).$$

➤ Partial-wave decomposition of the direct transition amplitude  $\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p})$  for an infinite plane-wave pulse: Making use of the partial-wave representation of the (free-electron) Volkov states, this **direct transition amplitude reads for an infinite plane-wave pulse**

$\mathbf{A}_c = A_o \mathbf{u} e^{-i(\omega t + \phi^{(\text{cep})})}$  and for circularly-polarized light ( $\lambda = \pm 1$ ) as:

$$\begin{aligned}
& \mathcal{T}^{(\text{SFA: direct})}(\mathbf{p}) \\
&= -i \int_{-\infty}^{\infty} d\tau \langle \chi_{\mathbf{p}}^{(\text{Volkov})}(\tau; \mathbf{A}) | \mathbb{H}^{(\text{laser})}(\tau) | \Psi_i(\tau) \rangle \\
&= -i \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} d\tau e^{iS^{(\text{Volkov})}(\tau; \mathbf{A})} e^{-i\varepsilon_i \tau} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} \\
&\quad \times \left[ A_0 e^{-i(\omega t + \phi^{(\text{cep})})} Y_{\ell_p, m_p}(\vartheta_p, \varphi_p) \sum_{q=0, \pm 1} (-1)^q u_q \langle \ell m, 1(-q) | \ell_p m_p \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n\ell \rangle \right. \\
&\quad \left. + A_0 e^{i(\omega t + \phi^{(\text{cep})})} Y_{\ell_p, m_p}(\vartheta_p, \varphi_p) \sum_{q=0, \pm 1} u_q^* \langle \ell m, 1q | \ell_p m_p \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n\ell \rangle \right] + \frac{\mathbf{A}^2(\tau)}{2} \sum_{\ell_p=0}^{\infty} \sum_{m_p=-\ell_p}^{\ell_p} \langle \varepsilon_p \ell_p m_p | n\ell m \rangle \\
&= -i \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} d\tau e^{iS^{(\text{Volkov})}(\tau; \mathbf{A})} e^{-i\varepsilon_i \tau} \\
&\quad \times \left[ A_0 e^{-i(\omega t + \phi^{(\text{cep})})} \sum_{\ell_p=0}^{\infty} \sum_{q=0, \pm 1} Y_{\ell_p, m+q}(\vartheta_p, \varphi_p) (-1)^q u_q \langle \ell m, 1(-q) | \ell_p, m-q \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n\ell \rangle \right. \\
&\quad \left. + A_0 e^{i(\omega t + \phi^{(\text{cep})})} \sum_{\ell_p=0}^{\infty} \sum_{q=0, \pm 1} Y_{\ell_p, m+q}(\vartheta_p, \varphi_p) u_q \langle \ell m, 1q | \ell_p, m+q \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n\ell \rangle \right] + \frac{\mathbf{A}^2(\tau)}{2} \langle \varepsilon_p \ell m | n\ell m \rangle.
\end{aligned}$$

For a circularly-polarized beams, we can use either the real or complex-valued vector potential in the *quadratic* term since  $\mathbf{A}^2(t) = A_o^2 f^2(t) (\cos^2(\dots) + \lambda^2 \sin^2(\dots)) = A_o^2 f^2(t)$ .

In the **electric-dipole approximation**, moreover, the term in the last line vanishes if  $|\varepsilon_p \ell_p m_p\rangle$  and  $|n\ell m\rangle$  are eigenfunctions of the same

(atomic) Hamiltonian,  $\langle \varepsilon_p \ell_p m_p | n \ell m \rangle = \delta_{\ell_p, \ell} \delta_{m_p, m} (-i)^{\ell_p} \int dr P_{\varepsilon_p \ell_p}(r) P_{n \ell} = 0$  and, hence, the  $\mathbf{A}^2(t)$  term from the electron-field interaction operator  $\mathbb{H}^{(\text{laser})}$  does not contribute in this particular case. This applies, for instance, if a Coulomb or distorted central-field potential *and* the corresponding (free-electron) Coulomb-Volkov or, respectively, distorted-Volkov state are utilized together in the computations.

In the direct amplitude  $\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p})$  above, moreover, a simple factor  $\langle m'_s | m_s \rangle = \delta_{m'_s, m_s}$  occurs in addition to the given expressions if the spin-projection of the electron is taken into account in the representation of the initial state and the final (Volkov) wave of the outgoing electron; this simple factorization just shows that the electron-field interaction does not depend on the spin (projection) of the electron and, hence, leaves the spin-projection unaffected.

➤ **Partial-wave decomposition of the direct transition amplitude  $\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p})$  for a finite and circularly-polarized pulse:** For a finite pulse with envelope  $f^{(\text{env})} \equiv f^{(\text{envelope})}(t)$  and vector potential  $\mathbf{A} = A_o e^{-i(\omega t + \phi^{(\text{cep})})} \mathbf{u} f^{(\text{env})}(t)$ , the direct transition amplitudes reads as

$$\begin{aligned} \mathcal{T}^{(\text{SFA: direct})}(\mathbf{p}) &= -i \int_{-\infty}^{\infty} d\tau \left\langle \chi_{\mathbf{p}}^{(\text{Volkov})}(\tau; \mathbf{A}) \left| \mathbb{H}^{(\text{laser})}(\tau) \right| \Psi_i(\tau) \right\rangle \\ &= -i \sqrt{\frac{2}{\pi}} \mathcal{F}^{(\text{Volkov})}[-; \omega; f^{(\text{env})}; \mathbf{A}] \left( \sum_{\ell_p=0}^{\infty} \sum_{q=0, \pm 1} Y_{\ell_p, m_p}(\vartheta_p, \varphi_p) (-1)^q u_q \langle \ell m, 1(-q) | \ell_p, m - q \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n \ell \rangle \right) \\ &\quad -i \sqrt{\frac{2}{\pi}} \mathcal{F}^{(\text{Volkov})}[+; \omega; f^{(\text{env})}; \mathbf{A}] \left( \sum_{\ell_p=0}^{\infty} \sum_{q=0, \pm 1} Y_{\ell_p, m_p}(\vartheta_p, \varphi_p) u_q^* \langle \ell m, 1q | \ell_p, m + q \rangle \langle \varepsilon_p \ell_p \| \mathbf{p} \| n \ell \rangle \right) \\ &\quad -i \frac{1}{\sqrt{2} \pi} \mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{env})}; \mathbf{A}] \langle \varepsilon_p \ell m | n \ell m \rangle \\ \mathcal{F}^{(\text{Volkov})}[\pm; \omega; f^{(\text{env})}; \mathbf{A}] &= A_o e^{\pm i \phi^{(\text{cep})}} \int_{-\infty}^{\infty} d\tau f^{(\text{envelope})}(\tau) e^{-i(\varepsilon \mp \omega) \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} \\ \mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{env})}; \mathbf{A}] &= \int_{-\infty}^{\infty} d\tau \mathbf{A}^2(\tau) e^{-i \varepsilon \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} \end{aligned}$$

Here, we have introduced the two **pulse-envelope integrals**  $\mathcal{F}^{(\text{Volkov})}[\pm; \omega; f^{(\text{env})}; \mathbf{A}]$  and  $\mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{env})}; \mathbf{A}]$  in order to separate the contribution of the time-dependent laser pulse with its frequency, envelope, carrier-envelope phase and polarization from the (effective)



electron-field interaction to the transition amplitudes. These pulse-envelope integrals refer to standard integrals as they frequently appear in SFA computations. For a time-harmonic pulse of infinite duration  $f^{(\text{envelope})}(t) = 1$ , these pulse-shape integrals can be evaluated analytically, especially for circularly-polarized laser pulses. For other pulses, these integrals are often solved numerically, while the Volkov phase  $S^{(\text{Volkov})}(t; \mathbf{A})$  may still be evaluated analytically.

- **Partial-wave decomposition of the direct transition amplitude  $\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p})$  for a finite and circularly-polarized pulse in the coupled basis:** For a finite pulse with envelope  $f^{(\text{env})} \equiv f^{(\text{envelope})}(t)$  and vector potential  $\mathbf{A} = A_o e^{-i(\omega t + \phi^{(\text{cep})})} \mathbf{u} f^{(\text{env})}(t)$ , the direct transition amplitudes reads for states of well-defined total angular momentum  $j, m$  as

$$\begin{aligned} \mathcal{T}^{(\text{SFA: direct})}(\mathbf{p}) &= -i \int_{-\infty}^{\infty} d\tau \left\langle \chi_{\mathbf{p}}^{(\text{Volkov})}(\tau; \mathbf{A}), m'_s \left| \mathbb{H}^{(\text{laser})}(\tau) \right| n\ell jm \right\rangle \\ &= \dots \end{aligned}$$

- In JAC, the pulse-envelope integrals  $\mathcal{F}^{(\text{Volkov})}[\pm; \omega; f^{(\text{env})}; \mathbf{A}]$  and  $\mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{env})}; \mathbf{A}]$  are implemented for a number of frequently applied pulse envelopes; their use is simply controlled by a (singleton) variable `envelope::AbstractEnvelope` which may take the values `InfiniteEnvelope()`, `RectangularEnvelope()`, `SinSquaredEnvelope()`, `GaussianEnvelope()`.

## Envelopes and Volkov phases of common laser pulses:

- **Pulse envelope  $f^{(\text{env})}(t)$  and carrier-envelope phase  $\phi^{(\text{cep})}$ :** A laser pulse is commonly parametrized by its frequency, (real-valued) pulse envelope  $f^{(\text{env})}(t)$ , the carrier-envelope phase  $\phi^{(\text{cep})}$ , the (real-valued) amplitude  $A_o$  as well as the (complex-valued and unit) polarization vector  $\mathbf{u}$ ; these pulses are then formally applied in terms of the — complex or real-valued — vector potential. For circularly-polarized light, this vector potential can be written as

$$\mathbf{A}_c(t) = A_o f(t) \mathbf{u} e^{-i(\omega t + \phi^{(\text{cep})})}$$

$$\mathbf{A}(t) = \Re[\mathbf{A}_c(t)] = \frac{A_o}{\sqrt{2}} f(t) [\cos(\omega t + \phi^{(\text{cep})}) \mathbf{e}_x + \lambda \sin(\omega t + \phi^{(\text{cep})}) \mathbf{e}_y].$$

Similar formulas apply for linearly-polarized light with  $\lambda = 0$  and  $A_o \rightarrow \sqrt{2} A_o$ ; however, linearly-polarized light is less relevant if only the *direct* and no *rescattering* amplitudes are considered. Unpolarized light is usually not considered by the strong-field community but could be treated by taking a proper superposition of circularly-polarized light.

## 10. Collision- and field-induced atomic responses

- **Volkov phase for circularly-polarized pulses with  $\lambda = \pm 1$ :** For a (in)finite pulse with well-defined carrier-envelope phase and for photoelectrons with asymptotic momentum  $\mathbf{p} = (p, \vartheta_p, \varphi) = (\sqrt{2\varepsilon_p}, \vartheta_p, \varphi_p)$  in spherical coordinates the Volkov phase can be written as:

$$\begin{aligned}
 S^{(\text{Volkov})}(t; \mathbf{A}) &= \frac{1}{2} \int^t d\tau (\mathbf{p} + \mathbf{A}(\tau))^2 = \frac{1}{2} \int^t d\tau (\mathbf{p}^2 + 2\mathbf{A}(\tau) \cdot \mathbf{p} + \mathbf{A}^2(\tau)) \\
 &= \underbrace{\frac{p^2}{2}}_{\varepsilon_p} t + \frac{A_o}{\sqrt{2}} \int^t d\tau f(\tau) [p_x \cos(\omega\tau + \phi^{(\text{cep})}) + \lambda p_y \sin(\omega\tau + \phi^{(\text{cep})})] + \frac{A_o^2}{4} \int^t d\tau f^2(\tau) \\
 &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int^t d\tau f(\tau) \cos(\omega\tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int^t d\tau f^2(\tau).
 \end{aligned}$$

In the last line, use is made of the addition theorem of the cosine and the allowed values of the helicity  $\lambda = \pm 1$ .

- **Volkov phase for linearly-polarized pulses:** For a (in)finite pulse

$$S^{(\text{Volkov})}(t; \mathbf{A}) =$$

- **Pulse envelope (time) integrals:** From the decomposition of the *direct* SFA amplitude  $\mathcal{T}^{(\text{SFA: direct})}(\mathbf{p})$ , we find that the influence of the (time-dependent) laser pulse can be *factorized* from the contributions of the effective atom-field interaction and captured in terms of the (so-called) pulse envelope (time) integrals

$$\mathcal{F}^{(\text{Volkov})}[\pm; \omega; f^{(\text{env})}; \mathbf{A}] = A_o e^{\pm i \phi^{(\text{cep})}} \int_{-\infty}^{\infty} d\tau f^{(\text{envelope})}(\tau) e^{-i(\varepsilon \mp \omega)\tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})}$$

$$\mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{env})}; \mathbf{A}] = \int_{-\infty}^{\infty} d\tau \mathbf{A}^2(\tau) e^{-i\varepsilon_i \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})}$$

### Infinite pulse (continuous beam):

- **Pulse envelope:**  $f^{(\text{env})} \equiv 1$

➤ **Volkov phase for a circularly-polarized pulse:** From the general expression above, the Volkov phase simplifies to:

$$S^{(\text{Volkov})}(t; \mathbf{A}) = \varepsilon_p t + \underbrace{\frac{A_o p \sin \vartheta_p}{\sqrt{2}\omega}}_a \sin(\omega t + \phi^{(\text{cep})} - \lambda \varphi_p) + \underbrace{\frac{A_o^2}{4}}_{U_p} t$$

$$e^{i S^{(\text{Volkov})}(t; \mathbf{A})} = e^{i(\varepsilon_p + U_p)t} e^{i a \sin(\omega t + \phi^{(\text{cep})} - \lambda \varphi_p)} = e^{i(\varepsilon_p + U_p)t} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s \omega t} e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)},$$

where  $U_p = A_o^2/4$  is the **ponderomotive energy, i.e. the cycle-averaged kinetic energy of a classical electron moving in the oscillating electric field of the laser pulse**. Moreover, the constant  $a$  is just used as short-hand notation in the expressions below.

➤ **Pulse envelope (time) integrals for a circularly-polarized pulse:** These integrals can be simplified with the identity  $\int dx e^{i x y} = 2\pi \delta(y)$  to

$$\begin{aligned} \mathcal{F}^{(\text{Volkov})}[\pm; \omega; f^{(\text{infinite})}; \mathbf{A}] &= A_o e^{\pm i \phi^{(\text{cep})}} \int_{-\infty}^{\infty} d\tau e^{-i(\varepsilon_i \mp \omega)\tau + i S^{(\text{Volkov})}(\tau)} \\ &= A_o e^{\pm i \phi^{(\text{cep})}} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \int_{-\infty}^{\infty} d\tau e^{i[(s \pm 1)\omega + \varepsilon_p - \varepsilon_i + U_p]\tau} \\ &= 2\pi A_o e^{\pm i \phi^{(\text{cep})}} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \delta((s \pm 1)\omega + \varepsilon_p - \varepsilon_i + U_p) \\ \mathcal{F}^{(\text{quad, Volkov})}[f^{(\text{infinite})}; \mathbf{A}] &= \int_{-\infty}^{\infty} d\tau \mathbf{A}^2(\tau) e^{-i \varepsilon_i \tau + i S^{(\text{Volkov})}(\tau)} = \frac{A_o^2}{2} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \int_{-\infty}^{\infty} d\tau e^{i[s\omega + \varepsilon_p - \varepsilon_i + U_p]\tau} \\ &= 4\pi U_p \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \delta(s\omega + \varepsilon_p - \varepsilon_i + U_p) \end{aligned}$$

### Rectangular pulse:

➤ **Pulse envelope:** For a pulse of  $n_p$  optical cycles (integer), the pulse envelope and duration are given by

$$f(t) = \begin{cases} 1 & 0 \leq t \leq T_p, \\ 0 & \text{otherwise} \end{cases}, \quad T_p = n_p \frac{2\pi}{\omega}.$$

➤ **Volkov phase for a circularly-polarized pulse:** For such a rectangular pulse envelope, the Volkov phase needs to be evaluated piecewise in *three* separate regions

$$S^{(\text{Volkov})}(t \leq 0) = \varepsilon_p t$$

$$\begin{aligned} S^{(\text{Volkov})}(0 \leq t \leq T_p; \mathbf{A}) &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int_0^t d\tau \cos(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int_0^t d\tau \\ &= \varepsilon_p t + \underbrace{\frac{A_o p \sin \vartheta_p}{\sqrt{2} \omega}}_a [\sin(\omega t + \phi^{(\text{cep})} - \lambda \varphi_p) - \sin(\phi^{(\text{cep})} - \lambda \varphi_p)] + U_p t \end{aligned}$$

$$\begin{aligned} S^{(\text{Volkov})}(t > T_p; \mathbf{A}) &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int_0^{T_p} d\tau \cos(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int_0^{T_p} d\tau \\ &= \varepsilon_p t + \underbrace{\frac{A_o p \sin \vartheta_p}{\sqrt{2} \omega}}_a [\sin(\omega T_p + \phi^{(\text{cep})} - \lambda \varphi_p) - \sin(\phi^{(\text{cep})} - \lambda \varphi_p)] + U_p T_p \end{aligned}$$

➤ **Pulse envelope (time) integrals for a circularly-polarized pulse:** For this Volkov phase, the pulse-envelope integrals can be solved analytically

with  $a = \frac{A_o p \sin \vartheta_p}{\sqrt{2} \omega}$

$$\begin{aligned}
& \mathcal{F}^{(\text{Volkov})} [\pm; \omega; f^{(\text{rectangular})}; \mathbf{A}] \\
&= A_o e^{\pm i \phi^{(\text{cep})}} \int_{-\infty}^{\infty} d\tau f^{(\text{rectangular})}(\tau) e^{-i(\varepsilon_i \mp \omega) \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} \\
&= A_o e^{\pm i \phi^{(\text{cep})}} \int_0^{T_p} d\tau e^{-i(\varepsilon_i \mp \omega) \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} = A_o e^{\pm i \phi^{(\text{cep})}} e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \int_0^{T_p} d\tau e^{-i(\varepsilon_i \mp \omega - \varepsilon_p - U_p) \tau + i a \sin(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p)} \\
&= e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \int_0^{T_p} d\tau e^{i [(s \pm 1) \omega + \varepsilon_p - \varepsilon_i + U_p] \tau} \\
&= -i e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \sum_{s=-\infty}^{\infty} \frac{J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)}}{(s \pm 1) \omega + \varepsilon_p - \varepsilon_i + U_p} \left( e^{i [(s \pm 1) \omega + \varepsilon_p - \varepsilon_i + U_p] T_p} - 1 \right) \\
& \mathcal{F}^{(\text{quad}, \text{Volkov})} [f^{(\text{rectangular})}; \mathbf{A}] \\
&= \int_{-\infty}^{\infty} d\tau \mathbf{A}^2(\tau) e^{-i \varepsilon_i \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} = \frac{A_o^2}{2} \int_0^{T_p} d\tau e^{-i \varepsilon_i \tau + i S^{(\text{Volkov})}(\tau; \mathbf{A})} \\
&= \frac{A_o^2}{2} e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \int_0^{T_p} d\tau e^{-i(\varepsilon_i - \varepsilon_p - U_p) \tau + i a \sin(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p)} \\
&= \frac{A_o^2}{2} e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \sum_{s=-\infty}^{\infty} J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)} \int_0^{T_p} d\tau e^{i (s \omega + \varepsilon_p - \varepsilon_i + U_p) \tau} \\
&= 2 U_p e^{-i a \sin(\phi^{(\text{cep})} - \lambda \varphi_p)} \sum_{s=-\infty}^{\infty} \frac{J_s(a) e^{i s (\phi^{(\text{cep})} - \lambda \varphi_p)}}{s \omega + \varepsilon_p - \varepsilon_i + U_p} \left( e^{i (s \omega + \varepsilon_p - \varepsilon_i + U_p) T_p} - 1 \right)
\end{aligned}$$

sin<sup>2</sup> pulse:

➤ **Pulse envelope:** For a pulse of  $n_p$  optical cycles (integer), the pulse envelope and duration are given by

$$f(t) = \begin{cases} \sin^2\left(\frac{\omega}{2n_p} t\right) & 0 \leq t \leq T_p, \\ 0 & \text{otherwise} \end{cases}, \quad T_p = n_p \frac{2\pi}{\omega}.$$

➤ **Volkov phase for a circularly-polarized pulse:** For such a sin<sup>2</sup> pulse envelope, the Volkov phase need again to be evaluated piecewise in three separate regions

$$S^{(\text{Volkov})}(t \leq 0) = \varepsilon_p t$$

$$\begin{aligned} S^{(\text{Volkov})}(0 \leq t \leq T_p; \mathbf{A}) &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int_0^t d\tau \sin^2\left(\frac{\omega}{2n_p} \tau\right) \cos(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int_0^t d\tau \sin^4\left(\frac{\omega}{2n_p} \tau\right) \\ &= \varepsilon_p t + \frac{3}{8} U_p t - \frac{U_p n_p}{2\omega} \sin\left(\frac{\omega}{n_p} t\right) + \frac{U_p n_p}{16\omega} \sin\left(\frac{2\omega}{n_p} t\right) \\ &\quad + a \sum_{k=-1}^1 \frac{c_k}{1 + \frac{k}{n_p}} \left[ \sin\left(\omega \left(1 + \frac{k}{n_p}\right) t + \phi^{(\text{cep})} - \lambda \varphi_p\right) - \sin(\phi^{(\text{cep})} - \lambda \varphi_p) \right] \end{aligned}$$

$$\begin{aligned} S^{(\text{Volkov})}(t > T_p; \mathbf{A}) &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int_0^{T_p} d\tau \sin^2\left(\frac{\omega}{2n_p} \tau\right) \cos(\omega \tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int_0^{T_p} d\tau \sin^4\left(\frac{\omega}{2n_p} \tau\right) \\ &= \varepsilon_p t + \frac{3}{8} U_p T_p - \frac{U_p n_p}{2\omega} \sin\left(\frac{\omega}{n_p} T_p\right) + \frac{U_p n_p}{16\omega} \sin\left(\frac{2\omega}{n_p} T_p\right) \\ &\quad + a \sum_{k=-1}^1 \frac{c_k}{1 + \frac{k}{n_p}} \left[ \sin\left(\omega \left(1 + \frac{k}{n_p}\right) T_p + \phi^{(\text{cep})} - \lambda \varphi_p\right) - \sin(\phi^{(\text{cep})} - \lambda \varphi_p) \right]. \end{aligned}$$

- **Pulse envelope (time) integrals for a circularly-polarized pulse:** These integrals could be solved analytically by applying the Jacobi-Anger expansion to all factors of the form  $\exp(-iz \sin \theta)$ . This leads to five infinite summations and is therefore not so practical for numerical computations since each summation should include about 5 to 10 terms for reasonable convergence. Instead, the integrals can be simpler solved numerically by using the analytical expression for the Volkov phase from above.

### Gaussian pulse:

- **Pulse envelope:** For a Gaussian envelope with FWHM  $T_p$ , which is taken also as pulse duration, the pulse envelope is given by

$$f(t) = \exp \left( -4 \ln(2) \left( \frac{t}{T_p} \right)^2 \right).$$

- **Volkov phase for a circularly-polarized pulse:** With the error function  $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$  and the abbreviation  $\xi = \phi^{(\text{cep})} - \lambda \varphi_p$ , the Volkov phase of a Gaussian envelope can be written as

$$\begin{aligned} S^{(\text{Volkov})}(t; \mathbf{A}) &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int^t d\tau f(\tau) \cos(\omega\tau + \phi^{(\text{cep})} - \lambda \varphi_p) + \frac{A_o^2}{4} \int^t d\tau f^2(\tau) \\ &= \varepsilon_p t + \frac{A_o p \sin \vartheta_p}{\sqrt{2}} \int^t d\tau \exp \left( -4 \ln(2) \left( \frac{t}{T_p} \right)^2 \right) \cos(\omega\tau + \phi^{(\text{cep})} - \lambda \varphi_p) + U_p \int^t d\tau \exp \left( -8 \ln(2) \left( \frac{t}{T_p} \right)^2 \right) \\ &= \varepsilon_p t + U_p \sqrt{\frac{\pi}{\ln(4)}} \frac{T_p}{4} \text{erf} \left( 2\sqrt{\ln(4)} \frac{t}{T_p} \right) \\ &\quad + \frac{A_o p \sin \vartheta_p T_p}{\sqrt{2}} \sqrt{\frac{\pi}{\ln(2)}} e^{-\frac{\omega^2 T_p^2}{\ln(65536)}} \left[ e^{-i\xi} \text{erf} \left( \frac{i T_p^2 \omega + 8 \ln(2) t}{4 T_p \sqrt{\ln(2)}} \right) - e^{i\xi} \text{erf} \left( \frac{i T_p^2 \omega - 8 \ln(2) t}{4 T_p \sqrt{\ln(2)}} \right) \right] \end{aligned}$$

- **Pulse envelope (time) integrals for a circularly-polarized pulse:** As for a  $\sin^2$  pulse, the pulse-envelope integrals are better solved numerically by using the analytical expression for the Volkov phase from above. If the trigonometric and error functions are available, such a 1-dimensional integration should be quite easy.

### Vector potentials and fields in dipole approximation:

- **Electric field:** For a linearly-polarized laser field, the electric field is often taken as:

$$\mathbf{E}(t) = \mathbf{E}_o \cos(\omega t) \mathbf{e}_x, \quad \mathbf{A}(t) = -\frac{\mathbf{E}_o}{\omega} \sin(\omega t) \mathbf{e}_x.$$

- **Vector potential:**  $\mathbf{E}(t) = \frac{\partial \mathbf{E}(t)}{\partial t}.$

### Time-dependent dipole amplitudes:

- **Continuum orbital of free electrons with asymptotic momentum  $\mathbf{p}$ ,  $|\mathbf{p}\rangle = e^{-i\mathbf{p}\cdot\mathbf{r}}$ :** Free electrons are described by (continuum solutions of the) Hamiltonian

$$H_o |\mathbf{p}\rangle = \frac{p^2}{2} |\mathbf{p}\rangle.$$

- **Time-dependent dipole amplitude:** If the electron is initially in the bound-state  $|\phi_o\rangle$  of the atom, the time-dependent dipole amplitude is given by

$$\mathbf{d}(\mathbf{p}) = \langle \mathbf{p} | \mathbf{r} | \phi_o \rangle.$$

- **Time-dependent dipole amplitude for non-relativistic hydrogenic 1s orbitals:** If the bound electron is initially in the 1s orbital, the dipole amplitude is given by

$$\mathbf{d}(\mathbf{p}) = -i 2^{7/2} \alpha^{5/4} \frac{\mathbf{p}}{\pi (p^2 + \alpha)^3}.$$



### Approximations to the Volkov phase:

- **Kinetic *versus* canonical momentum of a particle in an em field:** The (dressed) kinetic momentum  $\pi(\mathbf{p}, t) = \mathbf{p} + \mathbf{A}(\mathbf{r}, t)$  of a particle with charge  $e$  differs from its canonical momentum  $\mathbf{p}$  by the (coupling of the local) vector potential and, hence, the dressing of the em field. Often, one considers the motion of electrons in either a linearly- or circularly-polarized field.
- **Volkov phase:** The classically accumulated action of the electron, if it propagates in a laser field, reflects the dressing of the particle by the field; in the SFA, this action appears in the (so-called) Volkov phase

$$S(\mathbf{p}, t, t') = \int_{t'}^t dt'' \frac{[\mathbf{p} + \mathbf{A}(\mathbf{r}, t)]^2}{2} + I_p$$

- **Saddle point of the time-dependent momentum:** The saddle point fulfills the equation  $\nabla_{\mathbf{p}} S(\mathbf{p}, t, t') = 0$

$$\mathbf{p}^{(\text{saddlepoint})} = -\frac{1}{t - t'} \int_{t'}^t d\tau \mathbf{A}(\tau).$$

- **Saddle-point approximation to the Volkov phase:** This approximation leads for the  $q$ -th harmonic to three equations for the canonical momentum  $\mathbf{p}_s$  at the saddle point

$$\mathbf{p}_s(t, t') = \frac{1}{t - t'} \int_{t'}^t dt'' \mathbf{A}(t''), \quad \frac{[\mathbf{p} + \mathbf{A}(t')]^2}{2} = -I_p, \quad \frac{[\mathbf{p} + \mathbf{A}(t)]^2}{2} = q\omega - I_p.$$

The last two relations simply reflect the **conservation of energy**, namely, for the *release* of the electron into the continuum at the *ionization* time  $t'$  and for its recombination with the parent ion at the (*recombination*) time  $t$ . Both of these times are generally complex because  $I_p > 0$ .

### Time-dependent dipole moment $\mathbf{D}(t)$ :

➤ Time-dependent dipole moment:

$$\mathbf{D}(t) = \int_{-\infty}^t dt' \int d^3\mathbf{p} \, \mathbf{d}^*(\mathbf{p} + \mathbf{A}(t)) \mathbf{E}(t') \mathbf{d}(\mathbf{p} + \mathbf{A}(t')) e^{-iS(\mathbf{p},t,t')} + \text{c.c.}$$

➤ Time-dependent dipole moment in saddle-point approximation: In the saddle-point approximation, the dipole moment with  $\mathbf{p}^{(\text{sp})} \equiv \mathbf{p}^{(\text{saddle-point})}$  to:

$$\mathbf{D}^{(\text{saddle-point approx})}(t) = \int_{-\infty}^t dt' \left( \frac{2\pi i}{(t - t' - i\epsilon)} \right) \mathbf{d}^*(\mathbf{p}^{(\text{sp})} + \mathbf{A}(t)) \mathbf{E}(t') \mathbf{d}(\mathbf{p}^{(\text{sp})} + \mathbf{A}(t')) e^{-iS(\mathbf{p}^{(\text{sp})},t,t')} + \text{c.c.},$$

and where  $\epsilon$  is ...

### Frequency-dependent power spectrum $\mathbf{D}(q\omega)$ :

➤ Frequency-dependent dipole moment in saddle-point approximation: For the  $q$ -th order of the high-harmonic, the dipole moment in saddle-point approximation is given with  $\mathbf{p}^{(\text{sp})} \equiv \mathbf{p}^{(\text{saddle-point})}$  by

$$\mathbf{D}^{(\text{saddle-point approx})}(q\omega) = i \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' \left( \frac{2\pi i}{(t - t' - i\epsilon)} \right) \mathbf{d}^*(\mathbf{p}^{(\text{sp})} + \mathbf{A}(t)) \mathbf{E}(t') \mathbf{d}(\mathbf{p}^{(\text{sp})} + \mathbf{A}(t')) e^{iq\omega t - iS(\mathbf{p}^{(\text{sp})},t,t')} + \text{c.c.}$$

➤ Frequency-dependent dipole moment in saddle-point approximation: In this approximation, the frequency-dependent dipole moment of the  $q$ -th harmonic can be expressed as a sum of products [*field*  $\times$  *dipole amplitude*], and which just need to be evaluated at the saddle points:

$$\mathbf{D}(q\omega) = i \sum_s \frac{2\pi}{\sqrt{\det(S'')}} \left( \frac{2\pi}{t_s - t'_s} \right) \mathbf{d}^*(\mathbf{p}_s + \mathbf{A}(t_s)) \mathbf{E}(t'_s) \mathbf{d}(\mathbf{p}_s + \mathbf{A}(t'_s)) \exp[-iS(\mathbf{p}_s, t_s, t'_s) + iq\omega t_s].$$

Here  $S'' = \frac{\partial^2 S(\mathbf{p}, t, t')}{\partial t \partial t'} \big|_{(\mathbf{p}_s, t_s, t'_s)}$  denotes the Hessian matrix of the action at the saddle point. The saddle-point approximation is closely related to the classically allowed trajectories of a free electron in a strong laser field.

- **Power spectrum of high harmonics,  $\mathbf{D}(q\omega)$ :** The (so-called) power spectrum of the emitted harmonic radiation is obtained from the Fourier transform of the dipole acceleration  $\frac{\partial^2 \mathbf{D}(t)}{\partial t^2}$ .

### Semi-classical trajectories of electrons in Lewenstein's model:

- **Harmonics of well-defined order:** In practice, only a very small fraction of the released electrons find their way back to the parent ion and will recombine eventually. Obviously, the harmonic order is determined by the (dressed) kinetic momentum  $\mathbf{p} + \mathbf{A}(t)$  at the recombination time.
- **Long and short trajectories:** There are exactly two trajectories per half cycle which return the electron, and with the same energy, to the parent ion. Both trajectories will therefore contribute to the same harmonic order, though they are often referred to as *long and short trajectories* because of the different travel time of the electron along these trajectories.
- **Dipole phase of the short and long trajectories:** For the harmonics at the plateau, the dipole phases of the short and long trajectories clearly differ from each other because of the different travel times along these orbits, while the phases approach each other towards the cut-off [cf. Paufler *et al.* (2019), Fig. 1]. Moreover, the dipole phase generally depends linearly on the intensity of the incident beam.

### 10.8.b. Rotating-frame approximation [background]

#### Rotating-frame:

- **Rotating-frame:** The time-dependent Schrödinger equation of an (atomic) electron in a short-range potential and an external circularly-polarized electro-magnetic field can be transformed into a time-independent equation, if we make use of coordinates that rotate with the frequency of the external field around its propagation direction ( $z$ -axis). In this rotating framework, the Hamiltonian in atomic units reads as

$$\mathbb{H} = -\frac{\Delta}{2} + V(\mathbf{r}) - \omega l_z + \mathcal{E}x,$$

where  $V(\mathbf{r})$  is a short-range potential,  $l_z$  the projection of the orbital angular momentum and  $\omega$  the frequency of the laser field. The rotating-frame coordinates can be utilized to find an equation for the (complex-value) energy of an electron in a circularly-polarized field. Moreover, such a frame leads to the (so-called) *rotation-frame approximation*, in which the slow-varying and fast-oscillating terms in the

Schrödinger equation are separated from each other, and where the fast-oscillating terms are just treated *effectively* in some time-averaged mode.

### 10.8.c. Kramers-Henneberger frame [background]

#### Kramers-Henneberger framework:

- **Kramers-Henneberger framework:** In this framework, the **electron in a (strong external) oscillating field remains at rest**, i.e. the coordinates follow the motion of the electron. The transformation of the wave function and Schrödinger equation from the laboratory to the Kramers-Henneberger coordinates then requires a time-dependent unitary transformation which is given for a monochromatic and linearly-polarized field by

$$\psi^{(\text{KH})} = \exp\left(i \frac{\mathbf{r} \cdot \boldsymbol{\mathcal{E}}}{\omega} \sin \omega t\right) \psi^{(\text{Schroedinger})}, \quad i \frac{\partial \psi^{(\text{KH})}}{\partial t} = -\frac{\Delta}{2} \psi^{(\text{KH})} + V\left(\mathbf{r} + \frac{\boldsymbol{\mathcal{E}}}{\omega^2} \cos \omega t\right) \psi^{(\text{Schroedinger})}.$$

While this transformation is formally exact, it is useful especially in the **high-frequency limit**, in which the electron-laser interaction is much larger than the (unperturbed) binding energy of the electron. In this limit, the time-dependent Schrödinger equation can be reduced to a time-independent equation with a potential

$$V^{(\text{KH})}(\mathbf{r}) = \frac{1}{2\pi} \int_0^{2\pi} d(\omega t) V\left(\mathbf{r} + \frac{\boldsymbol{\mathcal{E}}}{\omega^2} \cos \omega t\right),$$

that is just the *zero-time* Fourier component of the original potential above. In this high-frequency limit, the (1D) electronic wave functions just describe **two probability clouds which are separated by  $2a = \mathcal{E}/\omega$** , i.e. **twice the amplitude of the oscillating electron is the field**. This separation of the probability density is known also as *dichotomy*.

### 10.8.d. Guo-Aberg-Crasemann (GAC) theory [background]

#### Differential GAC ionization cross sections:

- Lowest-order perturbation theory typically fails to explain the the shape of the envelope of the individual ATI photoelectron peaks. Perturbation theory also fails to predict the dependence of the strength of the ATI peaks on the intensity of the laser light, if the laser intensity exceeds  $1 \text{ TW cm}^{-1}$ .
- **Differential transition-rate formula:** Within the GAC theory, the lowest-order transition matrix element can be utilized together with the (integer) constraint  $z = m - n$ , in order to obtain a **differential transition-rate formula for the ionization of electron that have absorbed  $q = lm$  photons** (Guo *et al.*, 1989)

$$\frac{d\omega}{d\Omega} = \frac{(2m^3\omega^5)^{1/2}}{4\pi^2} |\Phi_i(\mathbf{p} - q\mathbf{k})|^2 q^2 \left(q - \frac{E_b}{\omega}\right)^{1/2} |\mathcal{J}_{q+z}|^2 |\mathcal{J}_z|^2,$$

where  $\Phi_i(\mathbf{p} - q\mathbf{k})$  is the Fourier transform of the initial-state wave function with binding energy  $E_b$ . The angular and polarization dependences of this differential transition-rate formula are determined by  $\mathbf{p} - q\mathbf{k}$  in  $\Phi_i$  as well as by the arguments of the two **elliptically polarized Bessel functions  $\mathcal{J}_t$** .

- In the nonrelativistic limit and for a large photon-number, the final state can be reduced to a single but modified Volkov state, if the ponderomotive energy is an integer multiple of the photon energy. Therefore, the scattering amplitude strictly exists only in the integer case, where it becomes a product of the original KFR amplitude and the overlap between the final plane-wave state and the Volkov state, and vanishes otherwise.

### 10.8.e. Twisted light beams [background]

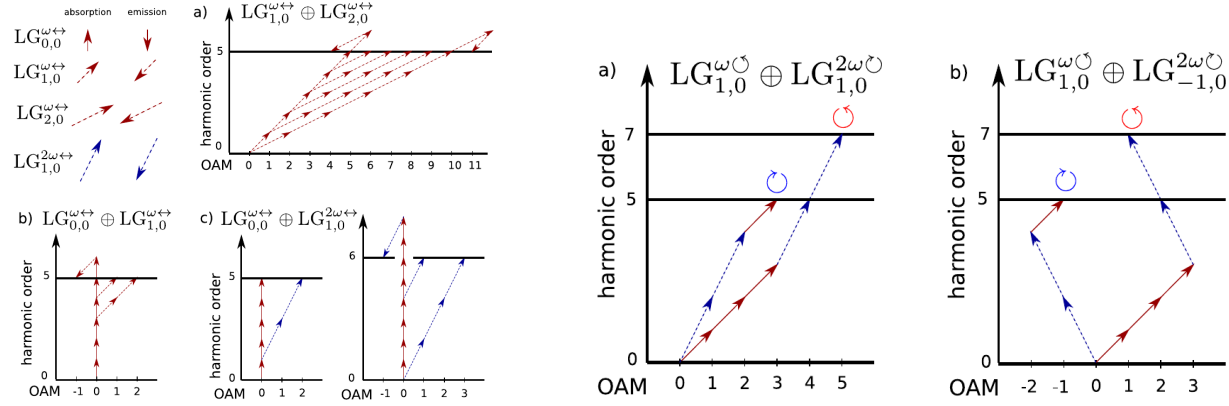


Figure 10.4.: **Photon-coupling diagrams in HHG.** (Left) Three different scenarios of HHG with superpositions of two linearly-polarized (Laguerre-) Gaussian beams are shown and can be utilized in order to control and manipulate the OAM of the generated harmonics. Different arrows from the left-upper corner here represent the absorption and emission of photons from different beams. (a) Superposition of two linearly-polarized LG beams with the same photon energy but different OAM. This scheme gives rise to **multiple couplings for the generation of each harmonic order and, hence, each harmonic may carry different values of OAM.** (b) Non-collinear superposition of a strong Gaussian beam with a weaker LG beam gives rise to the spatially separated xuv-vortices with a well defined OAM. (c) Non-collinear superposition of a strong Gaussian with its second harmonic. Similar to (b), we get spatially separated xuv-vortices, each with well-defined that carry a well-defined OAM as well. (Right) Photon-coupling diagrams of HHG with with bicircular twisted beams. (a) Superposition of two LG beams with the same OAM. For each harmonic order, **there is only one possible diagram which gives rise to xuv vortices with well-defined OAM.** Each of these harmonic is circularly-polarized. (b) Superpositions of two LG beams with opposite OAM. Since the number of photons absorbed from the  $\omega$ -beam always differs by one from the number of photons absorbed from the  $2\omega$  beam, the modulus of the OAM of each xuv vortex is  $|\ell| = 1$ .

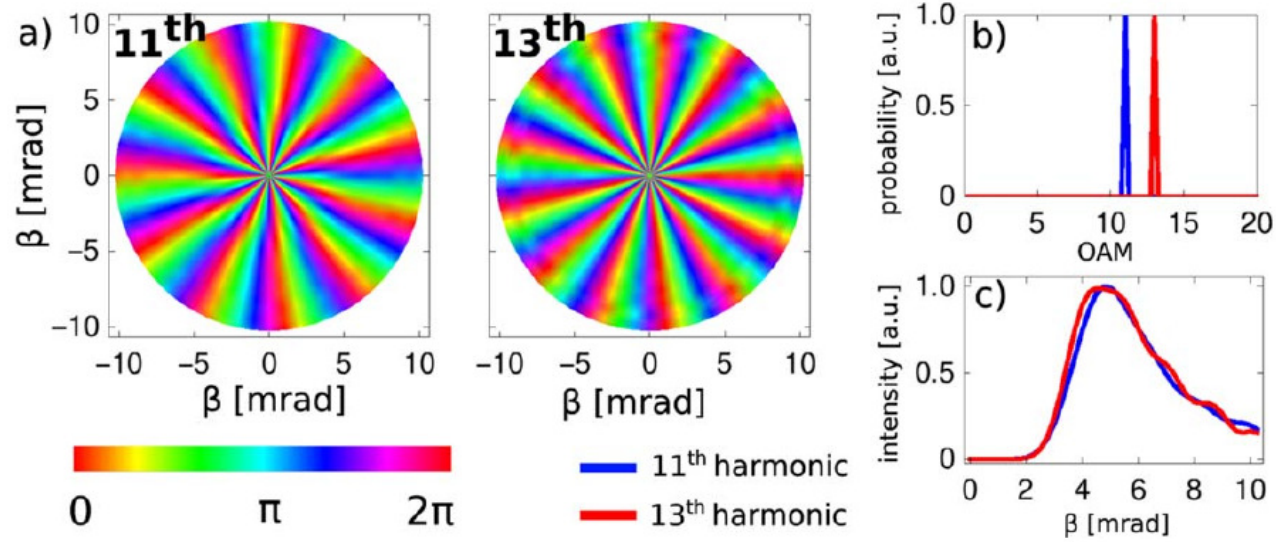


Figure 10.5.: Phase profile and spectrum of HH, generated with a linearly-polarized LG beam: (a) Phase profiles of the 11th and 13th harmonic at the detector, and where the OAM (number of phase changes of  $\pi$ ) is equal to the harmonic order. (b) OAM of the 11th (blue) and 13th (red) harmonic as obtained by a Fourier transform along the azimuthal coordinate. (c) Intensity distributions of the 11th (blue) and 13th (red) harmonic in the far-field. From Paufler *et al.* (2019, Fig. 3).

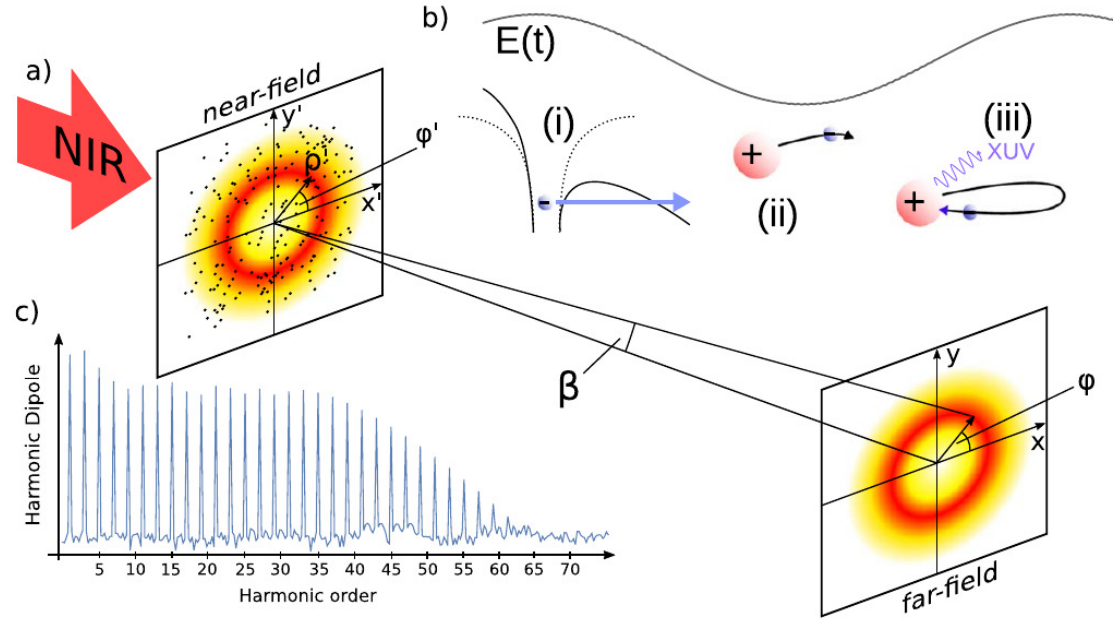


Figure 10.6.: HHG in the near- and far-field. (a) Superposition of the far-field due to locally generated HH in the near field and as described by the Fraunhofer diffraction formula. (b) Illustration of the simple man's three step model: (i) release of the electron by tunnel ionization, (ii) propagation and acceleration of the *free* electron in the strong laser field and (iii) recombination of the electron with the parent ion under the emission of a high-energetic photon at multiple laser frequency. (c) Typical high-harmonic spectrum as generated with a linearly-polarized laser field, and where only odd harmonic orders contribute to the spectrum. From Paufler *et al.* (2019, Fig. 2).



# 11. Time-evolution of many-electron atomic state functions and density matrices

## 11.1. Time-dependent approximations of many-electron states

### Time-dependent methods:

- **Time-dependent theory:** The response of multi-electron atoms to strong laser fields with intensity  $\sim 10^{14}$  W/cm<sup>2</sup> can be typically described only by explicitly time-dependent approaches. For short and intense light pulses, for example, the ionization rate is known to change rapidly during the pulse, and this makes the use of just a monochromatic field incorrect in the theoretical description. For laser intensities  $\gtrsim 10^{16}$  W/cm<sup>2</sup>, moreover, the electric field becomes even stronger than the inter-atomic fields, leading to a breakdown of perturbation theory. Then, the time-dependent Schrödinger equation need to be integrated explicitly in order to properly deal with the shape and intensity of the light pulses, although the *limits* of perturbation theory are not yet well understood in this time and intensity domain.
- **Light sources for studying electron dynamics in atoms:** New light sources and technologies facilitate nowadays various experiments with intense attosecond extreme-ultraviolet (XUV) pulses in order to resolve in time the ejection of electrons from the atomic target.
- **New coherent light sources:** Recently developed light sources include attosecond lasers, high-order-harmonic generation (HHG) sources or free-electron lasers. These novel light will pave the way for studying the interaction of matter with intense femtosecond or even sub-femtosecond radiation pulses in the visible and XUV regime.
- **New light sources:** Recent advances in the generation of ultra-short and extreme ultraviolet (XUV) pulses at free-electron lasers (FEL), attosecond high harmonic pulses or few-cycle optical laser pulses have pave the way for imaging and controlling the electronic and nuclear dynamics in molecules, and with many exciting applications in physics, chemistry and elsewhere. In particular, table-top HHG sources of femtosecond and sub-femtosecond XUV pulses enable one to observe the dynamics at the attosecond time scale.

## 11. Time-evolution of many-electron atomic state functions and density matrices

- **X-ray free-electron lasers (XFEL):** Various XFEL's worldwide have recently extended the range of nonlinear processes due to intense ionizing radiation ( $> 10^{15}$  PW/cm<sup>2</sup>).
- **FEL versus synchrotron sources:** Although both are based on accelerator technology, FEL (may) emit *coherently* because of its multi-electron coherence, while synchrotron radiation is always emitted incoherently due to its independently radiating electrons. Therefore, FEL are able to combine the intensity and coherence of an (optical) laser with the broad spectral coverage of synchrotrons.
- **Third-generation synchrotrons:** Modern synchrotron facilities support ionization studies of atoms and molecules across a wide energy range, using quite stationary conditions, and with much higher resolution than ever before. Moreover, these spectroscopic studies are often combined with synchronized laser pulses.
- The development of sub-femtosecond radiation pulses enables one to explore the electron dynamics in atoms *or* the (combined) electron and nuclei dynamics in molecules with a high degree of temporal and spatial resolution.
- **Femto-slicing:** Ultra-short x-ray pulses are nowadays an indispensable tool for visualizing ultra-fast processes in molecules, liquids and solids. Such ultra-short pulses can be generated by femto-slicing, i.e. if the relativistic electrons in an undulator are accompanied by some ultra-short and co-propagating laser pulse. This technique enforces x-ray pulses with just 100 fs duration and at a time-scale that is comparable to atomic ordering phenomena in solids.
- **Femto-slicing:** This technique was first proposed by Zholents and Zolotarev in 1996 in order to generate ultra-short x-ray pulses at synchrotron facilities, and it was later demonstrated experimentally at the Advanced Light Source (ALS) in Berkeley. A first undulator-baser femto-slicing source was completed at BESSY II in Berlin in 2004. This technique has been further advanced during recent years in high-flux beamline and by using novel Zone Plate Monochromator (ZPM).
- **Short-pulse, short-wavelength radiation:** There are several approaches known for achieving ultra-short and high-energetic photon pulses:
  - The conversion of fs laser pulses to higher photon energy by (i) HHG, (ii) by plasma generation with intense laser pulses, and which then emits x-rays, or (iii) by relativistic Thomson scattering.
  - The time structure of electron bunches can be changed in a storage ring, for instance, if the (so-called) momentum-compaction factor is changed or if the laser-induced energy modulation is modified (**femto-slicing**), or by further compression of electron bunches in linear accelerators and especially at free-electron laser (FEL). In this regime, however, only laser-based techniques (femto-slicing and seeded FELs) facilitate a natural synchronization between the laser and the x-ray pulses for pump-probe experiments.
- **Need for new time-dependent theoretical models:** To support modern experiments with intense atto-second pulses, new time-dependent models and methods need to be developed beyond the current standard schemes, such as the single-active-electron approximation.

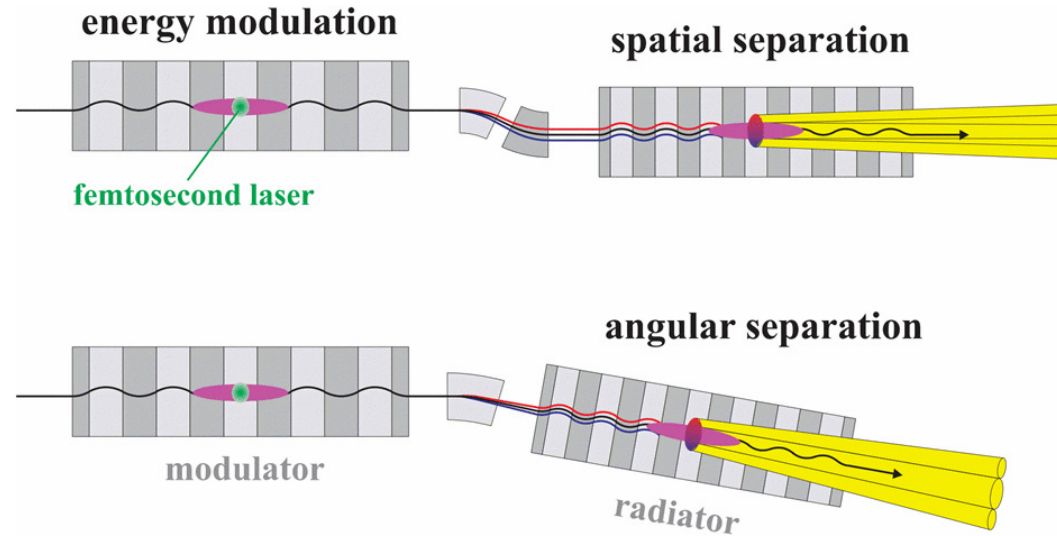


Figure 11.1.: Generation of short x-ray pulses by laser-induced energy modulation of electrons and subsequent spatial (top) and angular (bottom) separation.  
From Ref. DOI: 10.1109/PAC.2005.1590500.

- **Time-dependent Hartree-Fock (TDHF) method:** In this method, the time evolution of the electronic orbitals is accounted for during the interaction with an external field or collision partner by following the (time-dependent) mean field of the total electron density in the given potential. This method therefore properly treats the nuclear interaction and the *mean field* of the electrons but averages over all electronic correlations. In practice, such a mean-field approximation significantly reduces the dimension of the  $N$ -particle quantum system from  $3N$  spatial coordinates to just three coordinates for the *mean* density. **The TDHF method is an initial value problem that typically starts from the wave function of the static ground state of the system.**
- **Time-dependent RAS method with space partition:** In this method, the wave functions are expanded in terms of Slater determinants with explicitly time-dependent CI coefficients. The Slater determinants are usually based on two type of time-independent orbitals: (i) Orbitals that are just defined in an inner region close to the atomic nucleus and (ii) orbitals in an outer region with zero-contribution to the inner region (Miyagi and Madsen, 2017).
- **Space partition methods:** A partitioning of space has been widely utilized for describing atom-electron collisions since the very first advent of the R-matrix theory. In all these models, a configuration-interaction (CI) expansion of the many-electron wave function is typically made in some inner region in order to deal with electronic correlations. In the outer region, in contrast, the electrons are supposed to move

## 11. Time-evolution of many-electron atomic state functions and density matrices

independently of each other in just a long-range effective potential, and without that further exchange and correlation contributions are taken into account. This piecewise definition of the wave function then requires to make sure that it remains continuously differentiable across the surface between the two regions.

- **Time-dependent MCHF (TD-MCHF) method:** This method is presently seen as the most accurate and widely used technique in order to describe the many-electron dynamics in explicitly time-dependent potentials, such as the laser-induced dynamics of  $N$ -electron atoms. When compared to the space-partition methods, the TD-MCHF method has the great advantage that, for a sufficiently large (radial) domain of the orbitals, all single- and multi-electron interactions (continua) can be taken into account, at least in principle.
- **Time-evolution with separable (atomic) potentials (TESP):** Galstyan *et al.* (2018) describe a new and **computationally inexpensive method for studying the interaction of complex atoms or molecules with intense ultrashort laser pulses within the single active electron approximation**. With this method, they have analyzed the photoionization of water molecules from the highest occupied molecular orbital and calculated, in particular, the ionisation yield for different orientations of the molecule with regard to the polarization of the incident pulse.
- **TESP method:** This method is an approximation since the exact solution would require to incorporate an infinite number of separable potentials in the representation of the kernel. This method is therefore especially useful for pulses with high frequency where only the lowest (few) levels play a crucial role for the ionization of the system.
- **Central idea of the TESP method:** The main idea of this method is to work in **momentum space and to replace the kernel of the Coulomb potential by a sum of  $N$  symmetric separable potentials which each support just a single bound state of the system**. The use of separable potentials enables one to reduce the  $N$ -dimensional time-dependent Schrödinger equation (TDSE) to a system of  $N$  one-dimensional Volterra integral equations which only depend on time. This method is known also by Separable Potentials for Atoms and Molecules (SPAM).
- **Weaknesses of the TESP method:** The separable potential is not necessarily unique and does usually not represent the correct asymptotic behaviour of the potential. Moreover, the method is not gauge invariant and the question about proper gauges will need to be explored in further detail.
- **Time-resolved electron dynamics:** Various experimental techniques have been developed in order to perform time-resolved studies of the electron dynamics in atoms and molecules, such as **re-collision imaging, attosecond streaking or time-resolved photoionization studies**. Until the present, however, most of these observations have been simulated only in effective single-electron models, and with little care about the many-electron dynamics in realistic systems. For an accurate interpretation of such experiments, however, either the time-dependent (many-electron) Schrödinger equation need to be solved or, at least, many-electron correlation contributions has to be taken into account.

Moreover, since perturbation theory is not appropriate in the strong-field regime, either a direct numerical integration of the TDSE or further advances of the strong-field theory are required.

### Time-evolution of ASF:

- A reliable description of the time-dependent (TD) many-electron dynamics has attracted recent interest in order to theoretically support a real-time analysis and control of the ultrafast electronic and nuclear dynamics of atoms and molecules in intense laser pulses.
- A computational and conceptual simple approach to the many-electron dynamics is the TD configuration-interaction singles (TD-CIS) method in which only singly excited configurations, relative to the Hartree-Fock ground state, are taken into account in the configuration interaction expansion.
- Miyagi and Madsen (2013) make use of the TD-CIS method by performing an optimization of the orbitals as well as the expansion coefficients at each time step in the evolution. This separate optimization makes it possible to construct a reasonable accurate wave function with just a relatively small number of electronic configurations. For the optimization, Miyagi and Madsen (2013) utilized the Dirac-Frenkel-McLachlan TD variational principle.

## 11.2. Time-dependent statistical tensors

### Motivation:

- In physics, Liouville's theorem is known from classical statistical and Hamiltonian mechanics, and it asserts that the phase-space distribution function is constant along the trajectory of the system.
- Similarly, the quantum-mechanical analog of Liouville equation describes the time evolution of a mixed state. The quantum form can be obtained by the standard replacements of classical variables with quantum operators and Poisson brackets with commutators.
- The Liouville equation for the atomic density matrix  $\rho$  reads

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [\mathbb{H}, \rho] - \Gamma \rho, \quad \mathbb{H} = \mathbb{H}^{(\text{atom})} + \mathbb{H}^{(e-\gamma)}$$

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where the first term in the Hamiltonian describes the (inner-) atomic and the atom-photon interactions, and the second term the relaxation matrix  $\Gamma$ . This relaxation matrix accounts for the atomic spontaneous decay due to either radiative or nonradiative (Auger) processes of the atom.

## 11.3. Time-integration of statistical tensors

### Motivation:

- Various methods can be applied to solve the coupled first-order ODEs for the time-evolution of the statistical tensors. Apart from those methods which solve the equations with given accuracy (but typically require the evaluation of the rhs at any given time  $t$ ), **we are mainly interested in shooting or predictor-corrector methods** which make only use of previous solutions of  $\rho$  and  $d\rho/dt = f$  on an equidistant time grid.

### Numerical methods:

- If we use a step-size  $h$  and define  $\rho(t_j) = \rho_j$ ,  $\frac{d\rho}{dt}(t_j) = f_j$ , the following integration formulas can be applied.
- **Euler's methods:**

$$\rho_{j+1} = \rho_j + h f_j$$

- **Adams-Bashford methods:**

$$\rho_{j+1} = \rho_j + h \left[ \frac{3}{2} f_j - \frac{1}{2} f_{j-1} \right]$$

$$\rho_{j+1} = \rho_j + h \left[ \frac{23}{12} f_j - \frac{16}{12} f_{j-1} + \frac{5}{12} f_{j-2} \right]$$

$$\rho_{j+1} = \rho_j + h \left[ \frac{55}{24} f_j - \frac{59}{24} f_{j-1} + \frac{37}{24} f_{j-2} - \frac{9}{24} f_{j-3} \right]$$

## 11.4. Time evolution of statistical tensors. Formalism

### 11.4.a. Liouville equation for the atomic density matrix

#### Vector potential and state multipoles:

- In the electron-photon interaction, the vector potential of the electromagnetic field is typically chosen to fulfill  $\text{div} \mathbf{A}(\mathbf{r}_i, t) = 0$ .
- When the electron-photon interaction Hamiltonian  $\mathbb{H}^{(e-\gamma)}$  is applied upon the density operator  $\rho$ , we shall consider only processes with one photon.
- Moreover, we assume a vector potential for a monochromatic field with frequency  $\omega$  and wave vector  $\mathbf{k} = (\vartheta_k, \varphi_k)$  ( $|\mathbf{k}| = \frac{\omega}{c}$ ) with regard to the coordinates in the laboratory system.
- **Envelope of the vector potential:** For a pulse with (real) envelope  $f(t)$ , the vector potential then includes two terms

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) f(t) e^{-i\omega t} + \mathbf{A}^*(\mathbf{r}) f^*(t) e^{i\omega t}.$$

#### Liouville equation in the representation of well-defined angular momenta:

- **Liouville equation:** In an atomic basis with well-defined total angular momenta and parity, the Liouville equation can be re-written as

$$\begin{aligned} \frac{\partial}{\partial t} \langle \alpha \mathbb{J}_\alpha M_\alpha | \rho | \beta \mathbb{J}_\beta M_\beta \rangle &= -\frac{i}{\hbar} (E_\alpha - E_\beta) \langle \alpha \mathbb{J}_\alpha M_\alpha | \rho | \beta \mathbb{J}_\beta M_\beta \rangle \\ &\quad - \frac{i}{\hbar} \sum_{\nu \mathbb{J}_\nu M_\nu} \left( \langle \alpha \mathbb{J}_\alpha M_\alpha | \mathbb{H}^{(e-\gamma)} | \nu \mathbb{J}_\nu M_\nu \rangle \langle \nu \mathbb{J}_\nu M_\nu | \rho | \beta \mathbb{J}_\beta M_\beta \rangle - \langle \alpha \mathbb{J}_\alpha M_\alpha | \rho | \nu \mathbb{J}_\nu M_\nu \rangle \langle \nu \mathbb{J}_\nu M_\nu | \mathbb{H}^{(e-\gamma)} | \beta \mathbb{J}_\beta M_\beta \rangle \right) \\ &\quad - \sum_{\gamma \mathbb{J}_\gamma M_\gamma} \langle \alpha \mathbb{J}_\alpha M_\alpha | \Gamma | \gamma \mathbb{J}_\gamma M_\gamma \rangle \langle \gamma \mathbb{J}_\gamma M_\gamma | \rho | \beta \mathbb{J}_\beta M_\beta \rangle \end{aligned}$$



### 11.4.b. Time-dependent statistical tensors of atomic lines

#### Time-dependent statistical tensors:

- **Statistical tensors:** With the substitutions of the statistical tensors from above and the notations  $[ab...c] \equiv (2a+1)(2b+1)...(2c+1)$ , the Liouville equation can be written as Grum-Grzhimailo, 2012)

$$\begin{aligned}
 i\hbar \dot{\rho}_{kq}(\alpha \mathbb{J}_\alpha, \beta \mathbb{J}_\beta) &= -2\pi \sqrt{\frac{\hbar}{c k}} \sum_{\nu \mathbb{J}_\nu K Q} \\
 &\left[ f(t) e^{-i(\omega - \omega_{\alpha\nu})t} \sum_{LM\lambda} g_\lambda (-1)^{J_\alpha + J_\beta + K + L} [LK]^{1/2} \langle KQ, LM | kq \rangle \left\{ \begin{matrix} J_\alpha & J_\beta & k \\ K & L & J_\nu \end{matrix} \right\} D_{M\lambda}^L(\varphi_k, \vartheta_k, 0) \left( \langle \alpha \mathbb{J}_\alpha \| \mathbb{T}_L^{(m)} \| \nu \mathbb{J}_\nu \rangle + i\lambda \langle \alpha \mathbb{J}_\alpha \| \mathbb{T}_L^{(e)} \| \nu \mathbb{J}_\nu \rangle \right) \tilde{\rho}_{KQ}(\nu \mathbb{J}_\nu, \beta \mathbb{J}_\beta) \right. \\
 &- f^*(t) e^{i(\omega - \omega_{\nu\alpha})t} \sum_{LM\lambda} g_\lambda^* (-1)^{J_\beta + k + J_\nu + L} [Lk]^{1/2} \langle kq, LM | KQ \rangle \left\{ \begin{matrix} J_\alpha & J_\beta & k \\ K & L & J_\nu \end{matrix} \right\} D_{M\lambda}^{L*}(\varphi_k, \vartheta_k, 0) \left( \langle \nu \mathbb{J}_\nu \| \mathbb{T}_L^{(m)} \| \alpha \mathbb{J}_\alpha \rangle - i\lambda \langle \nu \mathbb{J}_\nu \| \mathbb{T}_L^{(e)} \| \alpha \mathbb{J}_\alpha \rangle \right) \tilde{\rho}_{KQ}(\nu \mathbb{J}_\nu, \beta \mathbb{J}_\beta) \\
 &+ f(t) e^{-i(\omega - \omega_{\nu\beta})t} \sum_{LM\lambda} g_\lambda (-1)^{J_\alpha + J_\beta + K} [LK]^{1/2} \langle KQ, LM | kq \rangle \left\{ \begin{matrix} J_\alpha & J_\beta & k \\ L & K & J_\nu \end{matrix} \right\} D_{M\lambda}^L(\varphi_k, \vartheta_k, 0) \left( \langle \nu \mathbb{J}_\nu \| \mathbb{T}_L^{(m)} \| \beta \mathbb{J}_\beta \rangle + i\lambda \langle \nu \mathbb{J}_\nu \| \mathbb{T}_L^{(e)} \| \beta \mathbb{J}_\beta \rangle \right) \tilde{\rho}_{KQ}(\alpha \mathbb{J}_\alpha, \nu \mathbb{J}_\nu) \\
 &- f^*(t) e^{i(\omega - \omega_{\beta\nu})t} \sum_{LM\lambda} g_\lambda^* (-1)^{J_\alpha + K + J_\nu} [Lk]^{1/2} \langle kq, LM | KQ \rangle \left\{ \begin{matrix} J_\alpha & J_\beta & k \\ L & K & J_\nu \end{matrix} \right\} D_{M\lambda}^{L*}(\varphi_k, \vartheta_k, 0) \left( \langle \beta \mathbb{J}_\beta \| \mathbb{T}_L^{(m)} \| \nu \mathbb{J}_\nu \rangle - i\lambda \langle \beta \mathbb{J}_\beta \| \mathbb{T}_L^{(e)} \| \nu \mathbb{J}_\nu \rangle \right) \tilde{\rho}_{KQ}(\alpha \mathbb{J}_\alpha, \nu \mathbb{J}_\nu) \Big] \\
 &- i\hbar \sum_{\gamma \mathbb{J}_\gamma} G_{kq}^{KQ}(\alpha \mathbb{J}_\alpha, \beta \mathbb{J}_\beta, \gamma \mathbb{J}_\gamma) e^{i\omega_{\alpha\gamma}t} \tilde{\rho}_{KQ}(\gamma \mathbb{J}_\gamma, \beta \mathbb{J}_\beta)
 \end{aligned}$$

## 11.5. Observables to be derived from time-dependent statistical tensors

### Motivation:

- If we solve the set of time-dependent (Liouville) equations for the state multipoles, we can obtain the atomic statistical tensors for
- (a) discrete atomic states  $\rho_{kq}(\alpha \mathbb{J}_\alpha; \beta \mathbb{J}_\beta)$       (b) for atomic states with one electron in continuum  $\rho_{kq}(\alpha_f \mathbb{J}_f, \varepsilon \kappa : \alpha \mathbb{J}_\alpha, \alpha'_f \mathbb{J}'_f, \varepsilon' \kappa' : \alpha \mathbb{J}_\alpha),$
  - (c) *nondiagonal* elements  $\rho_{kq}(\alpha_f \mathbb{J}_f, \varepsilon \kappa : \alpha \mathbb{J}_\alpha, \beta \mathbb{J}_\beta)$     and     $\rho_{kq}(\alpha_f \mathbb{J}_f, \varepsilon \kappa : \alpha \mathbb{J}_\alpha, \alpha'_f \mathbb{J}'_f, \varepsilon' \kappa' : \beta \mathbb{J}_\beta).$

## 12. Atomic descriptors

### Machine learning. Basic concepts, goals & notations:

- **Machine learning (ML):** Methods in ML basically apply statistical algorithms whose performance improve with training, similar as in daily life. ML approaches are therefore able to learn the rules that underlie a given dataset. These approaches access some available portion of data and build automatically a model to make predictions for so-far unknown systems.
- **Machine learning (ML) in quantum chemistry and material science:** ML methods circumvent the task of solving the SE explicitly by using instead the data from a finite subset of well-known solutions in order to estimate solutions for (yet) unknown systems and materials. Since, more generally, many research fields require a frequent solution of the SE, ML methods may enable one to explore quantum behavior in much larger spaces, such as the (so-called) chemical compound space in material science.
- **Goals of machine learning:** The goal of ML is to automatically derive a function (or relation) that, for a specific set of input data, is able to predict the desired output values to an acceptable degree of fidelity.
- **Machine learning algorithms:** These algorithms generally establish a nonlinear map between input data (descriptors) and the specific property that need to be predicted; their efficiency mainly depend on how well the input data are represented by the various descriptors.
- **Artificial-intelligence methods:** The emergence of contemporary artificial-intelligence methods has substantially altered and enhanced the role of computers in science and engineering during the past years (Butler *et al.*, 2018).
- **Fourth paradigm of science:** The combination of artificial-intelligence methods with large data sets has been termed in the public discussion as fourth paradigm of science or fourth industrial revolution. This new paradigm includes in particular a rapidly increasing number of applications in chemistry and material science. This paradigm is also quite different from most traditional computations, where computers simply acts as ‘calculator’ and just employ some hard-coded algorithm as provided by some human expert (Butler *et al.*, 2018).
- **Inverse design:** This new paradigm in designing molecules and materials start from the functionality and then searches for some (ideal) molecular structure, for which this functionality is realized. In contrast to quantum-chemical methods, here the input is the desired property, while the output is a corresponding (geometrical) structure and composition of the molecule. Typically, however, a given function does not

## 12. Atomic descriptors

map uniquely to just *one* molecular structure but to a distribution of *probable or nearby* geometrical structures (Sanchez-Lengeling and Aspuru-Guzik, 2018).

- **Deep learning algorithms** aim for generating data distributions by training with large data sets. The **loss function** is hereby a measure how the empirically observed and the generated distribution differ from each other.
- **High-throughput calculations** of atomic level representations (state vectors) and processes is usually highly time-consuming. This suggests to make use of ML approaches in order to predict atomic data as they are needed, for instance, in astro and plasma physics. Once a ML model has been trained on an atomic (training) set, ML based computations are expected to be very fast.
- **High-throughput virtual screening (HTVS)**: This simulation method has its roots in the pharmaceutical industry for drug discovery in order to screen a (very) large number of synthesized or potentially useful molecules. While HTVS appears in spirit quite similar to inverse material design, it differs in philosophy since HTVS also includes automation and time-critical performance with the goal to identify ‘promising candidates’, and which are later further processed by more expensive methods.

### Feature selection and engineering in atomic physics:

- **Feature engineering**: Like in (human) learning, a machine-learning algorithm might learn more effectively by using one *particular* format rather than other formats (Butler *et al.*, 2018). Therefore, the raw input data need to be converted into a more suitable form for a given algorithm, a process that is known as **featurization** or **feature engineering**. In practice, however, it is by far not obvious which particular descriptor will eventually give rise to the best performance of an machine-learning algorithm, and special intuition and experience are typically required for each particular field of application.
- **Feature engineering**: The selection and transformation of (given) input data into proper descriptors is a highly non-trivial task and requires special insight into a particular research field. In practice, this transformation has to be based more on intuition than a systematic treatment, since descriptors need to be computed frequently and easily.
- **Role of descriptors**: Machine learning typically starts with a rather silent and unspectacular task, namely the **choice of proper descriptors, i.e. the choice of useful parameters that connects available data sets with some learning method**. If the choice of descriptors is inappropriate, it remains usually unclear of what can be learned from the (given) descriptor-property relations.
- **Descriptors** or (so-called) features generally define (vector) variables owing to some particular parametrization of data, suitable for ML. In this parametrization, **domain knowledge is very important in order to obtain a best set of descriptors**. Moreover, these descriptors should be independent of each other. Different ML methods help identifying more (and less) relevant descriptors, although some ambiguity in choosing these descriptors usually remains.

- **Atomic descriptors:** The definition of proper (atomic) descriptors is central for building models for machine learning and for predicting the physical properties and behaviour of atomic systems. These descriptors are also known also as **feature transformations** in the literature.
- **Descriptors for atomic (or molecular) states:** In electronic structure theory, the (electronic) state of an atom or molecule need to be transformed into a (more or less) **simple vector representation, called descriptor**. A set of such descriptors are then utilized as input for training a machine learning model on one or a few selected properties, and as associated with one or several atomic states.
- **Atomic descriptors:** A fast ML scan are often faster by a few (2-3) orders of magnitude, when compared with full quantum-mechanical computations, and may be applied as a preliminary step before detailed computations are made for selected structures and processes.
- **Data parallelism:** Since the descriptors of a *given* atomic system are usually independent from those of other systems, the computation of descriptors can easily be parallelized. Any useful implementation of such feature transformations should therefore **consider a parallel descriptor creation for multiple samples**.
- **Property-labelled atomic fragments:** Since not all atomic properties can likely be derived from a single set of descriptors, it is desirable to construct so-called property-labelled atomic fragments in order to simplify the feature selection process.
- **Property-Labelled Atomic Fragments (PLAF):** Following ideas from material science, it might be desirable to represent atomic (many-electron) states by graphs and to associate fragement descriptors to certain parts of these graphs. However, not much work has been done in this direction so far.
- **Fragement descriptors:** For each atomic property  $q(r)$ , such as electron densities, density convolutions, etc., one may also consider the minimum  $[\min(q)]$ , maximum  $[\max(q)]$ , total sum  $[\sum q]$ , average  $[\text{avg}(q)]$  as well as the standard deviation  $[\text{std}(q)]$  of property  $q$  as potential descriptors in order to encode an atomic level or the underlying electron configuration.
- **Primary features of an atom or ion:**
  - ionization potential (IP) and electro-negativity (EA);
  - energies of the highest-occupied and lowest-unoccupied shell;
  - radii of maximum charge distribution of all individual shells, calculated in a rather simplified shell model.

## 12.1. In JAC implemented atomic descriptors

None.

## 12.2. In JAC partly-implemented atomic descriptors

### 12.2.a. Descriptors for electronic densities (Descriptor)

#### Feature transformations:

- A feature transformation of the electron density is often applied in material science and will likely help also to characterize atomic (shell) structures and levels.

#### Use & notations:

- Using JAC: Perform an `Atomic.Descriptor(feature::AbstractFeature, ..., Descriptor.Settings(...))` or call directly functions from the module `Descriptor`.
- In JAC, we shall provide a list of features to which an approximate electron density can be transformed to.

#### 4D surfaces of spatial densities:

- **Use of a 4-dimensional unit sphere:** Bartok *et al.* (2010) projected the electron densities of all atoms (in some given unit cell) upon the surface of a four-dimensional unit sphere. This can be achieved by a very **similar transformation as applied for constructing the Riemann sphere**

$$(\varphi, \vartheta, \vartheta_o) = [\tan^{-1}(y/x), \cos^{-1}(z/|\mathbf{r}|), |\mathbf{r}|/r_o], \quad r_o > r_{\text{cut}}/\pi$$

- The use of this transformation has the advantage that all the information from the 3D spherical region inside the cutoff is now **encoded by three angles of the 4D surface**, and including the radial dependence of the (electron) density.

- **4D spherical harmonics**  $U_{mm'}^{(j)}$  : For such a four-dimensional unit sphere, the 4D spherical harmonics  $U_{mm'}^{(j)}$ , also known as the **Wigner matrices**, provide a natural complete basis for the interior of the 3D sphere and without the need for radial basis functions. An approximate projection of the atomic density upon the 4D sphere is then obtained by just using a subset of expansion coefficients  $c_{mm'}^{(j)} = \langle U_{mm'}^{(j)} | \rho \rangle$ .

### Bispectra of electronic densities:

- **Bispectrum of an atomic density:** A descriptor of the electron density can be formed also by means of the bispectrum of the projection coefficients  $(c_{mm'}^{(j)})$  of some atomic or shell density upon a 4D sphere as well as the standard Clebsch-Gordan coefficients

$$B_{j_1, j_2, j} = \sum_{m_1, m'_1 = -j_1}^{j_1} \sum_{m_2, m'_2 = -j_2}^{j_2} \sum_{m, m' = -j}^j (c_{m'm}^{(j)})^* \langle j_1 m_1, j_2 m_2 | j m \rangle \langle j_1 m'_1, j_2 m'_2 | j m' \rangle c_{m'_1 m_1}^{(j_1)} c_{m'_2 m_2}^{(j_2)}.$$

- **Bispectrum of an atomic density:** The elements of the three-index array  $\mathbf{b} = (B_{j_1, j_2, j})$  from above are invariant with respect to rotations of the 4D space, and hence also to rotations of the 3D space. In practice, one can easily limit the spatial resolution in describing the atomic density by truncating the summation to  $j, j_1, j_2 \leq J_{\max}$ .

### Partial radial distribution functions (PRDF):

- **Partial radial distribution function (PRDF):** These functions have been widely applied in the analysis of x-ray powder diffraction patterns in crystallography as well as for text mining in computer science. In physics, the PRDF representation may encode the distribution of pairwise distances  $d_{ab}$  between two (given) atoms or atomic levels of type  $a$  and  $b$ .
- **PRDF:** In molecular physics and material science, the PRDF can be seen as the density of atom-type  $b$  in a shell of radius  $r$  that is centered around atom  $a$ . If averaged over all atoms of a given type, the discrete PRDF representation is given by (Schütt *et al.*, 2014)

$$g_{ab}(r) = \frac{1}{N_a V_r} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \Theta(d_{a_i b_j} - r) \Theta(r + dr - d_{a_i b_j}),$$

where  $N_a, N_b$  are the (total) number of atoms of type  $a, b$ , and  $V_r$  is the volume of the sphere. In solid-state physics, one usually considers the atoms in the unit cell. The PRDF representation has the advantage that it is not fixed to a certain number of atoms in the unit cell of the training materials and, hence, can be used also in order to predict the properties of other (related) systems.

### 12.2.b. Descriptors for pairs of atomic levels

#### Feature transformations:

- Descriptors for a single atomic level might include: various radii, one-electron binding energies, bispectrum of atomic density; effective atomic charges for shells/subshells.
- Descriptors for pairs of atomic levels: overlap integrals of valence electrons.
- **Shell-coupling labeled atomic fragments:** It still need to be worked out how the coupling information of atomic levels can be transformed into useful features.
- **Cocatenation of descriptors:** All fragment-based atomic descriptors can be concatenated quite easily in order to represent a particular level uniquely. From this concatenated vector descriptor, one then has to **filter out low-variance as well as highly-correlated features in order to ensure a stable learning process.**

## 12.3. Methods of machine learning

### Machine learning. A short overview:

- **Machine learning (ML):** Frankly speaking, ML methods can be understood as a collection of computational methods which make use of data to predict yet unknown, though helpful new information. **ML is closely related to data mining** which applies machine learning and other methods to unveil information that is already within the data but did not (yet) become apparent so far.
- **Machine learning (ML):** The widespread use of ML methods in engineering sciences, social sciences, financial sciences, statistics, marketing, etc., has lead to many new methods and techniques which are independent of the research field they were developed originally.
- **Machine learning** includes several generic tasks, rather independent of the particular application: (i) Modelling of existing data by means of probability distributions; (ii) clustering and classification of data; (iii) regression analysis; and (iv) feature reduction. Different – formal and numerical – techniques have been developed and applied in order to deal with each of these tasks.
- **Mathematics behind ML methods:** These methods usually return a statistics-based model for some given data set, and which is then utelized in order to interpolate between the known data. A high accuracy in fitting the available data (low bias) often results in a rather high variance *between* these data points. Therefore, the accuracy of the fitting need to be tested by some cross-validation with test data or with experiment.



- **Branches of machine learning:** Three branches (classes) of ML methods are often distinguished: (i) Supervised learning; (ii) unsupervised learning as well as (iii) reinforcement learning (RL).
- **Supervised learning:** This approach is the **most mature and powerful learning approach** and, hence, has been applied in a large number of machine-learning studies in the physical and natural sciences, such as in the mapping of chemical compositions to some property of interest, picture recognition and elsewhere.
- **Supervised learning** aims for learning some conditional distribution  $P(\mathbf{y}|\mathbf{x})$ , and by assigning labels  $\mathbf{y}$  to the classification data  $\mathbf{x}$  based on training data from the distribution  $P(\mathbf{y}, \mathbf{x})$ . For example, supervised learning may aim to ‘learn’ a function  $y = f(x)$  from a given data set.
- **Unsupervised learning** aims to identify certain structures within a given distribution  $P(\mathbf{x})$ , such as some clustering of data.
- **Reinforcement learning** tries to learn some correct behavior due to (so-called) reinforcement signals-rewards or punishments. The agent’s goal is to obtain rewards with a high probability (Dunjko *et al.*, 2016).
- **Generative models for machine learning:** While there are various ways for building generative models, the main three approaches are: (i) variational autoencoders (VAEs); (ii) reinforcement learning (RL); and (iii) generative adversarial networks (GAN).
- **Quantum machine learning:** Analogue to quantum computing, this field aims to devise and implement explicit quantum algorithms (software) for machine learning that are faster than any known algorithms on some classical computers. Although a number of quantum algorithms are meanwhile well established, there are still many hardware and software challenges to be solved (Biamonte *et al.*, 2016). The use of quantum instead of classical algorithms is also known as **quantum speedup**. Quantum software makes in particular use of quantum algorithms to process information.
- **Statistical regression techniques:** In the last few years, various statistical regression techniques have been applied in order to approximate effectively the properties of systems, for which a rather small number of accurate and demanding reference calculations can be performed. To make use of these regression techniques, atomic-scale representations (descriptors) need to be developed to encode the **fundamental symmetries and properties of a class of systems**. Well-selected descriptors can hereby substantially improve the performance of the regression; good descriptors may also offer insights into the chemistry of the system. For instance, Willat *et al.* (2018) report a data-driven analysis of the *similarity* between pairs of elements that resembles the periodic table of the elements.

### 12.3.a. Supervised learning methods

#### Concepts & notations:

- **Supervised learning models:** These models can be used to predict output values from either a discrete set (e.g. classification of materials) or a continuous set of data (e.g. polarizability). To make predictions from a discrete set requires classification, while regression is needed to forecast continuous data.
- **Kernel-based learning methods:** These methods are based on the mapping of (atomic or molecular) data upon a high-dimensional feature space. This mapping is made implicitly by using a **kernel function**, e.g., a Gaussian kernel  $k(x, y) = \exp(xy/\sigma^2)$  or some Laplacian kernel  $k(x, y) = \exp(xy/\sigma)$ . Here, the kernel can be interpreted as a **measure to characterize the similarity between the given and predicted data**. The predicted property is then computed as a linear combination of kernel functions that depend on the material of interest and the training materials (Schütt *et al.*, 2014).

#### Advantages & limitations:

- Since the regression coefficients  $\{c_i\}$  arise from a nonlinear model, i.e. due to a nonlinear transformation of the training data, **such a kernel-based ML model is specific to some selected property and cannot be applied to any other properties or regions of compound space**.

#### Kernel ridge regression (KRR) method:

- **Regression model based on the Coulomb matrix:** Rupp *et al.* (2012) apply a ML model, in which the energy of a molecule is expressed as a sum over weighted Gaussians

$$E^{(\text{estimate})}(\mathbf{M}) = \sum_i^N c_i \exp \left[ -\frac{d(\mathbf{M}, \mathbf{M}_i)^2}{2\sigma^2} \right]$$

where  $i$  runs over all molecules  $\{\mathbf{M}_i\}$  from the training set. The training on the available reference data  $\{\mathbf{M}_i, E_i^{(\text{reference})}\}$  then results in a set of regression coefficients  $\{c_i\}$  as well as the length-scale parameter  $\sigma$ . In such a regression model, each molecule  $i$  from the training set contributes not only by its distance but also due to its regression coefficient  $c_i$ .

- **Kernel ridge regression:** In this regularized model, the norm of regression coefficients  $\{c_i\}$  is restricted to ensure the transferability of some model towards some unexplored species. For a given length-scale parameter  $\sigma$  and regularization parameter  $\lambda$ , the regression coefficients

are obtained by determining the minimum of the function (Rupp *et al.*, 2012)

$$\min_{\{c_i\}} \sum_i \left( E^{(\text{estimate})}(\mathbf{M}_i) - E_i^{(\text{reference})} \right)^2 + \lambda \sum_i c_i^2 \quad \Rightarrow \quad \mathbf{c} = \frac{\mathbf{E}^{(\text{reference})}}{(\mathbf{K} + \lambda \mathbf{I})}, \quad K_{ij} = \exp \left[ -\frac{d(\mathbf{M}_i, \mathbf{M}_j)}{2\sigma} \right].$$

$\mathbf{K}$  is called the Kernel matrix of all training molecules, while  $\mathbf{I}$  here denotes the identity matrix.

- **Locality of the kernel ridge regression:** The locality of this model is measured by the length scale  $\sigma$ ; this parameter determines a range outside of which any training molecule  $\mathbf{M}_i$  only contributes with (a rather) negligible weight to the selected property. Usually, the length scale  $\sigma$  is determined by some ML method and becomes smaller as the size of the training set increases, i.e. a model is said to become more *local* as more training data are available.

### 12.3.b. Neural network (NN) methods

#### Concepts & notations:

- **Deep neural network (DNN) model:** In these model, atomic or molecular representations are transformed first by a linear and later nonlinear function across several stages (layers) of the network. For a given task and associated loss function, the parameters for each layer (weights) are then optimized via the **backpropagation algorithm**.
- **Deep learning:** Since the DNN architecture transforms the original data into some other representation, more suitable for tasks like classification or generation, deep learning is often characterized as **representation learning**.
- **Deep neural network (DNN):** A DNN refers to multiple layers of neurons; each layer receives its input from the neuron activation of the previous layer, perform a simple transformation (computation), and transmits the (non-linear) activation to the next layer. In a DNN, therefore, all neurons of a given network implement altogether a nonlinear mapping of input (activation) data upon output data. A DNN learns from given test data by adapting the weights of each neuron due to **backpropagation techniques**.

### 12.3.c. autoencoder methods

#### Concepts & notations:

- **Autoencoder (AE) model:** Such model includes two steps, namely, the encoding of descriptors into some lower-dimensional (latent) space, and the mapping of the latent vector back to the original representation. These AE models often work better if the latent vector are generated by means of probability distribution so that a (single) descriptor is no longer represented as single point but rather as **probability distribution in the latent space**.
- In AE models, systems and properties are represented as continuous and differentiable vectors from some probabilistic manifold (Sanchez-Lengeling and Aspuru-Guzik, 2018).
- **Latent vector spaces:** These are continuous vector space and, hence, enable one to apply direct gradient-based optimization procedures. Nevertheless, the manifold of (atomic or molecular) data may lead to many local minima, so that other optimization approaches are also necessary.
- **Multilevel variational AE:** These AE refer to structured architectures and are presently promising research directions in ML, including so-called **reinforcement learning (RL) methods**.

### 12.3.d. Other methods

#### Concepts & notations:

- **Active learning approaches** attempt to provide guidance to optimize a particular property for some large and unexplored class of systems. So far, however, very little is known how some available or possible experimental set-ups should be sampled in order to obtain optimal output. Here, **active learning techniques aim to predict optimal future experiments** that enable one to better understand a given problem. In particular, such active machine-learning approaches may help directly select future experiments, a feature that has been discussed, for instance, in crystallography.

## 12.4. Feature transformations & applications of machine learning

### 12.4.a. Feature transformation and engineering

#### Requirements & notations:

- The recent boom in ML applications in molecular physics and material science has led to a plethora of (atomistic) descriptors that are — more or less — suitable for ML algorithms. However, a proper software implementation of these descriptors is either not accessible so easily for the users or is widely scattered across different programs and libraries.
- **Least absolute shrinkage and selection operator (LASSO):** In the selection of proper features, it is usually desirable to determine a small set of parameters that is able to keep all relevant information about the given data.
- **Feature selection:** This term comprises a rather widespread set of techniques that are used in statistical analysis in different fields, and the **least absolute shrinkage and selection operator (LASSO)** is just one of them.
- **Feature selection:** To reduce the size of the feature space, one often defines rules for linear and non-linear combinations of the primary features. This then usually gives rise to a very large number of candidate descriptors.

#### Properties of good descriptors:

- In material science, the properties of good (molecular) descriptors have been summarized at various places in the literature; cf. Himanen *et al.* (2019). In particular, such descriptors should be:
  - (a) **invariant with regard to a spatial translation** of the coordinate system;
  - (b) **invariant with regard to a rotation** of coordinates;
  - (c) **unique**, i.e. there should be a single way to construct a descriptor from the (atomic) structure and occupation of the unit cell, and the descriptor itself just refers to a single property of the material;
  - (d) **continuous**, i.e. small changes in the atomistic structure of the unit cell should translate into small changes in the descriptor;
  - (e) **computationally cheap** since the computation of descriptor should be significantly faster than any direct computation of the property of interest.
- **Properties of useful descriptors:** The following properties are considered to be important if not even necessary (Ghiringhelli *et al.*, 2015) but are very similar to the criteria above:

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- (a) A vector descriptor  $\mathbf{d}_i$  should uniquely characterize the system or process of interest.
- (b) Different (similar) systems or processes should be characterized by different (similar) vector descriptors.
- (c) The computation of the vector descriptor should be (much) cheaper than the property of interest.
- (d) The vector dimension  $\Omega$  of the descriptor should be as low as possible (for a certain request of accuracy).

### 12.4.b. Applications in molecular physics

#### Special concepts & notations of ML in molecular physics:

- **Molecular graphs:** Molecular systems can be quite readily described by graphs in which vertices represent the atoms and edges the chemical bonds. In such a representation, **fragment descriptors characterize subgraphs of the full 3D molecular network**. From this perspective, **different materials can be considered as coloured graphs**, where different colors represent different atoms and interatomic interactions. Such a graphical perspective also enables one to represent the individual parts of a molecular graph by linear combinations of fragment descriptors and, hence, to simplify the computation, storage and interpretation of the different descriptors.
- **Molecular graphs:** Following semi-empirical rules from bond theory, every molecule can be easily expressed as an **undirected graph where each atom is a node and the bonds are the edges**. In these graphs, all hydrogen atoms are usually treated implicitly in order to keep the size of the graphs moderate.
- **Molecular graphs:** SMILES strings form an established standard for molecular graphs; these strings follow the typical text encoding of the standard chemical notation (e.g., H<sub>2</sub>O or C<sub>2</sub>H<sub>5</sub>OH). Other and more advanced representation use weighted graphs with various vector features in order to assign bonding type, aromaticity, charge, and distance to the edges and nodes of the graph (Sanchez-Lengeling and Aspuru-Guzik, 2018).
- **Molecular graphs:** Since there is generally no unique translation between the molecular structure and some corresponding graph, the use of different such ‘translations’ can either appear to be advantageous (e.g., for further data augmentation) or disadvantageous, if different graphs cause noise in the ML process.
- **Chemical space project:** The chemical space formally comprises the set of all possible molecular and solid-state compounds which, obviously, still contains huge unexplored regions. For pharmacologically relevant small molecules, the number of structures is estimated to be on the order of  $10^{60}$  (Sanchez-Lengeling and Aspuru-Guzik, 2018). In the chemical space project, a total of  $166.4 \times 10^9$  billion molecules with at most 17 heavy atoms have been (formally) summarized.

- **Compound space in quantum chemistry:** ML models are often based on measuring distances in compound space in order to extract useful information about the stoichiometry and the configurational variation of different molecules. This requires of course a **measure measure of molecular (dis)similarity** that should be invariant with regard to translations, rotations and the particular ordering of atoms.
- **Gaussian approximate potentials (GAP):** Even for rather small systems, the GAP model for molecular potential energy surface is orders of magnitude faster than standard plane-wave DFT codes, although significantly more expensive and accurate than simple analytical potentials (Bartok *et al.*, 2010).

### Molecular descriptors:

- **Molecular descriptor:** A better representation of data requires less computational resources in order to *learn* the underlying patterns. For example, a representation that can span all of chemical space would need to capture all the symmetries of the Schrödinger equation, such as the permutational, rotational, reflectional as well as translational invariance for particles of the same type.
- **Molecular descriptor:** The Coulomb matrix and other descriptors often refer in counting atoms to their nuclear charge, although other criteria, such as the electron configuration or number of valence electrons could be used as well.
- **Molecular descriptor:** The finding of good molecular representations is presently an open research area. While there are various representations available, **no single representation seems to work for all properties of interest**. More general, those representations that encode the relevant physics will result in a better learning process.
- **Types of molecular descriptors:** Three such types are often distinguished, namely, discrete (e.g., text), continuous (e.g., vectors and tensors) or weighted graphs. Although each graphs can be re-expressed also as sparse matrices, graphs are quite different of how they are processed within the models of machine learning (Sanchez-Lengeling and Aspuru-Guzik, 2018).
- **Mulliken electro-negativity of an atom:**  $E^{(\text{MN})} = -(IP + EA)/2$  ; it is simply formed from the ionization potential (IP) and the electro-negativity (EA) of the atom or ion.
- **Coulomb matrix:** This matrix representation encodes the Coulombic forces between the nuclear charges of each atom.
- **Coulomb matrix:** This molecular descriptor has not always been found useful in ML and this applies, in particular, to periodic solids.
- **Coulomb matrix:** For single molecules with nuclear charges  $\{Z_i\}$  and positions  $\{\mathbf{r}_i\}$  of all atoms, the Coulomb matrix has been found a good (molecular) descriptor

$$C_{ij}^{(\text{molecule})} = \begin{cases} 0.5 Z_i^{2.4} & \text{for } i = j \\ \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} & \text{for } i \neq j. \end{cases}$$

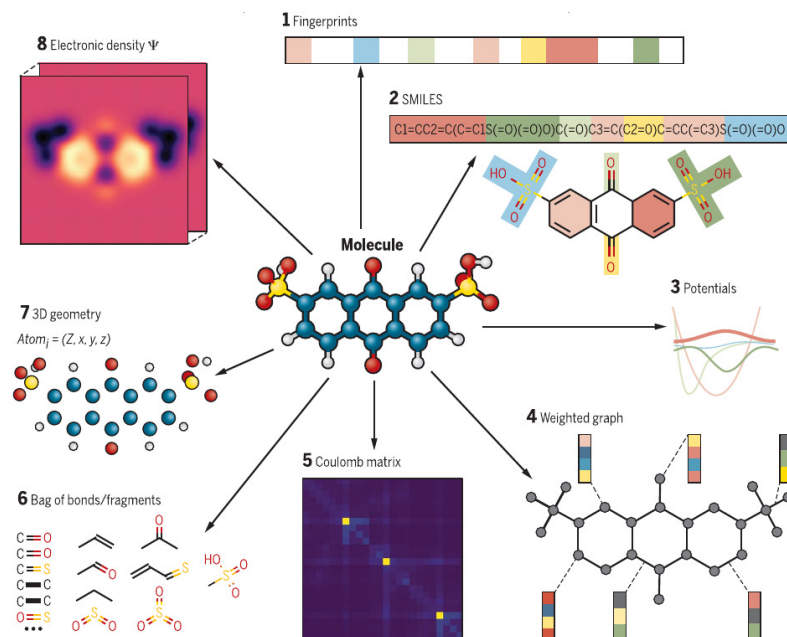


Figure 12.1.: Different types of molecular descriptors that can be applied to some molecule: (1) A fingerprint vector that quantifies the presence or absence of certain molecular environments; (2) SMILES for simple text encoding of the chemical species; (3) various potential energy functions that model the interactions and symmetries of the molecule; (4) a graph with atoms and bond weights; (5) Coulomb matrix; (6) a bag of bonds and fragments; (7) 3D geometry with associated atomic charges; and (8) encoding of the electronic density; taken from: Sanchez-Lengeling and Aspuru-Guzik (2018).

The Coulomb matrix is invariant under rotation and translation but cannot be applied so easily to infinite periodic crystals.

- **Galvez matrix of molecular graphs:** The construction of descriptors can be inspired also by (so-called) topological charge indices or Kier-Hall electro-topological state indices. In this construction scheme, a **Galvez matrix**  $M = A \cdot D$  is formed by multiplying the adjacency matrix  $A$  of the graph by the reciprocal square distance matrix ( $D_{ij} = (1/r_{ij}^2)$ ). Obviously, this is a  $n \times n$  quadratic matrix with  $n$  being the number of atoms in the unit cell. From the Galvez matrix, various descriptors of some reference property  $\mathbf{q}$  can be calculated by



(Isayev *et al.*, 2017):

$$T = \sum_{i=1}^{n-1} \sum_{j=i+1}^n |q_i - q_j| M_{ij}, \quad T_{\text{bond}} = \sum_{i,j \in \text{bonds}} |q_i - q_j| M_{ij}.$$

- **Feature matrix** ( $X_{ij,n} = g_{ab}(r_n)$ ): Matrix of the PRDF of all pairs of atoms  $(a, b)$ , evaluated for some cut-off radius  $r_n$ . The distance of two molecules or crystals is then defined by the Frobenius norm between these those matrices; these distances can be directly used also for some of the kernels of ML methods. The feature matrix is a global descriptor for the similarity of molecules, which is invariant under translation, rotation, and the particular choice of the unit cell (Schütt *et al.*, 2014).

## Applications:

- **Potential energy surface (PES)**: ML approaches has been used to predict the Born-Oppenheimer potential energy surface (PES) for a set of atoms without explicit molecular computations. For example, Bartok *et al.* (2010) modeled the bulk phases of carbon, silicon, germanium, iron and gallium nitride, based on a unified framework in forming atomistic descriptors. These authors also developed a framework for automatically generating finite range interatomic potential models from quantum-mechanically calculated atomic forces and energies.

### 12.4.c. Applications in solid-state physics and material science

#### Special concepts & notations of ML in material science:

- **Machine learning in material science**: ML methods will likely augment or even supplant in the (near) future the time consuming and often intuition-based, trial-and-error experimentation for the design and discovery of new materials.
- **Machine learning in material science**: Methods in ML may help optimize several properties simultaneously with the best trade-off, for example, by maximizing one property, while keeping another property bound near to some required value. In a **Pareto plot** with axis due to these properties, this means to identify the boundary for one given property, which the materials cannot cross without deteriorating the value of some other properties.

## 12. Atomic descriptors

- **Machine learning in crystallography:** Computationally efficient ML models have been applied during recent year in order to predict molecular properties of many crystals with similar accuracy as obtained from DFT. These models are especially useful to systematically screen millions of crystals with only milliseconds per single prediction (Faber *et al.*, 2016).
- **Material Genome Initiative (MGI):** In 2011, Obama announced this initiative to maintain the US manufacturing competitiveness by halving the time it takes to discover new materials. Since then, this initiative has been supported and sustained by various US agencies. **New materials are sought in order to reduce the costs and environmental friendliness**, with special focus upon Kevlar and Li-based batteries and their potential replacements.
- **Inverse material design:** Since it appears intractable to explore the huge space of (different classes of) materials, neither computationally nor experimentally, the **inverse design aims to discover tailored materials by starting directly from some desired functionality** and to combine available databases with methods from machine learning.
- **Inverse material design:** Various approaches to inverse material design have been proposed and benefitted from recent developments in machine learning. In particular, **deep generative models** have been applied to numerous classes of materials including the rational design of prospective drugs, synthetic routes to organic compounds as well as a further optimization of photovoltaics and redox flow batteries (Sanchez-Lengeling and Aspuru-Guzik, 2018).
- **Structure maps:** Originally, these maps refer to simple scatter plots that display two physical properties *versus* each other for a number of compounds or materials, such as ionization potentials, valences, ionic radii, etc. These structure plots have been frequently used in material science in order to identify class of systems whose physical properties come already close to some desired behaviour. In particular, the Periodic Table is a particular structure map that establishes trends in the chemical properties of all atoms, if one moves along its rows or columns.
- **Structure maps:** Various well-known structure maps in chemistry and material science are based on symmetric combinations, e.g., sums or differences, of ionic radii which are computed by means of pseudopotential. Since the use of coordinates do not require extra computation nor measurements, they can be easily applied in structure maps for clustering physical properties other than crystal structure or melting temperatures, etc.
- **Structure maps:** ML methods can extend traditional structure maps towards three or more dimensions and, hence, remove the subjectivity or ambiguity in the decisions of where to draw the boundaries for clusters and to replace simple boundaries by more sophisticated and flexible manifolds (Gubernatis and Lookman, 2018).
- **Ashby plot:** Historically, an Ashby plot displayed the Young's modulus *versus* the density of some material in order to show overlays of metals, polymers, ceramics, foams, etc. This structure map has been applied in material engineering in order to select the most appropriate material for a particular application.

- **Molecular fragments:** This concept from molecular physics has been adopted in material science during the last years to design crystalline materials and has helped improve the molecular nomenclature and representation.
- **Property-Labelled Material Fragments (PLMF):** Fragments or (vector) descriptors that are just associated with a certain parts of a molecular or material graph.

### Descriptors for solid-state physics and material science:

- **Descriptors for material science:** Coulomb matrix, Ewald sum matrix, sine matrix, Many-body Tensor Representation (MBTR), Atom-centered Symmetry Functions (ACSF) and Smooth Overlap of Atomic Positions (SOAP); cf. Himanen *et al.* (2019).
- **Smooth overlap of atomic positions (SOAP):** The SOAP formalism provides an elegant framework in order to construct a rotationally-invariant representation (descriptors) of the atomic density that can be used for machine-learning purposes. While the formalism itself provides a complete representation of structural correlations of a given order within an atomic environment, the quality and the computational cost of the regression scheme can be further improved by modifying the representation and by including chemical intuition (Willat *et al.*, 2018). For example, the use of multiple kernels due to different interatomic distances was found to lead to an improved machine learning behaviour.
- **Descriptors for material science:** To encode the atomistic structure of some molecule or material, the descriptor either depicts a local atomic environment or the structure as a whole. Global descriptors encode information about the whole atomistic structure, such as the size, temperature variation, etc.
- **Voronoi cells:** A Voronoi tessellation is a partitioning of space into regions based on some predefined subset of points, called seeds, sites, or generators. For each of these seeds, there is a region consisting of all points closer to that seed than to any other one; these regions are called Voronoi cells. The Voronoi cells of a crystal coincide with the so-called Wigner-Seitz cells of each atom, if the atomic sites are taken as seeds. **The tessellation of a crystal is unique and insensitive to the particular choice of unit cell.**

### Applications:

- **Formation energy of elpasolites:** Faber *et al.* (2016) introduced a newly developed ML model to investigate and predict the formation energies of all  $2 \times 10^6$  elpasolites that can be (formally) constructed from all main-group elements up to Bi. These predictions helped identify a new elemental order of descending elpasolite formation energy, including crystals with quite peculiar atomic charges.
- **Formation enthalpy of binary compounds:** Curtarolo *et al.* (2003) built a ML model for predicting the formation enthalpy of binary compounds, and which was based on the formation enthalpies of the same elements but in other chemical and solid-state structures.

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- **High-throughput density functional theory (HT-DFT) calculations:** In materials science, large data bases have been generated by HT-DFT calculations and in a few cases by high throughput experiments.

### 12.4.d. Other applications

#### ML in text mining:

- **Text mining:** Because of the rapid increase of information, available to researchers via the web and scientific literature, navigation has become more and more difficult. Here, **text mining became a popular approach to identifying and extracting information from unstructured text sources.**
- Text mining aims for extracting facts and relationships in a structured form in order to create specialized databases, to transfer knowledge between domains or, more generally, to support decision-making (Butler *et al.*, 2018).

## 13. Semiempirical estimates

### 13.1. In JAC implemented estimates for atomic properties and data

#### 13.1.a. Data from the periodic table of elements (PeriodicTable)

##### Symbols, atomic mass and ionization potentials:

- In JAC, the (mean) atomic masses of all elements are obtained from a call of `[PeriodicTable.]get(Z::Int64)` or `[PeriodicTable.]get(sy::Symbol)`, if `sy` refers to a valid element symbol.
- In JAC, the first ionization potential of a given element with nuclear charge  $Z$  or symbol `Sy` is obtained from a call of `[PeriodicTable.]get("", Z::Int64)` or ...
- Atomic mass:

#### 13.1.b. Isotope data (PeriodicTable)

:

- Detailed isotope data are required, for instance, to calculate hyperfine  $A$ ,  $B$  parameters, isotope-shift parameters, and at various places elsewhere.
- The isotope data need to be specified for the nuclear model `nm::Nuclear.Model`, if such properties are to be calculated.
- In JAC, a few selected isotope-specific data can be obtained by a call to `[PeriodicTable.]getIsotope(" ", ..., Z::Int64)`. However, no attempt is made to provide data for all isotopes and elements; instead we encourage the user to add further data as the need arises in specific applications.

### 13.1.c. Binding energies of inner- and valence-shell electrons (PeriodicTable)

#### Binding energies:

- In JAC, an estimate for the binding energy of an  $n\ell$ -electron in the neutral atom can be obtained from `[PeriodicTable.]get("ionization potential: inner-shell", shell::Shell, Z::Int64)`.

### 13.1.d. Atomic radii, susceptibilities and polarizabilities (PeriodicTable)

#### Atomic polarizabilities:

- In JAC, ... can be obtained from `[PeriodicTable.]get( )`.
- Further details

#### Atomic radii:

- In JAC, ... can be obtained from `[PeriodicTable.]get( )`.
- **Atomic radii:** The concept of atomic and ionic radii has been found helpful for understanding, explaining or even predicting various physico-chemical properties of atoms, ions and molecules. However, this is quite different to the use of such radii in crystal chemistry where they are used in order to estimate and to explain the binding lengths in crystal lattices.
- **Atomic radii:** Ghosh (2002) applied computed theoretical radii in order to estimate a number of size-dependent physical properties of isolated atoms: (1) the diamagnetic part of the magnetic susceptibility  $\chi^{(\text{diamagnetic})}$  for all elements up to xenon, (2) the atomic polarizability  $\alpha$  and (3) the global hardness  $\eta$  for all elements of the periodic table.

## 13.2. In JAC partly-implemented estimates for atomic properties and data

### 13.2.a. Weak-field ionization of effective one-electron atoms

#### Property & notations:

- **Field ionization:** by a quasi-static external field:  $A^{(*)} + F \mathbf{e}_z \longrightarrow A^+ * e^-$ .
- **Formal quantum notation:**  $|\alpha \mathbb{J}\rangle \longrightarrow \dots$
- Not yet implemented.
- In JAC, all estimates on the field-ionization rates of atoms are always based on a non-relativistic, single-electron approach. No attempt has (yet) been made to generalize this approximation towards real many-electron atoms and ions with their fine-structure.

#### Motivation:

- Ionization of atoms by an external electric field is a fundamental atomic process that plays an important role, for instance, in the formation of charge-state distributions in (dilute) plasma under strong fields.
- **Vice versa:** The observations of temporal variations in the line intensities of ions, that are produced by field ionization, can help determine spectroscopically the macroscopic-field distribution in plasma.
- Since the field-ionization probability grows (very) rapidly with the electric field strength  $F$ , the field strength can be derived from accurate measurements of the ionization probabilities.

#### Further information:

- **Ionization probabilities are often calculated within the WKB approximation, i.e. in the weak-field limit.** In general, field ionization probability depends critically on the projection of the total orbital angular momentum upon the direction of the field.

### 13. Semiempirical estimates

- In most field-ionization probability computations, a quasi-static and homogeneous electric field is assumed as it occurs, for example, for macroscopic-scale fields in plasma. This assumption is in contrast to many local fields that may occur at the atomic scale.
- For the case of a single electron with binding energy  $E$  in the valence shell ( $n\ell$ ) and outside of closed shells otherwise, the quasi-classical escape rate is given by (Fisher *et al.*, 1998)

$$\Gamma(E, \ell, m) = B_{n\ell}^2 \frac{(2\ell + 1)(\ell + m)!}{2^{m+1} k^m m! (\ell - m)!} \left( \frac{2k^2}{F} \right)^{2Z/k - m - 1} \exp\left(-\frac{2k^3}{3F}\right)$$

where  $Z$  is the charge of the parent ion as seen by the electron are large  $r$ ,  $k = \sqrt{2|E|}$  is the modulus of the (electron's) wave vector and  $B_{n\ell}$  is the amplitude that characterizes the outgoing electron wave.

#### 13.2.b. Tunnel ionization rates

##### Tunnel ionization rates:

- **ADK rate for tunnel ionization:** The first step in the strong-field photoionization by a linearly-polarized laser field (with  $\gamma < 1$ ) is often modeled by means of the Ammosov-Delone-Kainov (ADK) rate for the tunnel ionization of an atom in an oscillating electric field. This rate is given by (Chen *et al.*, 2019)

$$W^{(\text{ADK})}(|\mathcal{E}(t)|) = |c_{n^*\ell^*}|^2 f(\ell, m) I_p \left( \frac{2\kappa}{|\mathcal{E}(t)|} \right)^{2n^* - |m| - 1} \exp\left(-\frac{2\kappa}{3|\mathcal{E}(t)|}\right), \quad n^* = \frac{Z^{(\text{ion})}}{\sqrt{2I_p}}, \quad \ell^* = n^* - 1$$

$$|c_{n^*\ell^*}|^2 = \frac{2^{2n^*}}{n^* \Gamma(n^* + \ell^* + 1) \Gamma(n^* - \ell^*)}, \quad f(\ell, m) = \frac{(2\ell + 1)(\ell + |m|)!}{2^{|m|} |m|! (\ell - |m|)!}, \quad \kappa = (2I_p)^{3/2}.$$

In this notation,  $(n^*, \ell^*)$  are effective quantum numbers, while  $(\ell, m)$  are the orbital and magnetic quantum numbers of the (single-active) valence electron, and  $Z^{(\text{ion})}$  is the charge of the residual ion.

- **ADK rate for tunnel ionization:** Tong and Lin (2005) found that the ADK rates significantly overestimate the (static) ionization rate if calculated numerically in an barrier-suppressing electric field. In the near- and over-the-barrier regimes, these authors suggested instead



the **modified ADK rate**

$$W^{(\text{modified ADK})}(|\mathcal{E}(t)|) = W^{(\text{ADK})}(|\mathcal{E}(t)|) \exp\left(-\mu \frac{[Z^{(\text{ion})}]^2}{I_p} \frac{|\mathcal{E}(t)|}{\kappa}\right), \quad 6 < \mu < 10 \quad \dots \text{fitting parameter.}$$

For a few atoms and ions, the fitting parameters  $\mu$  is given by Tong and Lin (2005).

- **PPT rate for tunnel ionization:** The ADK rate for tunnel ionization is the limes of an extremely strong laser field ( $\gamma \rightarrow 0$ ) of a more general model by Perelomov, Popov, and Terentev (PPT) from (1967) which was originally derived for arbitrary values of the Keldysh parameter  $\gamma$ . In this PPT model, the ionization rate is given by

$$W^{(\text{PPT})}(|\mathcal{E}(t)|, \omega) = |c_{n^*\ell^*}|^2 f(\ell, m) I_p \left(\frac{2\kappa}{|\mathcal{E}(t)|}\right)^{2n^* - |m| - 1} (1 + \gamma^2)^{|m|/2 + 3/4} A_m(\omega, \gamma) \exp\left(-\frac{2\kappa}{3|\mathcal{E}(t)|} g(\gamma)\right)$$

$$g(\gamma) = \frac{3}{2\gamma} \left[ \left(1 + \frac{1}{2\gamma^2}\right) \sinh^{-1} \gamma - \frac{\sqrt{1 + \gamma^2}}{2\gamma} \right], \quad A_m(\omega, \gamma) \dots \text{see literature,}$$

while all other entities are the same as in the ADK rate above.

- **Total ionization probability from tunnel ionization rate:** For a given laser pulse  $\mathcal{E}(t)$ , the total ionization probability is given by

$$\mathcal{P}^{(\text{tunnel rate})} = 1 - \exp\left(\int_{-\infty}^{\infty} dt W^{(\text{tunnel rate})}(|\mathcal{E}(t)|, \dots)\right),$$

and where  $W^{(\text{tunnel rate})}$  refers to one of the tunnel ionization rates from above.

### 13.2.c. Electron-impact ionization. Cross sections

#### Semi-empirical electron-impact excitation and ionization cross sections:

- **Temperature dependence of cross sections and rate coefficients:** Vriens and Smeets (1980) analyzed how the electron-impact excitation, ionization and de-excitation cross sections and rate coefficients depend on the electron energy and temperature as well a few other parameters. They cover a rather wide range of electron-impact energies from *sudden* up to *adiabatic* collisions. In particular, **Vriens and Smeets (1980)**

### 13. Semiempirical estimates

constructed a set of simple analytical formulas for the electron-impact cross sections and rate coefficients as well as for the total depopulation and three-body recombination, although it appears rather difficult to follow this paper in detail, and especially to which entities the given formulas refer and when they are valid.

- **Electron-impact cross sections for CR simulations:** CR models have been applied in the literature in order to simulate different nonequilibrium plasmas; these models typically require the cross sections or rates for all major electronic transfer processes. While different approximate cross-section and rate formulas are available from the literature, these formulas often have a limited range of validity, and there occur serious discrepancies among the different approximations. Vriens and Smeets (1980) here provide practical formulas that are accurate over a reasonable wide range of primary energies and which are applicable for different transitions.
- Two characteristic energies of electron-impact processes refer to the binding energy  $E^{(\text{binding})}$  of the (least-bound) valence electron and to the kinetic energy of the incident electrons  $E^{(\text{impact})}$ .
- **Two regimes for electron-impact processes:** (i) In the sudden regime of rather high impact energies,  $E \gtrsim 4 E^{(\text{binding})}$ , there is generally good agreement between the binary-encounter and the Bethe-Born approximation. (ii) For low collision energies  $E^{(\text{binding})} \lesssim E \lesssim 4 E^{(\text{binding})}$  the binary-encounter cross sections are larger (up to  $\sim 40\%$ ) than the classical three-body as obtained by Monte-Carlo trajectory calculations.

#### Kolbenstvedt model for the electron-impact ionization:

- Haque and coworkers (2010) explored a so-called Kolbenstvedt model for the electron-impact ionization of the  $K$ -,  $L$ - and  $M$ -shells of neutral atoms and ions.

## 13.3. Further estimates on atomic properties, not yet considered in JAC

### 13.3.a. Electron and positron stopping powers (StoppingPower)

#### Property & notations:

- **Stopping power:** due to the penetration of electrons and positrons through matter:  $A^{(*)} \dots$

#### Motivation:

- **Stopping powers of matter for electrons are important** for many applications involving energy deposition. In radiation physics, chemistry, biology and medicine, it is important to have simple but accurate estimates about the stopping power of energetic electrons in various media for (Gümüs, 2005).
- Until the present, no simple and practical model exists for the stopping power of electrons with energies below 10 keV.

#### Approximate stopping power formulas:

- The stopping power of materials arise from two types of processes, namely collisional and radiative processes. The collisions of the incident particles with the target material is most important and mainly arises from collisions between the incident particles and the atomic electrons.

$$\frac{dE}{dx} = \left( \frac{dE}{dx} \right)^{(\text{collision})} + \left( \frac{dE}{dx} \right)^{(\text{radiative})}$$

- For incoming electrons, a modified collisional stopping power formula for incoming electrons can be written as given by Sugiyama (1985) or Rohrlich and Carlson (1954)
- **Full Bethe-Bloch formula:**

$$-\frac{dE}{dx} = \left( \frac{e^2}{4\pi\epsilon_o} \right) \frac{4\pi z^2 N_A Z \rho}{mc^2 \beta^2 A} \left[ \ln \left( \frac{2mc^2 \beta^2}{I} \right) - \ln(1 - \beta^2) - \beta^2 \right]$$

### 13.3.b. Stopping power of multiply-charged ions

#### Motivation:

- **Stopping power of multiply-charged ions:** The energy loss and the range of penetration of multiply-charged ions in matter is relevant for different fields, from radiation damage and dosimetry to radiation chemistry and biology, to nuclear and health physics, and at several places in science and technology (Ziegler and Manoyan, 1988).
- **Stopping power of multiply-charged ions:** The stopping power of medium and heavy ions generally depends on the charge and velocity of the incident ions. In particular, the velocity need to be compared with the (so-called) Bohr velocity  $\mathbf{v}^{(\text{Bohr})} \approx 25 \text{ keV/amu}$ , i.e. the velocity of electrons in the conduction band of a solid. While ions with  $\mathbf{v} < \mathbf{v}^{(\text{Bohr})}$  undergo adiabatic collisions with the target electrons and, hence, experience only a small stopping power in the material, the stopping power increases for ions with nuclear charge  $Z$  with the velocity for  $\mathbf{v} > \mathbf{v}^{(\text{Bohr})}$  until a peak occurs at about  $\mathbf{v}^{(\text{peak})} \approx 3 \mathbf{v}^{(\text{Bohr})} Z^{2/3}$ . For velocities  $\mathbf{v} > \mathbf{v}^{(\text{peak})}$ , the interaction of the ions with the target electrons become less relevant owing to the shorter effective interaction time and, thus, the stopping power decreases with increasing velocity of the ions (Ziegler and Manoyan, 1988).
- **SRIM code:** This code estimates stopping powers and ranges for different ions and target materials. Since an earlier version from 1985, a few major upgrades have been published about every six years, and with good number of citations ( $\sim 700$ ) every year. In the SRIM-2010 version, a number of major improvements have been made (Ziegler *et al.*, 2010): (1) Further experimental stopping powers were added to the database and now contains a total of about 28,000 stopping powers; (2) improved corrections were made for the stopping power of ions in various compounds; (3) a number of additional computations of stopping powers have been carried out for heavy ions and now lead to more accurate predictions; (4) the development of a self-contained SRIM module for the stopping powers and range values of ions that can be invoked by other software tools; (5) incorporation of interatomic potentials for selective ion-atom collisions.

#### Empirical rules:

- **Stopping power of ions in different target materials:** Apart from the charge and velocity of the incident ions, the stopping power also depends on the target materials. For a hydrocarbon target gas, the stopping power can be derived approximately from the stopping powers of pure carbon and hydrogen targets by following **Braggs empirical rule**. A number of earlier works discussed the possibility of finding the stopping power for other targets by using the results of hydrocarbon target gases.
- **Empirical Bragg rule for stopping powers:** This rule tells that the stopping power of a compound target can be estimated by using a linear combination of the stopping powers of the individual elements. While this rule has been found reasonably accurate within about 20 %,

all further improvements of this rule failed since the stopping power depend of course also on the detailed electronic structure and the excitation energies in the target.

- **Sigmund's theory of stopping power (1982):** This theory allows for rather arbitrary electronic configurations of the target, and it also takes the detailed internal motion of the electrons into account. This theory has been applied by Sabin and coworkers to evaluate stopping powers for both, individual elements and for the stopping of protons in hydrocarbons. This theory often predicts stopping powers which agree with experiment by a few percent.
- **Brandt-Kitagawa rules:** Ziegler and Manoyan (1988) apply the (so-called) Brandt-Kitagawa rules in order to apply the known stopping powers *one* ion to other ions. In practice, these rules scale the proton stopping powers to those of other ions at the same velocity by making a few simple assumptions: (i) The heavy ions will loose all electrons that are slower than the velocity of the incident ion relative to the target material; (ii) the size of the ions shrinks due to the electron loss to the size of hydrogenic ions of charge  $Z^{(\text{eff})}$ . – However, the presentation and notation by Ziegler and Manoyan (1988) is quite cumbersome, although the parametrizations look overall rather simple. Moreover, all the write-ups by Ziegler (1988) and by Ziegler and coworkers (1999, 2010) are rather sophisticated and do not make use of standard atomic notations.
- **Stopping power at high ion velocities:** Two assumptions are often made for light ions with incident velocities much higher than those of the projectile electrons: (i) All electrons are stripped off the ions; (ii) even light and medium-heavy ions are much heavier than the target electrons. These assumptions apply for light ions with incident energies between 1 MeV/u and 10 GeV/u.

### Empirical theories:

- **Bohr's model for the stopping power of ions in matter:** Following Bohr, the energy loss of ions, passing through matter, can be divided into two contributions: (i) a nuclear contribution due to the (positive) charge of the ions in the material and (ii) due to the (quasi-) free electrons of the material, and which is often dominant. Bohr's considerations are mainly based on the relative masses and the abundances of the target electrons and ionic cores. For incident ions with nuclear charge  $Z$  and valence electron with orbital frequency  $\omega$ , a simple model gives rise to the energy loss that can be extended towards relativistic energies ( $\gamma = 1/\sqrt{1 - v^2/c^2}$ ) (Ziegler 1999)

$$\frac{dE}{dx}^{(\text{non-relativistic})} = 4\pi Z^{(\text{target})} \frac{Z^2 e^4}{m v^2} \ln \left( \frac{m v^3}{Z e \omega} \right) \quad \Rightarrow \quad \frac{dE}{dx}^{(\text{relativistic})} = 4\pi Z^{(\text{target})} \frac{Z^2 e^4}{m v^2} \ln \left( \frac{\gamma^2 m v^3}{Z e \omega} \right)$$

### 13.3.c. Stark broadening of spectral lines in plasma

#### Motivation:

- **Stark broadening of spectral lines:** This broadening has been found very important in (so-called) DA and DB white dwarf atmospheres.
- Apart from white dwarfs, Stark broadening of spectra is also an important pressure-broadening mechanism for various types of other stars.
- Various semi-empirical calculations of the Stark widths and shifts have been performed in the impact approximation by using Griems (1968) formula.
- For selected lines, it was shown that Stark broadening can change the observed widths by 10-45 %.

#### Semi-empirical approximations:

- **Lorentzian profile of isolated lines:** For isolated lines  $|\alpha_i \mathbb{J}_i\rangle \rightarrow |\alpha_f \mathbb{J}_f\rangle$  with level energies  $E_i$  and  $E_f$ , the line profile is often assumed to be Lorentzian, shifted by the energy  $d$  and with the (total) line widths  $\Gamma$  due to the (plasma) Stark broadening.

$$F(\omega) = \frac{(\Gamma/2\pi)}{(\omega - \omega_{if} - d)^2 + (\Gamma/2)^2}, \quad \omega_{if} = \frac{E_i - E_f}{\hbar}.$$

where

- **Energy shift and (total) widths of the Stark-broadened line:** Both, the energy shift  $d$  as well as the (total) widths  $\Gamma$  can be expressed in terms of the velocity distribution  $f(v)$  of the electrons in the plasma, its density  $N^{(\text{elec})}$ , the impact parameter  $b$  of the incident electrons as well as the elastic and inelastic (electron-impact excitation) cross sections for **excitations of the initial and final levels to neighbored levels**.

$$\Gamma = N^{(\text{elec})} \int dv v f(v) (\sigma^{(\text{elastic})} + \sigma^{(\text{inelastic})}); \quad d = N^{(\text{elec})} \int dv v f(v) \int_{R_1}^{R_{\text{Debye}}} db 2\pi b \sin(\phi_p)$$

and where  $\phi_p$  is a **plasma-specific phase shift**. Further details on the Stark broadening of spectral lines are given by Dimitrijevic and Sahel-Brechot (1996).

- In 1968, Griem suggested simple semiempirical formulas for the Stark line shift and widths in impact approximation which is based on some original formula by Baranger (1958) as well as an effective Gaunt factor by Seaton (1962) and Regemorter (1962). With these formulas,

the Stark linewidths and Stark line shifts can be obtained by:

$$\frac{\Gamma}{[a.u.]} = 8 \left(\frac{\pi}{3}\right)^{3/2} \frac{\hbar}{m a_o} N_e \left(\frac{E_H}{kT}\right)^{1/2} \left[ \sum_{i'} |\langle i' | r | i \rangle|^2 g_{se} \left(\frac{E}{\Delta E_{i'i}}\right) + \sum_{f'} |\langle f' | r | f \rangle|^2 g_{se} \left(\frac{E}{\Delta E_{f'f}}\right) \right]$$

$$\frac{d}{[a.u.]} = -8 \left(\frac{\pi}{3}\right)^{3/2} \frac{\hbar}{m a_o} N_e \left(\frac{E_H}{kT}\right)^{1/2} \left[ \sum_{i'} \left(\frac{\Delta E_{i'i}}{|\Delta E_{i'i}|}\right) |\langle i' | r | i \rangle|^2 g_{sh} \left(\frac{E}{\Delta E_{i'i}}\right) + \sum_{f'} \left(\frac{\Delta E_{f'f}}{|\Delta E_{f'f}|}\right) |\langle f' | r | f \rangle|^2 g_{sh} \left(\frac{E}{\Delta E_{f'f}}\right) \right]$$

In these formulae,  $E_H$  is the hydrogen ionization energy,  $N_e$  is the free-electron density of the perturber levels,  $T$  is the electron temperature,  $E = 3/2 kT$  the mean energy of the perturbing electron and  $g_{se}$ ,  $g_{sh}$  are the effective Gaunt factors which are calculated and tabulated by Griem. These Gaunt factors are slowly varying functions of  $x_{j'j}$  where  $x_{j'j} = E/\Delta E_{j'j}$  is the energy difference between a perturbing level  $j'$  and the perturbed initial/upper (final/lower) level  $j$ .

- The atomic matrix elements need often to be obtained from *ab-initio* Hartree-Dirac-Fock computations, and the summation over the levels is obtained by making use of the table by Moore (1958).

### 13.3.d. Atomic electron-momentum densities

#### Definition & notations:

- For a given atomic level  $(\alpha\mathbb{J})$ , the (radial electron) momentum density  $I(p; \alpha\mathbb{J})$  and the one-electron momentum density  $\Pi_{n\kappa}(p; \alpha\mathbb{J})$  and is given by (Koga and Thakkar, 1996)

$$I(p; \alpha\mathbb{J}) = 4\pi p^2 \Pi(p; \alpha\mathbb{J}), \quad \Pi(p; \alpha\mathbb{J}) = \frac{1}{4\pi p^2} \sum_{i=1}^N \langle \psi_\alpha | \delta(p - p_i) | \psi_\alpha \rangle.$$

- The radial one-electron momentum density  $I$  is used to calculate the corresponding **moments of the momentum density**

$$\langle p^k \rangle = \int_0^\infty dp p^k I(p; \alpha\mathbb{J}), \quad -2 \leq k \leq 4$$

- These moments are often applied in:

- density functional theory: since  $\langle p \rangle / \pi$  is close to the Dirac-Slater exchange energy;
- x-ray crystallography: since  $\langle p^3 \rangle$  is roughly proportional to the initial value of the so-called Patterson function
- Compton profiles: since  $J(q) = \frac{1}{2} \int_{|q|}^\infty dp p^{-1} I(p)$  is twice the peak height of the isotropic Compton profile.



# 14. Beams of light and particles

## 14.1. Helmholtz wave equation

### Propagation of light in free space:

- **Helmholtz wave equation:** If we consider the propagation of light in free space, the Maxwell equations simplify and the spatial structure of their solution satisfy the well-known **Helmholtz wave equation**, an elliptic partial differential equation

$$\nabla^2 u(\mathbf{r}) + k^2 u(\mathbf{r}) = 0.$$

This equation follows from the (full) time-dependent wave equations due to the **separation of variables**.

- **Harmonic solution of the Helmholtz equation:**

$$u(\mathbf{r}) = C_1 e^{i\mathbf{k}\cdot\mathbf{r}} + C_2 e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad k = |\mathbf{k}| = \frac{\omega}{c}.$$

- The solution in time is a linear combination of sine and cosine functions with angular frequency  $\omega$ , while the form of the spatial solution of the Helmholtz equation depends rather sensitively on the given boundary conditions.
- **Vector potential of optical beams:** There exist various expressions to represent the vector potential of optical beams of different kind and spatial structure, and which are solutions of the Helmholtz equation. These vector potentials represent different spatial structures and phases.
- Below, several of these solution are provided for different beams in terms of the (scalar) amplitudes of the corresponding light fields.
- **Synonym notions of vortex beams:** helically phased light beams; optical vortex beams with a field dependence  $e^{im\varphi}$ , ... .

### Paraxial approximation to the Helmholtz equation:

- **Paraxial approximation:** The Helmholtz equation still represents a complicated partial differential equation; in the science of optics, one often has well-defined paraboloidal waves or Gaussian beams in which the field change along the propagation direction is small compared to the change in perpendicular direction;  $\partial u / \partial z \ll \partial u / \partial x, \partial u / \partial y$ .
- For these conditions, the Helmholtz equation simplifies to

$$\nabla_{\perp}^2 u(\mathbf{r}) + 2ik \frac{\partial u}{\partial z}(\mathbf{r}) = 0.$$

- **Conditions for the paraxial approximation:** The restrictions upon the variation of the amplitude function  $u$  is often also written in the form

$$\left| \frac{\partial u}{\partial z} \right| \ll |k u| \quad \text{and} \quad \left| \frac{\partial^2 u}{\partial z^2} \right| \ll |k^2 u|.$$

- The paraxial approximation is obtained if the ansatz  $\psi(\mathbf{r}) = u(\mathbf{r}) e^{ikz}$  is used in the Helmholtz equation and if the term  $\sim \frac{\partial^2 u}{\partial z^2}$  is neglected, when compared with  $\sim \frac{\partial \psi}{\partial z}$ .

## 14.2. Symmetries of light beams

### 14.2.a. Orbital and spin angular momentum

#### Angular momentum of photons:

- **Angular momentum of photons:** Following Maxwell's theory, the angular momentum quantum numbers of the photon are integers [in units of the Planck constant  $\hbar$ ] in the usual three-dimensional settings. For the propagation of light in reduced dimensions, in contrast, photons can also have some half-integer total angular momentum. Such an half-integer quantization of the total angular momentum is known from the quantum Hall effect and can be measured by using noise measurements. Therefore, new forms of quantization arises for photons in a beam, similar as known for electrons in reduced dimensions, .
- **Applications of the angular momentum of photons:** The angular momentum of photons may cause various optomechanical effects in optical trapping as well as with the manipulation of – microscopic and mesoscopic – particles. This angular momentum can be utilized also to remotely detect rotations of light in astronomy at radio-frequencies. In QIP, the angular momentum of light is utilized in order to create high-dimensional entanglement, quantum dense coding or for the identification of different objects.
- **Jones vector:** For a paraxial beam, the two-component complex vector field  $\mathcal{E}(t)$  generally describes the amplitudes of both polarizations ( $\mathcal{E}$ -field) in the plane perpendicular to the beam axis. For a helicity basis and the use of polar coordinate  $(\rho, \varphi)$  in this plane, the angular momentum (AM) operators can generate only rotations of the field around the beam axis. For a paraxial beam, this AM operator includes the  $3 \times 3$  Pauli matrix  $s_z = \hbar \sigma_z$ , which rotates the polarization direction homogeneously across the beam, and the projection of the orbital angular momentum  $l_z = -i\hbar \frac{d}{d\varphi}$ , which rotates the spatial beam profile but leaves the polarization unchanged otherwise. Both of these rotations keep the light field ( $\mathcal{E}$ -field) transverse to the beam propagation so that the projections of the spin and orbital angular momenta are conserved independently.
- **Photon propagation in 3 dimensions:** The free (3-dimensional) propagation of photons follows Maxwells equations and, hence, only the total angular momentum  $\mathbf{j} = \mathbf{l} + \mathbf{s}$  and its projection upon the quantization axis  $j_z = l_z + s_z$  is conserved owing to the rotational invariance of the equations.
- **Measurement of the photon's angular momentum:** The angular momenta of photons can be measured, for instance, by means of a Mach-Zehnder interferometer, quite independent of whether the AM is of type spin, orbital or total angular momentum. For this, the eigenstates of the light field, associated with the given AM operator, must pick up a phase factor by passing through the interferometer. This technique can be generalized also for half-integer and even rational eigenvalues of the AM operator if proper wave plates and prism are applied, such that the spatial and spin components of the light field rotates properly (Ballantine *et al.*, 2016). For example, a half-wave plate reverses

the sign of the spin quantum number  $\lambda = \pm 1$  but does not affect the orbital angular momentum and, hence, results in a torque of  $2\hbar\lambda$  per photon. In contrast, an ideal polarization-preserving Dove prism leads to an inversion of orbital angular momentum and results in a torque of  $2\hbar\ell$  per photon (Ballantine *et al.*, 2016).

### Beams with well-defined OAM:

- **Photons from twisted (OAM) beams:** For a beam with well-defined (projection of the) orbital angular momentum, the relevant quantum numbers are the eigenvalues [in units of  $\hbar$ ] of the spin and orbital angular momentum operators,  $l_z$  and  $s_z$ , respectively. While the spin quantum number  $\lambda = \pm 1$  characterizes the circular polarization of the beam, the orbital quantum number  $\ell = 0, \pm 1, \pm 2, \dots$  typically characterizes the phase  $e^{i\ell\varphi}$  of the spatial part of the light field. For paraxial beams, then, the conservation of the (projection of the) total angular momentum,  $j_z = l_z + s_z$  still ensures integer eigenvalues (Ballantine *et al.*, 2016).
- The conservation of the total angular momentum  $j_z = l_z + s_z$  follows from the rotational symmetry of the Maxwell equations. Since this symmetry is no longer fulfilled for a light beam with a given propagation direction, only the angular momentum (operator) as associated with the propagation of photons in the 2-dimensional cross section of the beam will be conserved owing to the Noether theorem. This angular momentum operator then just generates rotations of the beam around the propagation direction. Moreover, this *restricted* symmetry leads to a new form of total angular momentum with either half-integer or even rational eigenvalues. This quantization of the light field of optical beams can be verified also experimentally by analyzing the noise in the total angular momentum current (Ballantine *et al.*, 2016).
- **Photons from twisted (OAM) beams:** The total angular momentum operator  $j_z$  generates simultaneous rotations of the polarization *and* the spatial part of the light field, although generally through different angles. However, this projection of the total angular momentum is only conserved, e.g. a good quantum number, if the field can be (completely) expanded into eigenfunctions of  $j_z$  and if these eigenfunctions are, up to a phase factor, invariant under the associated rotations. For a monochromatic beam, the solutions must then fulfill the eigenvalue equations

$$(l_z + \gamma s_z) \mathcal{E} = j_z^{(\gamma)} \mathcal{E}, \quad \mathcal{E} = c_1 e^{i\ell_1\varphi} \mathbf{e}_1 + c_{-1} e^{i\ell_2\varphi} \mathbf{e}_{-1}$$

where  $\mathbf{e}_1 \mathbf{e}_{-1}$  are the polarization (unit) vectors in the helicity basis. Moreover, the radial dependence of these eigenmodes is *irrelevant* and omitted from the notation. Since the  $\mathcal{E}$  should be unchanged by a complete rotation  $(2n\pi)$ , both  $\ell_1, \ell_2$  must be integer. Since all modes are simply superpositions of two states with definite spin and orbital angular momenta, the gyroscopic factor  $\gamma$  and the eigenvalue

of the total angular momentum operators are given by

$$\gamma = \frac{\ell_2 - \ell_1}{2}, \quad j^{(\gamma)} = \frac{\ell_2 + \ell_1}{2}$$

### 14.2.b. Torus-knot angular momentum

#### Coordinated rotations (CR) of light fields:

- **Coordinated rotations (CR) of light fields:** These rotations describe symmetry transformations in which the spatial component of the light field is rotated by some azimuthal angle  $\phi_o$  around the beam axis ( $z$  axis), while the electric-field vector (polarization) is rotated by the angle  $\gamma \phi_o$ . Here  $\gamma$  is generally referred to as **gyroscopic factor** or **coordination parameter**.
- **Coordinated rotations (CR) of light fields:** These symmetry operations are generated by the linear combination of the OAM and SAM projection operators,  $j_z^{(\gamma)} = l_z + \gamma s_z$ , and whose (eigen-) values are independently conserved only within the paraxial regime. For paraxial beams, therefore, not only the eigenvalues  $\ell$  and  $\lambda$  are good quantum numbers but also the **torus-knot angular momentum**  $j^{(\gamma)}$ , although these values need no longer to be integer. The coordinated rotations are sometimes said to induce Möbius-stripe topologies.
- **Gyroscopic factor:** For monochromatic light, the gyroscopic factor  $\gamma$  can take only integer or half-integer values and can be mathematically related to the topology of a Möbius strip. For bichromatic fields, in contrast, the gyroscopic factor  $\gamma$  can take all rational values, at least in principle.
- **Monochromatic bicircular fields:** For monochromatic light, the gyroscopic factor  $\gamma$  for a coordinated rotation of the light field must be either integer or a half-integer, since the polarization ellipse of the overall beam coincides with itself only for a rotation of  $n\pi$  after each half-cycle,  $\gamma \propto n/2$ . However, this restriction does not apply to general electromagnetic fields. For bicircular fields, of course, only bichromatic superpositions need to be considered in order to analyze all the possible coordinated rotations for counter-rotating bicircular fields.
- **Symmetries of the electric-field:** Even for a monochromatic beam, the real-valued electric field  $\mathcal{E}(\mathbf{r}, t) = \Re(\mathcal{E}^{(\text{complex})} e^{-i\omega t})$  is generally not an eigenstate of the torus-knot angular momentum operator (symmetry operator). A well-defined TKAM can only be assigned if the

optical field fullfills the combined symmetry and time-translation operation of a coordinated rotation (Pisanty *et al.*, 2019)

$$R(\gamma\alpha) \mathcal{E}(R^{-1}(\alpha) \mathbf{r}, t) = \mathcal{E}(\mathbf{r}, t + \tau\alpha),$$

and where  $\tau$  [time] is a constant and  $R(\alpha)$  a  $2 \times 2$  rotation matrix for a rotation by the angle  $\alpha$  of the coordinates perpendicular to the beam axis.

### Beams with well-defined torus-knot angular momentum:

- **Beams with well-defined torus-knot angular momentum:** Pisanty *et al.* (2019) showed that the eigenvalues  $j^{(\gamma)}$  of the torus-knot angular momentum, known also as the **torus-knot topological charge**, are conserved for beams with a properly defined gyroscopic factor  $\gamma \in \mathbb{Q}$ . This topological can help classify the high-harmonics as generated from such bichromatic and bicircular beams. Since TKAM beams are invariant under coordinated rotations for the associated coordination factor  $\gamma \in \mathbb{Q}$ , the non-linear HHG process will preserve also the torus-knot topological charge, in addition to the conserved charges of the OAM and SAM.
- **Beams with well-defined TKAM:** These beams are not only invariant under coordinated rotations but also associated with a *combined* angular momentum operator  $j_z^{(\gamma)} = l_z + \gamma s_z$  of the (projections of the) orbital  $l_z$  and spin  $s_z$  angular momentum operators with regard to the beam axis. In the paraxial approximation, both the OAM and SAM (projections) are conserved and can be measured independently.
- **Symmetry classification of torus knots & Lissajous figures:** These knots can be characterized by two indices, namely the **symmetry order  $m$  of the (polarization) Lissajous figure** itself as well as the **spatial rotation number  $n$** , how often this Lissajous figure rotates if one goes once around the beam axis within the cross section of the beam. For each symmetry order  $m$ , the spatial rotation number  $n$  characterizes the spatial topology of the optical field (beam).
- **Construction of the torus:** From the Ferris-wheel diagram, the topology of a torus can be immediately read off if one follows the tips of the tre-foild and fold this together after going once around the beam axis. This twists the  $m$  tips of the tre-foil  $n$  times around and can be understood as  $m$  lines (symmetry order) on a torus that crosses its – inner – equatorial plane at  $n$  **torus knots** (spatial rotations). A similar analysis can be made for the eigenvalues of the torus-know angular momentum operator.
- **Torus-knot angular momentum:** Because of the algebraic identification of beam topology and the operator for a coordinates rotation, we can refer to the subgroup generator  $j^{(\gamma)}$  as the torus-knot angular momentum (TKAM). The name of this (formal) angular momentum is derived from the close relation of the generated coordinated rotation and the topology of the torus.

- **Concept of torus knot:** This concept appears in different optical situations, for instance, for generating special optical vortices (or so-called C-lines) and field lines. However, neither the torus nor the knots with its equatorial plane does exist as real-space 3D object for a given beams, although this concept help characterize the topology of beams with regard to their properties such a as paraxial, the possible Lissajous-type figures and others.

### $\omega - 2\omega$ bichromatic bicircular beams:

- **$\omega - 2\omega$  bichromatic bicircular fields:** These bichromatic fields with counter-rotating right- ( $\circlearrowright$ ) and left-handed circular ( $\circlearrowleft$ ) polarizations can be characterited by their *two* (well-defined) orbital angular momenta,  $\ell_1$  and  $\ell_2$ , or by just *one* torus-knot angular momentum  $j^{(\gamma)} = j^{(\gamma)}(\ell_1, \ell_2)$ . Indeed, the particular combination of  $(\ell_1, \ell_2)$  OAM uniquely determines the allowed gyroscopic factor  $\gamma$  for which the overall bicircular beam is invariant with regard to a coordinated rotation of the spatial and spin-components of the light beam.
- **TKAM charges of bichromatic beams:** For a bichromatic beam, the two (monochromatic) driving fields must have different TKAM charges in order to fullfill the overall dynamic symmetry of a coordinated rotation as the local phases of the light field depend on the frequencies.
- **$\omega - 2\omega$  bichromatic bicircular fields:** The two frequency components of a  $\omega - 2\omega$  bichromatic and bicircular beam with well-defined OAM have the TKAM quantum numbers  $j_1^{(\gamma)} = \ell_1 + \gamma$  and  $j_2^{(\gamma)} = \ell_2 - \gamma$ . For the  $q$ -t harmonic, this gives rise to the TKAM value  $j_q^{(\gamma)} = q j_1^{(\gamma)}$ , i.e. in a **linear increase of the TKAM with the order  $q$  of the harmonic**. Of course, the orbital angular momenta  $\ell_q$  can be obtained directly from the torus-knot angular momentum  $j_q^{(\gamma)}$ , and if the assigned (right- and left-handed) polarization of the  $\omega - 2\omega$  incident beam, e.g.  $\text{LG}_{\ell_1, p_1}^{\omega \circlearrowright} \oplus \text{LG}_{\ell_2, p_2}^{2\omega \circlearrowleft}$ , is taken into account.
- **$\omega - 2\omega$  bichromatic bicircular fields with  $\ell_1 = \ell_2 = 1$ :** For  $\text{LG}_{\ell_1, p_1}^{\omega \circlearrowright} \oplus \text{LG}_{\ell_2, p_2}^{2\omega \circlearrowleft}$  bicircular beam, one finds:  $j_1^{(\gamma)} = 2/3$ ,  $j_q^{(\gamma)} = 2/3 q$ .
- **$\omega - 2\omega$  bichromatic bicircular fields:** Counter-rotating circularly polarized beams at different frequencies help construct beams of light that are **invariant under coordinated rotations** for quite arbitrary rational gyroscopic factors  $\gamma$ . This additional freedom of bichromatic field for choosing a well-defined TKAM arise from the higher internal symmetry of these bichromatic superpositions. It was shown that these beams can be classified by means of the topology of a torus knot and, more specifically, by the eigenvalues  $j^{(\gamma)}$  of a (so-called) torus-knot angular momentum (operator)  $j_z^{(\gamma)} = l_z + \gamma s_z$ .
- **$\omega - 2\omega$  bichromatic bicircular fields:** These beams forms so-called **bicircular trefoil-shaped Lissajous figures**.
- **$\omega - 2\omega$  Bichromatic bicircular fields:** The tre-foil polarization figure of these beams rotates smoothly when one goes once around the beam axis (in the plane perpendicular to it). This can be read off immediately from a so-called **Ferris-wheel diagram** which display the Lissajous figure at different angles  $\varphi$  in the cross section of the beam. From such figures, it can be seen also that the internal rotation of the Lissajous figure induces a Möbius-strip topology to the polarization.

- $\omega - 2\omega$  bichromatic bicircular fields: The concept of monochromatic bicircular fields can be generalized towards bichromatic bicircular fields which possess a high symmetry order  $m$  in their (polarization) Lissajous figures. For a  $\omega - 2\omega$  bichromatic bicircular beam with a right-circularly polarized beam component at fundamental frequency  $\omega$  and a left-circularly polarized second harmonic, for example, the fundamental component rotates counterclockwise by  $120^\circ$ , while the  $2\omega$  component rotates clockwise by  $240^\circ$ . Therefore the polarization (electric-field vector) at all spatial points in the beam is symmetric with regard to a rotation by  $2\pi/3 = 120^\circ$ .
- $r\omega - s\omega$  bichromatic bicircular fields: A  $r\omega - s\omega$ , bichromatic beam with coprime numbers  $r, s$  generally has a  $(r + s)$ -fold symmetric Lissajous figure.
- $r\omega - s\omega$  bichromatic bicircular fields: For such a bichromatic beam with orbital angular momenta  $\ell_r$  and  $\ell_s$  of the right- and left-circularly polarized field components, the winded tips still confine to the surface of a torus, from which the two characteristic symmetry numbers can be read off: (1) the symmetry number  $m = r + s$  as number of points that appear with fixed angle  $\varphi_o$  in the cross each cross section of the torus and that is equal to the lobes of the Lissajous figure; (2) a signed (spatial) number  $n = r\ell_r - s\ell_s$  for the spatial symmetry. While  $|n|$  denotes the number of crossings in the – inner – equatorial plane of the torus, the characterizes the phase changes of the right- and left-circularly polarized beam components.



## 14.3. Light beams

### Light beams:

- **Characterization and properties of beams:** In studying light-matter interactions, **light beams** play a major practical role and, hence, their characterization and properties are very important in order to understand the details of the interaction.
- **Beams from applications:** Light beams are usually formed when the em field from a given source is projected by filters and blends into a beam. In some lighting devices, lamps or parabolic reflector are used to produce an artificially light beam with a more or less large divergence (for example, car headlights, spotlights, ect.).
- **Experimental beam parameters:** The geometry and behavior of a Gaussian beam are governed by a set of beam parameters which are defined slightly different for different kinds of beams but which are often used to characterize the beams. These beam parameters include:
  - **Beam width:** There are over five definitions of beam width.
  - **Beam quality:** Quantified by the beam quality parameter, M2.
  - **Beam divergence:** This is a measure of how the beam spreads with distance with regard to the focus plane.
  - **Beam profile:** A beam profile is the 2D intensity plot of a beam at a given location along the beam path. A Gaussian or flat-top profile is often desired for many applications. The beam profile indicates nuisance due to high-order spatial modes in a laser cavity as well as hot spots in the beam.
  - **Beam astigmatism:** A beam is called **astigmatic** when the vertical and horizontal focus of the beam is placed at different locations along the beam path.
  - **Beam wander or jitter:** The amount by which the centroid or peak value of the beam profile moves with time.

### Twisted (vortex) light beams:

- Charles Darwin (1932; 1887-1962) was one of the first who worked on **light with a spatial structure of the phase**.
- For circularly-polarized plane-wave light, the photons carry a projection of the angular momentum  $\Delta L_z = \pm\hbar$  upon the propagation direction.
- **Polarization state of a light beam:** In 1892, Poincare showed that the state of polarization of a light beam can be described as a point on the surface of a unit sphere now known as the Poincare sphere.

### 14.3.a. Gaussian beams

#### Characterization and use:

- **Gaussian beam:** In optics, a Gaussian beam is a beam of electromagnetic radiation whose **transverse electric field amplitude and, hence, its intensity distributions are approximately described by some Gaussian distribution.**
- Both, plane waves and Gaussian beams are solutions of the Maxwell equation *and* the homogeneous wave equation; they both generally possess a **polarization** but can be readily described in terms of complex amplitudes.
- **Complex-valued electric field amplitude  $u(\mathbf{r})$ :** In a Gaussian beam, the electric field amplitude

$$u(\rho, z) = u_0 \frac{w_0}{w(z)} \exp\left(\frac{-\rho^2}{w^2(z)}\right) \exp\left(-ikz - ik\frac{\rho^2}{2R(z)} + i\zeta(z)\right)$$

obeys the paraxial Helmholtz equation. This amplitude is sufficient in order to describe the properties of the beam since the electric field and magnetic field propagate together and obey the same wave equation.

- **Characteristic parameters:** In the definition of the electric-field amplitude above, we have
  - $\rho$  ... radial distance from the center axis of the beam;
  - $z$  ... the axial distance from the beam's narrowest point (the **beam waist**),
  - $k = \frac{2\pi}{\lambda}$  ... the wave number (in radians per meter),  $E_0 = |E(0, 0)|$
  - $w_0 = w(0)$  ... the waist size,
  - $w(z)$  ... the radius at which the field amplitude drops to  $1/e$  and, hence, the intensity to  $1/e^2$  at axis with regard to  $w_0 = w(0)$ ,
  - $R(z)$  ... the radius of curvature of the beam's wavefronts,
  - $\zeta(z)$  ... the Gouy phase shift, an extra contribution to the phase that is seen in Gaussian beams.
- In fact, many lasers emit beams with roughly a Gaussian profile; these beams are often called the TEM<sub>00</sub> fundamental modes of the laser's optical resonator. **Gaussian beams form a widespread model in laser physics.**

### 14.3.b. Vortex beams. Characterization and properties

#### General remarks:

- The recent years have seen a tremendous effort in generating and manipulating vortex beams together with a good number of new or promising applications, including the capture, manipulation and transport of nanoscopic particles (optical tweezer), high-resolution microscopy or for data transmission.

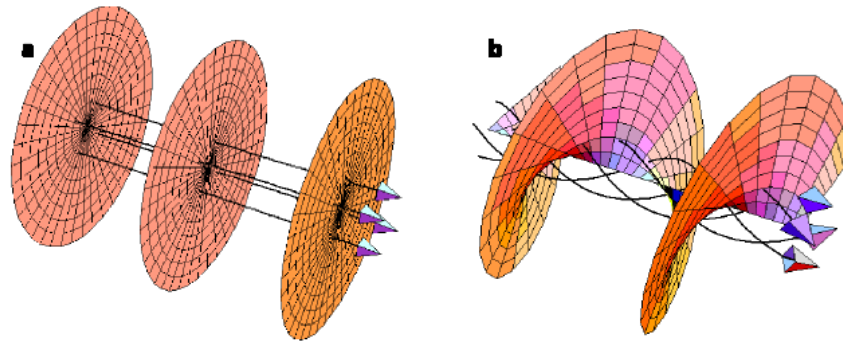


Figure 14.1.: Laser beams usually have planar wavefronts with wavevectors parallel to the beam axis. Beams with helical wavefronts have wavevectors which spiral around the beam axis and give rise to an orbital angular momentum; from Padgett and Allen (2000).

- Twisted photons carry both, spin angular momentum (SAM) as well as orbital angular momentum (OAM) along their propagation direction.
- **Topological charge** The  $z$ -projection of the OAM,  $m$ , is often called the topological charge or the **winding number of the beam**. This charge describes the number of the  $2\pi$  windings of the helical phase around the vortex in one wavelength.
- **Synonym notions of vortex beams:** helically phased light beams; optical vortices with a field dependence  $e^{im\varphi}$ .
- Optical vortex beams are well-known and have been routinely used for the last 20 years; a first demonstration dates back to Durnin *et al.* (1987).
- For optical vortices, charge values of  $m \leq 5000$  have been realized (Shen *et al.*, 2013).
- Reviews on optical vortex beams are given by Allen *et al.* (1999); Franke-Arnold *et al.* (2008), Zhan (2009) and Yao and Padgett (2011).

### Characterization of vortex beams:

- A vortex state of light carries a well-defined projection of the orbital angular momentum (OAM) with respect to the beam axis.
- **Wave functions:**  $\sim e^{im\varphi}$  are eigenfunctions of  $\ell_z = \frac{\partial}{\partial \varphi}$ .
- **Photon field:** For a quantized radiation field, each particle also carries a projection  $m\hbar$  of the OAM, that is part of the total angular momentum. In general, the spin and orbital angular momentum cannot be separated.
- In the paraxial approximation, the spin and OAM longitudinal components of the vortex state can be separated from each other. Beyond the paraxial limit, however, the spin-orbit interaction does not allow a simple separation of the spin and orbital angular momentum.

### Properties of vortex beams:

- For all points in the beam, the ratio between the azimuthal and  $z$ -components of the momentum is found to be  $\ell/k r$ .
- The linear momentum of each photon is given by  $\hbar k$ ; since the azimuthal component of the wavevector is  $m/r$  and is independent of the wavelength, the orbital angular momentum per photon is

$$p = \hbar k \quad \longrightarrow \quad p_\varphi = \hbar k \phi \quad \longrightarrow \quad \ell = r \times p_\varphi = r \times \frac{\hbar k}{r} = m\hbar$$

- However, OAM  $\neq$  SAM, despite the rather similar illustrations in the literatur; in particular, there exist also vortex states for spin-less waves, such as acoustic vortex waves.

### 14.3.c. Vortex beams. Generation

#### Generation of vortex beams with different photon energies:

- For intense, short-wavelength FEL radiation, optical methods can often not be applied due to strong limitations and difficulties in the fabrications of optical surfaces (Terhalle *et al.* 2011, Peele *et al.* 2002).
- **Twisted EUV beams:** Ribic and coworkers (2014) proposed an efficient scheme in order to generate intense coherent and twisted OAM beams in the EUV region. These beams can be realized by means of a seeded FEL, i.e. by using a (seeding) laser pulse with a transverse, staircaselike phase. For this phase pattern, in particular, the diffraction and mode selection drive the radiation profile towards a dominant OAM mode at saturation.
- **Twisted x-ray beams:** Hemsing and coworkers proposed two clever approaches for generating FEL vortex beams within the x-ray region:
  - (i) By using the interaction of an electron beam with a seeded laser within a helical undulator (Hemsing *et al.*, 2011);
  - (ii) by using a so-called echo-enabled harmonic generation (EEHG) scheme, in which two seed lasers and two magnetic chicanes are utilized in order to produce harmonic microbunches of an electron beam with a corkscrew distribution.

#### Generation of vortex beams by pitch-fork holograms:

- The superposition of a regular phase profile with some proper grating already results in a fork hologram that help generate vortex beams.
- Fork-like or pitch-fork holograms are known to diffract the light and to generate beams with OAM. Such holograms can be generated also dynamically by using a spatial light modulator and readily controlled by a computer.
- A pitchfork hologram is obtained adding a twisting and an oblique phase. The width of six  $2\pi$  phase ramps is highlighted.

#### Generation of vortex beams by spiral phase plates:

- A (plane-wave) light beam can acquire a non-zero OAM by crossing a spiral phase plate with an inhomogeneous thickness.
- **Spiral phase plates (SPP):** Such a SPP is a transparent dielectric plate with a thickness that varies as a smooth ramp; this variation in the thickness adds a phase shift to an incident field that increases linear with the azimuthal angle  $\varphi$ .
- **Light field:** If a SPP is placed into the waist of a Laguerre-Gaussian beam with well-defined quantum numbers,  $u_{\ell p}^{\text{LG}}$ , the complex light amplitude just behind the plate can be described by means of a phase-plate operator  $S(m_s, \alpha)$

$$\langle r, \varphi | S(m_s, \alpha = 0) | l, p \rangle = u_{lp}^{\text{LG}}(r, \varphi) e^{im_s \varphi},$$

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and where  $m_s$  is the phase shift per unit angle of the given SPP.

- SPP help explore high-dimensional entanglement with just two detector, while 6 detectors are required by other popular methods in order to prove the entanglement of the OAM degree of freedom for two entangled photons (Oemrawsingh *et al.*, 2004).
- The figure below shows the transformation of a  $\text{TEM}_{00}$  mode into a helical beam.

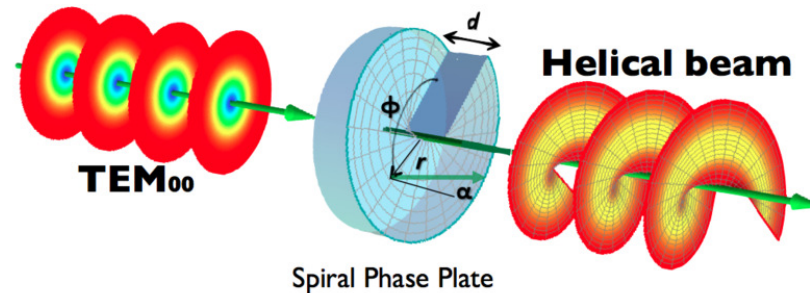


Figure 14.2.: Experimental scheme for generating light orbital angular momentum with spiral phase plates. Taken from Beijersbergen *et al.* (1994).

### Generation of vortex beams by q-plates:

- **q-plate:** A (so-called) q-plate is a device that is realized by means of liquid crystals, polymers or sub-wavelength gratings; this device exploits a change of sign if the polarization of the incoming light is modified.

### Generation of vortex beams by spatial light modulators:

- xxxxx A spatial light modulator (SLM) is an object that imposes some form of spatially varying modulation on a beam of light. A simple example is an overhead projector transparency. Usually when the phrase SLM is used, it means that the transparency can be controlled by a computer. In the 1980s, large SLMs were placed on overhead projectors to project computer monitor contents to the screen. Since then more modern projectors have been developed where the SLM is built inside the projector. These are commonly used in meetings of all kinds for presentations.

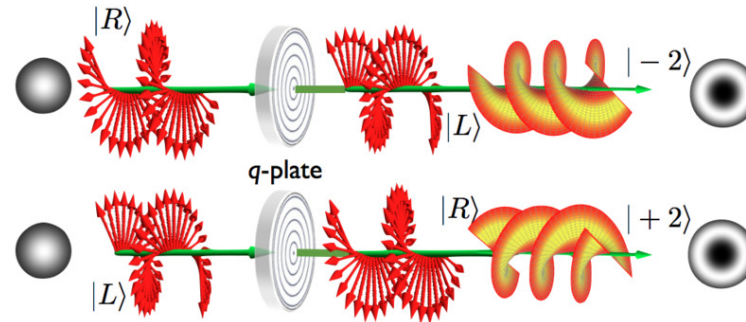


Figure 14.3.: The q-plate effect for left and right-hand circular polarizations.

### Generation of vortex beams by cylindrical mode converters:

- A Hermite-Gaussian beam can be converted into a Laguerre-Gaussian beam with well-defined OAM by using an **astigmatic** system with two well-aligned cylindrical lenses. In this scheme, these lenses are placed at some specific distance in order to introduce a well-defined relative phase between the horizontal and the vertical Hermite-Gaussian beams.

### Generation of vortex beams by helical undulators:

- X-ray vortex beams with photon energies  $\hbar\omega \approx 100$  eV have been generated in a helical undulator by Bahrtdt *et al.* (2013) and Hemsing *et al.* (2013).
- Another interesting approach has been suggested by Ribic and coworkers (2014). These authors proposed to modify the phase mask and to manipulate directly the seeding laser in order to change the transverse properties of the FEL light.

#### 14.3.d. Hermite-Gaussian beams

### Characterization and use:

- **Hermite-Gaussian modes**  $HG_{mn}$ : have a rectangular symmetry and are described by means of two mode indices  $m$  and  $n$ ; these mode indices give the number of nodes in the  $x$  and  $y$  directions respectively.

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- **Hermite-Gaussian modes:** These modes are a convenient description for the output of lasers whose cavity design is not radially symmetric but asymmetric in horizontal and vertical directions.

### 14.3.e. Laguerre-Gauss beams

#### Characterization and use:

- The Laguerre-Gaussian (LG) beams carry an intrinsic OAM like the intrinsic SAM for beams with a circular polarization (Allen *et al.* 1992, 2003). This appeared originally rather surprising as the OAM of LG beams arise from the helical phase distribution about the beam axis, and which coincides also with a phase singularity (Nye and Berry, 1974).
- **Laguerre-Gaussian modes  $u_{\ell p}^{\text{LG}}$ :** For a Laguerre-Gaussian beam with well-defined magnetic and radial quantum numbers  $(m, p)$ , the complex amplitude of the light field in the waist of the beam is defined as in the polar representation

$$u_{\ell p}^{\text{LG}}(r, \varphi) = \langle r, \varphi | m, p \rangle = R_{mp}(r) \Phi_m(\varphi) \quad \text{with} \quad \Phi_m(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}}$$

- **Laguerre-Gaussian modes  $u_{\ell p}^{\text{LG}}$ :** If the problem is cylindrically symmetric, these modes are the natural solution of the paraxial wave equation. They are often written in cylindrical coordinates by using Laguerre polynomials.

### 14.3.f. Bessel beams

#### Characterization and use:

- **Bessel beams:** A Bessel beam refers generally to an electromagnetic field whose amplitude is given by a Bessel function of the first kind. 5
- Although these beams are an idealization, true **Bessel beam are monochromatic and non-diffractive and, hence, do not not diffract and spread out** when they propagate. This behaviour is quite in contrast to other typical optical (or sound) waves if they are focused at some spot.
- Bessel beams are known to be **self-healing if they are obstructed at some point, i.e. they reform to a Bessel beam again further down the beam axis.**



- Pure Bessel modes generally carry a well-defined OAM; in particular, they typically include three components of the topological charge since only the (projection of the) total angular momentum is conserved for these beams. For this reason, the  $z$ -projections of the orbital and spin angular momentum are not defined independently.
- **Bessel modes  $|\kappa, m\rangle$ :** Bessel beams can be written also as a superposition over plane waves with well-defined (fixed) transverse momentum, longitudinal momentum as well as circular polarization

$$\psi(\mathbf{r}) = e^{-i\omega t + i k_z z} |\kappa, m\rangle, \quad |\kappa, m\rangle \propto e^{im\varphi} J_m(\kappa \rho)$$

- **Vector potential:** The vector potential of the Bessel beams is often written as Fourierintegral over Bessel states of different projections of the orbital angular momentum  $a_{\kappa m}(\mathbf{k}_\perp)$ ,

$$\mathbf{A} = e^{-i\omega t} \frac{1}{(2\pi)^2} \int d\mathbf{k}_\perp e^{-i\mathbf{k}\cdot\mathbf{r}} a_{\kappa m}(\mathbf{k}_\perp) \mathbf{e}_{\mathbf{k},\lambda}, \quad a_{\kappa m}(\mathbf{k}_\perp) = \sqrt{\frac{2\pi}{\kappa}} (-i)^m e^{-im\varphi_{\mathbf{k}}} \delta(k_\perp - \kappa)$$

$$\mathbf{e}_{\mathbf{k},\lambda} = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos \vartheta_k \cos \varphi_k - i\lambda \sin \varphi_k \\ \cos \vartheta_k \sin \varphi_k + i\lambda \cos \varphi_k \\ -\sin \vartheta_k \end{pmatrix} \quad \tan \vartheta_k = \frac{\kappa}{k_z}$$

and where  $\mathbf{e}_{\mathbf{k},\lambda}$  are known as polarization (unit) vector and  $\vartheta_k$  as the opening angle of the Bessel beam.

- **Plane-wave expansion:** Of course, every monochromatic plane-waves can be expanded also in terms of Bessel waves as they are both just two different bases in order to describe wave packets

$$e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} = \sum_{m=-\infty}^{\infty} e^{-i\omega t + i k_z z} i^m e^{-im\varphi_{\mathbf{k}}} |\kappa, m\rangle$$

- **Electron-photon interaction operator for Bessel beams:** For (a Bessel beam of) twisted photons, the transition operator reads as:

$$V^{(\text{tw})} = \alpha \mathbf{A}_{\varkappa m_\gamma k_z \lambda}(\mathbf{r}) \mathbf{p}.$$

$$\mathbf{A}_{\varkappa m_\gamma k_z \lambda}(\mathbf{r}) = \int \mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} a_{\varkappa m_\gamma}(\mathbf{k}_\perp) e^{-i\mathbf{k}_\perp \cdot \mathbf{b}} \frac{d^2 k_\perp}{(2\pi)^2}, \quad a_{\varkappa m_\gamma}(\mathbf{k}_\perp) = (-i)^{m_\gamma} e^{im_\gamma \varphi_k} \sqrt{\frac{2\pi}{k_\perp}} \delta(k_\perp - \varkappa).$$

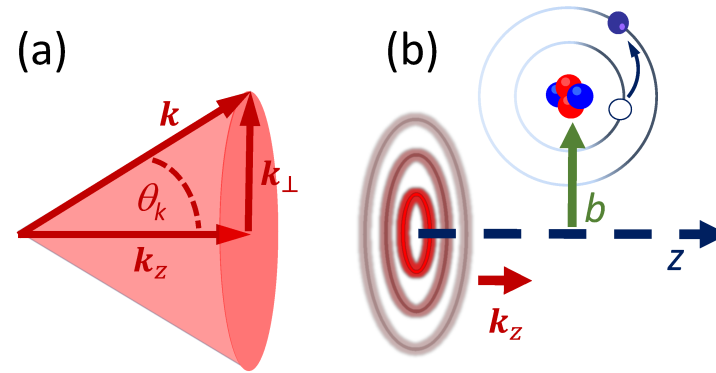


Figure 14.4.: (a) In momentum representation, the twisted light can be seen as a coherent superposition of plane waves. These plane waves with wavevectors  $\mathbf{k}$  are all lying on a cone with (polar) opening angle  $\vartheta_k = \arctan(|\mathbf{k}_\perp|/k_z)$  and with polarization vectors  $\mathbf{e}_{\mathbf{k},\lambda}$  which are perpendicular to  $\mathbf{k}$ . (b) For a given atom, the absorption amplitude depends on the position of the atom in a plane perpendicular to the propagation direction. The position of the target atom with regard to the beam axis is specified by the impact parameter (vector)  $\mathbf{b}$  (c-05-photobeam-interaction.eps).

In this expression, the factor  $e^{-i\mathbf{k}_\perp \cdot \mathbf{b}}$  specifies the position of a target atom within the incident wave-front, and which refers to the complex spatial structure of the Bessel beam.

### 14.3.g. Airy beams

#### Characterization and use:

- **Airy beams:** Similar to Bessel beams, the cross section of an ideal Airy beam has an area of principal intensity and with a series of adjacent, less luminous areas up to infinity. Airy beams can be derived from the Airy integral that was first developed by George Biddell Airy in the 180s in order to explain the optical caustics in a rainbow and elsewhere.
- An Airy beam preserves its shape of intensity during propagation and forms a parabolic curve, quite analogue to the trajectory of a free projectile as seen in a plane perpendicular to the propagation.
- Airy beam are freely accelerating, i.e. they bend to form a parabolic arc as they propagate (Berry and Balazs, 1979; Siviloglou *et al.*, 2007), although the linear momentum remains conserved for these beams since the intensity centroid of an Airy beam forms a straight line.

- Airy beam do also not diffract, i.e. they do not spread out after focussing.

### 14.3.h. Necklace ring beams

#### Characterization and use:

- **Necklace ring beams:** These beams refer to optical vector solitons that consist of incoherently coupled self-trapped ‘necklace’ beams; these beams can carry zero, integer or even some fractional angular momentum.
- Necklace ring beams exhibit a self-stabilizing mutual attraction between different beam components and a quasistable propagation for much larger distances than the corresponding scalar vortex solitons

### 14.3.i. Light beams with non-integer OAM

#### Characterization and use:

- **Beams with non-integer OAM:** These beams refer to structurally propagation invariant light beams carrying non-integer orbital angular momentum (OAM) using Hermite-Laguerre-Gaussian (HLG) modes.

### 14.3.j. Vector beams

#### Characterization and use:

- **Vector beams:** The vector beams need to be described in the product space of the optical SAM and OAM subspaces and are characterized by higher-order Stokes parameters.
- Vector beams exhibit a spatially variant polarization.
- Cylindrical vector beams are axially symmetric solution to the full electromagnetic (vector) wave equation.
- **Generation of vector beams:** These beams can be generated via different active and passive methods.

### 14.3.k. Traktor beams

#### Characterization and use:

- **Tractor beam:** These beams refer to optical fields that help attract one object to another from a distance.
- The concept of tractor beams originates from the novel *Spacehounds of IPC* by E. E. Smith (1931) and by re-coining an earlier ‘attractor beam’, in contrast to other, ‘repulser beams’.
- Tractor beam are defined to use (a negative) nonconservative radiation pressure, that differs from a gradient force, and which is directed towards the source. This generally requires a continuous redirection of momentum flux (Sukhov and Dogariu, 2010, 2011; Chen *et al.* 2011).
- Traktor beams are based on the maximization of forward scattering of light due to interference of different radiation multipoles. It was shown especially that an simultaneous excitation of multipoles is necessary in the particle in order to realize a negative (pulling) optical force.

### 14.3.l. Polarization radiation

#### Characterization and use:

- In electrodynamics, one generally distinguishes **two classes of emitted radiation: bremsstrahlung and polarization radiation**. While bremsstrahlung is produced by accelerated charges, polarization radiation can be emitted by a uniformly moving charge, although only in the presence of a medium.
- In dependence on the given medium or target geometry, one distinguishes various forms of polarization radiation: Cherenkov radiation, transition radiation, diffraction radiation as well as Smith-Purcell radiation.
- **Polarization radiation:** Electromagnetic radiation can be emitted not only by accelerated charges but also due to the motion of magnetic moments and higher multipoles. Until the present, however, this (so-called) polarization radiation has never been verified experimentally for any frequency of light.
- The main experimental difficulty for approving this radiation refers to the (very) small current of a magnetic moment that is suppressed by  $\sim 10^{-5}$  w.r.t. a corresponding charge current.
- A pure quasi-classical treatment of the polarization radiation is inconsistent since quantum corrections are of the same order for this type of radiation phenomena.

### 14.3.m. Manipulation of optical beams

#### Optical elements:

- **Dove prism:** This is a (type of) reflective prism that can be used to invert a given image. These prisms are often shaped from a truncated right-angle prism.
- If a beam enters the prism at one of the sloped faces and parallel to the longitudinal axis, it undergoes total internal reflection at the inside of the longest (bottom) face, and then leaves the prism at the opposite sloped face. Therefore, any image that passes through the prism is flipped (mirrored) and also also inverted but not laterally transposed.
- **Hologram:** A hologram usually refers to a three-dimensional image of an object that is created by holography, i.e. an optical technique for recording and reconstructing the amplitude and phase distributions of a coherent wave. Holography is often used to produce three-dimensional images or holograms.
- **Half-wave plate:** A wave plate, sometimes known as a retarder, designates an optical device that alters the polarization state of a light wave. While a half-wave plate shifts the polarization direction of linearly polarized light, a quarter-wave plate converts linearly-polarized light into circularly-polarized light and vice versa. Quarter-wave plate can be used also in order to produce elliptically-polarized light.

#### Mach-Zehnder interferometers:

- These interferometers make use of two separate beam splitters in order to split and recombine an input beam but from which the beam can emerge and detected at two outputs. The optical path lengths in the two arms of the interferometer may be nearly identical or may be different in order to introduce an extra delay path.
- If a beam is sent through the interferometer, the optical powers at the two outputs depends on in practice sensitively on the the precise difference in optical arm lengths as well as on the wavelength of the light.
- The Mach-Zehnder interferometer was first developed by Ludwig Mach and Ludwig Zehnder.

### 14.3.n. Optical forces of vortex beams

#### Optical forces:

- :
- A positive radiation force is relatively intuitive and occurs in the backscattering or absorption of the forward-directed momentum of a beam; it was first reported already by Nichols and Hull (1903).

### 14.3.o. Application of optical (vortex) beams

#### Remarks:

- Different applications of optical vortex beams and the angular momentum of light have been envisaged and are currently explored in research laboratories, although no real commercial application are yet known.
- **Fields of applications:** Cold atoms, trapped nanoparticles, micro manipulation and detection of spinning objects, remote measurement of the rotation of mesoscopic particles, entanglement and quantum information, optical data transmission, interaction with matter, microscopy and astrophysics.
- **X-ray magnetic circular dichromism** By using different OAM states in the measurements, the dipole and quadrupole contributions to the circular dichroism signal can be separated from each other.

#### Optical tweezer:

- **Optical tweezer:** These tweezers usually refer to single-beam gradient force trap that are realized by some highly focused laser beam. These focused beams provide an attractive or repulsive force on nano- or mesoscopic dielectric objects.
- Optical tweezers have been utilized to manipulate the orientation of particles or particle aggregates.
- In optical tweezers, the forces are typically on the order of piconewtons; they depends on the **refractive index** of the object.

### Optical phasors:

- **Phasor:** A complex constant in **complex wave notation** that encapsulates the amplitude; sometimes known also as sinor or complexor.

### Applications in quantum information theory:

- The orbital-angular momentum (OAM) of light has recently emerged as a promising candidate for quantum and classical information systems.
- In OAM beams, the spatial degrees of freedom provide a high-dimensional alphabet to quantum information processing which enables one to use qunits instead of qubits.
- **Quantum information encoding,** Higher-dimensional quantum information encoding has been discussed in the literature for possible future applications in quantum cryptography or quantum computations. The discrete, unbounded state-space of OAM promises in particular vastly enhanced data rates as well as an increased tolerance to eavesdropping in quantum communication.

## 14.4. Electron beams

### Electron beams:

- Electron beams are quite frequently applied in physics; such beams may refer, for instance, to some stream of electrons as obtained from a betatron. Electron beams are generally generated either by heat (thermionic emission), bombardment of surfaces with charged atoms or particles (secondary electron emission), or by means of strong electric fields (field emission).
- Electrons may be collimated by holes and slits. Because they are electrically charged, they can also be deflected, focused or accelerated by electric and magnetic fields.

### Twisted electron beams:

- Apart from twisted (vortex) solutions of the Dirac equation, a quasis-relativistic wave equation for twisted relativistic electron in arbitrary electric and magnetic fields can be derived by using a Foldy-Wouthuysen transformation.
- The interaction of twisted (vortex) electrons with electric and magnetic fields can be described quite readily, based on Lorentz transformations.

### 14.4.a. Gaussian electron beams

#### Characterization and use:

- It has been demonstrated experimentally that a Gaussian-profile model better describes the (equilibrium) electron beam than a beam with a uniform-profile model.

### 14.4.b. Vortex electron beams

#### General remarks:



- Electron vortex beams were first realized experimentally by Uchida and Tonomura (2010), Verbeeck, Tian and Schattschneider (2010) and McMorran *et al.* (2011). Uchida and Tonomura, in particular, generated an electron vortex beams with (electron) energy  $E = 300$  keV, a projection of the OAM with  $m \lesssim 100$  and by focusing the electron beam to a spot size of  $1.2$  Å.
- Vortex electrons can generally carry a rather large intrinsic projection of the orbital angular momentum (OAM)  $m \sim 100$  with respect to their propagation direction. Therefore, the magnetic moment of vortex electrons  $\mu \approx m \mu_B$  is similarly large, when compared with the Bohr magneton  $\mu_B$  due to the spin motion of the electron.
- The magnetic moment of twisted electrons due to their OAM comes in addition to the known magnetic moment due to the spin motion.
- Since Vortex electrons are sensitive to external magnetic fields, they can be utilized to probe atomic magnetism and, thus, open novel opportunities for electron microscopy.
- While vortex photon beams have been created and routinely used for several decades already, the vortex states of electrons and charged particles is a presently emerging field.

#### 14.4.c. Generation of vortex electron beams

##### Generation of vortex electron beams with different energies:

- Indeed, several new ideas were proposed in the literature in order to create electron vortex beams experimentally.

##### Generation of vortex electron beams by undulators:

- **Electrons in a helical modulator:** cf. Figure 14.4.c

##### Generation of vortex electron beams by transmission electron microscopes:

- Voloch-Bloch *et al.* (2013) generated Airy electron beams by using a holographic technique within a transmission electron microscope. Both, self-bending and self-healing features were observed in the experiments if the beam was obstructed by a small object during its propagation.

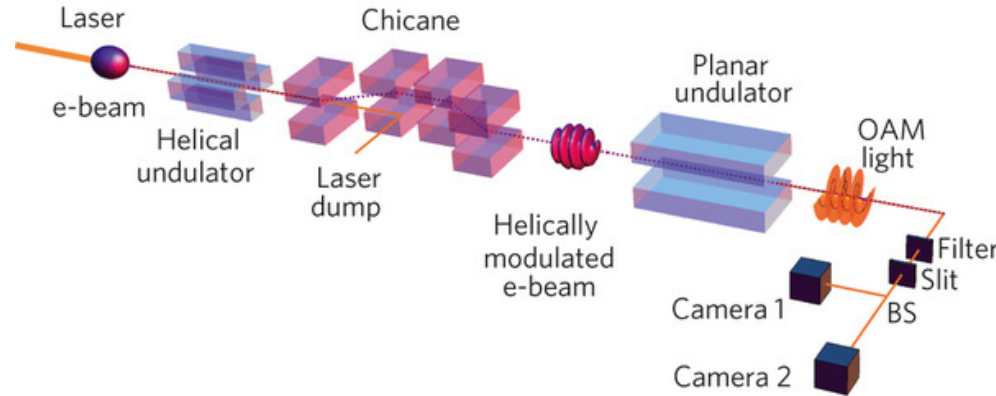


Figure 14.5.: An unmodulated relativistic electron beam interacts with a linearly polarized laser in a helical undulator, which gives the electrons an energy kick that depends on their position in the focused laser beam.

### Generation of vortex electron beams by holograms:

- Grillo *et al.* (2014) generated an electron Bessel beam by the diffraction of electrons at a nanoscale phase hologram. This hologram imposed a conical phase structure upon the electron wave-packet. The so obtained beams propagated for 0.6 m without measurable spreading and could reconstruct also its intensity distributions, if these beams were partly obstructed by an obstacle.

#### 14.4.d. Bessel electron beams

##### Characterization and use:

- Quasi-Bessel beams can be obtained within a good approximation, while it is not possible to generate an ideal Bessel beam because they are not normalizable in their total intensity,
- Wave function of a Bessel electron: In cylindrical coordinates  $r, \varphi, z$ , the wave function of electrons in a Bessel beam is given by

$$\psi(r, \varphi, z; t) = J_m(\kappa r) e^{i m \varphi} e^{-i(\omega t - k_z z)},$$

where  $J_m(x)$  is the  $m$ -th order Bessel function of the first kind and  $\kappa$  and  $k_z$  denote the transverse and longitudinal components of the wave vector, respectively.

- **Probability-density distribution of Bessel electron beams:** This wave function give rise to a probability-density distribution  $\mathcal{P} = \psi \psi^+$  that is independent of  $z$  and  $t$ :

$$\mathcal{P}(r, \varphi, z; t) = \mathcal{P}(r, \varphi, 0; 0) = [J_m(\kappa r)]^2.$$

- This shows that the **probability-density distribution is stationary in the transverse plane and independent of where this plane is taken.**
- The energy of the electron  $E = \hbar \omega$  defines the de Broglie wave length and the modulus of the wave vector by

$$k^2 = k_r^2 + k_z^2 = \frac{2m\omega}{\hbar} = \left( \frac{2\pi}{\lambda_{dB}} \right)^2.$$

- For Bessel beams with a nonzero  $m$  value, the electrons possess a non-uniform helical phase front with  $m$  dislocations in the phase, and where the handedness of the phase front is defined by the sign of  $m$ .
- **Current density of electron Bessel beam:** This current density circulates azimuthally in the transverse plane and introduces an (projection of the total) orbital angular momentum of  $m\hbar$  per electron.
- An Bessel electron beam with a nonzero  $m$  value possess exhibit a shape with multiple rings and with a null probability density at the origin.
- Bessel electron beams can be represented also as a coherent superposition of conical plane waves along a closed ring (circle).

#### 14.4.e. Airy electron beams

##### Characterization and use:

- Airy electron beams can be generated by diffraction of electrons through a nanoscale hologram, which imprints a cubic phase modulation on wavefunction of the electrons in the transverse plane.

#### 14.4.f. Application of twisted electron beams

##### Remarks:

- The scattering of twisted electrons can provide insights into the magnetic structure of the target materials.
- Beams with non-zero OAM helped explore the vacuum Faraday effect as well as Larmor and Gouy rotations.
- Bessel electron beams have been used in electron microscopy.

# 15. Symbolic evaluation of expressions from Racah's algebra

## 15.1. Racah's algebra in atomic and many-body physics

### 15.1.a. Advantages of using Racah's algebra

#### Goals and use of Racah's algebra:

- The theories of angular momentum and spherical tensor operators play a significantly role in atomic and nuclear physics, and at several places elsewhere. These two theories lead to algebraic expressions which are usually written in terms of generalized Clebsch-Gordan coefficients and/or Wigner  $3n-j$  symbols as well as the Wigner rotation matrices and spherical harmonics. Although the evaluation and simplification of such expressions is in principle a straightforward task, it can become extremely cumbersome, if more complex systems or physical scenarios are considered.
- Indeed, the study of open-shell atoms and nuclei quickly raises the question how the rotational symmetry of (closed) systems, i.e. the conservation of angular momentum, can efficiently be exploited in understanding many-particle systems. After the pioneering work by Wigner in the late thirties, Racah (1941, 1942, 1943) developed a powerful machinery, known as Racah algebra, to deal with such systems, and which is one of the fundamental concepts in the (quantitative) treatment of many-particle systems.
- In many-particle physics, an explicit re-coupling of the angular momenta is often required due to the use and sequence of different coupling schemes. In general, such recoupling transformations are written in terms of recoupling coefficients that need to be evaluated over and over again.
- **Spin-angular integration of many-particle matrix elements** In atomic and nuclear structure theory, the evaluation and spin-angular integration of many-particle matrix elements is typically based on standard quantities like the matrix elements of the unit tensor, the (reduced) coefficients of fractional parentage as well as a number of other reduced matrix elements for different products of creation and annihilation operators. These quantities arise rather frequently in both, configuration interaction approaches and in the derivation of perturbation expansions for many-particle systems by using symmetry-adapted configuration state functions.

## 15. Symbolic evaluation of expressions from Racah's algebra

- **Theory of angular momentum** In the treatment of quantum many-particle systems, the **theory of angular momentum offers two crucial advantages**: (i) The reduction of complicated many-electron matrix elements to a rather small number of *standard quantities* and (ii) an elegant and very powerful calculus which help simplify and evaluate sophisticated expressions.
- **Racah algebra techniques**: Owing to these advantages, the techniques from the theory of angular momentum, shortly known also as Racah algebra techniques (Racah 1941, 1942, 1943), have been utilized in a large number of applications and in quite different field of many-particle physics (Wigner 1959, Varshalovich *et al.* 1988).
- **Racah expressions**: With the symbolic evaluation of expressions from Racah's algebra, we wish to focus on the algebraic transformation of **(Racah) expressions** such as:

$$\begin{aligned} \text{Racahexpr} := & \sum_{j_1, j_2, l_1, \dots} (-1)^{2j_1-j_2+\dots} j_1^{3/2} [j_2] \dots \begin{pmatrix} \cdot & \cdot & j_1 \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} j_1 & j_2 & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \left\{ \begin{matrix} \cdot & j_3 & \cdot \\ j_1 & \cdot & \cdot \\ J & \cdot & j_2 \end{matrix} \right\} \dots \\ & \times \int d\Omega_1 Y_{\ell_1 m_1}(\Omega_1) Y_{\ell_2 m_2}(\Omega_2) \int d\beta d_{p_3 q_3}^{j_3}(\beta) d_{p_4 q_4}^{j_4}(\beta') \dots \end{aligned}$$

Here, the Clebsch-Gordan coefficients need not to shown explicitly in this expression since, apart from an additional phase, they are equivalent to the Wigner 3- $j$  symbols. Up to the present, we (must) also drop the rotation matrices and spherical harmonics which are not (yet) supported in JAC. We introduce this notation of **Racahexpr** with the intention for providing an (internal) data type which facilitates automatic manipulations and which is flexible enough to support a wide range of applications.

- **Racah expressions**: Such expressions may generally include any number of Wigner  $n$ - $j$  symbols of different kind as well as (various integrals over) the spherical harmonics and Kronecker and triangular deltas. Of course, the complexity of such Racah expressions increases rapidly as more Wigner symbols are involved in the product terms.
- The symbolic evaluation of typical expressions from Racah's algebra is naturally based on the knowledge of a large set of sum rules that may include rules with a (multiple) summations over dummy indices (Varshalovich *et al.* 1988). For complex and lengthy Racah expressions, moreover, the algebraic simplification can often be considerably accelerated if the graphical rules due to Yutsis *et al.* (1962) are taken into account.
- **Sum and orthogonality rules**: To obtain a simplification for complex Racah expressions, a large variety of sum and orthogonality rules have been implemented from the monograph by Varshalovich *et al.* (1988).
- In the past decades, various techniques in simplifying expressions from Racah's algebra have been developed, based either on graphical methods or on the explicit knowledge of special values and sum rules, as they can be found in some standard form in the literature. The direct application of these rules is however often laborious due to a large number of symmetric forms of the Wigner and related symbols.

- **Graphical loop rules:** These loop rules are typically used in order to find out about and to simplify those parts in a recoupling coefficient (or generally in any Racah expression) that belong together. The implementation of graphical rules even allows to easily simplify recoupling coefficients which include several ten angular momenta to an (completely equivalent) sum of products of Wigner 6- $j$  and/or 9- $j$  symbols, multiplied by proper weights.
- **Algebraic simplifications:** The simplification of expressions from Racah's algebra critically depends how easily **all equivalent symmetric forms of these expression are recognized internally**. Obviously, the symmetry of a Racah expression as a whole is closely related to the symmetries of all the Wigner  $3n-j$  symbols which are involved in the expression.
- **Classical symmetries of the Wigner symbols:** Apart from the classical symmetries of the Wigner symbols, there is an extended range of symmetries due to Regge (1958); these symmetries are however of minor practical importance.
- Although the mathematical background of angular momentum theory is today quite well understood, the treatment and simplification of typical expansions as they naturally arise by using Racah's algebra, is often very laborious.
- In JAC, we shall facilitate the symbolic evaluation of expressions from Racah's algebra and, in particular, for (complex) expressions for which the known algebraic and graphical methods start to become tedious and prone to making errors.

### 15.1.b. Frequently applied symbols and functions from Racah's algebra

#### Table of symbols and functions from the theory of angular momentum:

- The following symbols and functions from the **theories of angular momentum and irreducible tensor operators** occur very frequently in the computation and analysis of atomic and many-body systems

15. Symbolic evaluation of expressions from Racah's algebra

Symbol	Designation	Calls in JAC
$\begin{pmatrix} a & b & c \\ m_a & m_b & m_c \end{pmatrix}$	Wigner 3- $j$ symbol	<code>Wigner_3j()</code>
$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$	Wigner 6- $j$ symbol	<code>Wigner_6j()</code>
$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}$	Wigner 9- $j$ symbol	<code>Wigner_9j()</code>
$\left\{ \begin{array}{cccc} a & b & c & d \\ e & f & g & h \\ i & j & k & l \end{array} \middle  s \right\}$	Wigner 12- $j$ symbol of kind $s = 1, 2$	Not implemented.
$\begin{Bmatrix} - & a_2 & a_3 & a_4 \\ b_1 & - & b_3 & b_4 \\ c_1 & c_2 & - & c_4 \\ d_1 & d_2 & d_3 & - \end{Bmatrix}$	Sharp's symbol (Sharp 1955)	Not implemented.
$\langle a \ m_a, \ b \ m_b \mid c \ m_c \rangle$	Clebsch–Gordan coefficient	<code>ClebschGordan()</code>
$W(abcd; ef)$	Racah's $W$ coefficient	Not implemented.



Symbol	Designation	Calls in JAC
$d_{mm'}^j(\beta)$	Wigner $d_{mm'}^j(\beta)$ rotation matrix	<code>Wigner_d()</code>
$D_{mm'}^j(\alpha, \beta, \gamma)$	Wigner's $D$ -function	Not implemented.
$U_{mm'}^j(\omega; \Theta, \Phi)$	Rotation matrix $U(\omega)$	Not implemented.
$Y_{\ell m}(\vartheta, \varphi)$	Spherical harmonic	Not implemented.
$\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \otimes \mathbf{Y}_{l_2}(\vartheta_2, \varphi_2)\}_{LM}$	Bipolar spherical harmonic	Not implemented.
$\{\mathbf{Y}_{l_1}(\vartheta_1, \varphi_1) \otimes \{\mathbf{Y}_{l_2}(\vartheta_2, \varphi_2) \otimes \mathbf{Y}_{l_3}(\vartheta_3, \varphi_3)\}_{l_{23}}\}_{LM}$	Tripolar spherical harmonic	Not implemented.
$\mathbf{Y}_{jm}^l(\vartheta, \varphi)$	Vector spherical harmonic	Not implemented.
$\Omega_{jm}^l(\vartheta, \varphi)$	Spinor spherical harmonic	Not implemented.
$Y_{jm}^{ls}(\vartheta, \varphi)$	Tensor spherical harmonic	Not implemented.

### Brief explanation of symbols and functions:

- **Wigner  $3n-j$  symbols ( $n = 1, 2$ , and  $3$ ):** The Wigner  $3n-j$  symbols are all related to the (re-) coupling) of angular momenta between different coupling schemes. For  $n = 1, 2$ , and  $3$ , these symbols form the basic data types in the symbolic evaluation of expressions from Racah's algebra. Indeed, the Wigner  $3n-j$  symbols frequently arise in (almost) all applications of the theory of angular momentum.
- **$12-j$  symbols of first and second type. Sharp's symbol:** Wigner  $3n-j$  symbols of higher order ( $n \geq 4$ ) are rarely used in applications as their complexity increases rapidly with  $n$  and as several *kinds* of these symbols need to be distinguished (Varshalovich *et al.* 1988). In particular, there are two kinds of  $12-j$  symbols, called the *first* and *second* kind or  $12-j(1)$  and  $12-j(2)$  symbols, respectively. These symbols are often written as

$$\left\{ \begin{array}{cccc|c} a_1 & a_2 & a_3 & a_4 & s \\ b_1 & b_2 & b_3 & b_4 & \\ c_1 & c_2 & c_3 & c_4 & \end{array} \right\},$$

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where  $s = 1, 2$  selects the *kind*. Instead of the  $12-j(2)$  symbol of *second kind*, *Sharp's symbol* (Sharp 1955) is sometimes used that exhibits a slightly higher symmetry. For  $n \geq 4$ , the properties of the  $3n-j$  symbols are still a research topic in modern group theory.

- **Clebsch-Gordan coefficients:** The Clebsch-Gordan or vector coupling coefficients appear naturally as Fourier coefficients in the *re-coupling* of angular momenta; they are closely related to the Wigner  $3-j$  symbols. In JAC, we make use of the Condon-Shortley phase convention (Condon and Shortley 1935)

$$\langle j_1 m_1, j_2 m_2 | j_3 m_3 \rangle = (-1)^{j_1 - j_2 + m_3} [j_3]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}.$$

- **Racah's W coefficients:** The Racah W coefficients,  $W(abed; cf) = (-1)^{a+b+d+e} \begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ , are basically equivalent to the Wigner  $6-j$  symbols and were mainly applied in the earlier literature on the recoupling of angular momenta. In the JAC program, we only use the Wigner  $6-j$  symbols in all symbolic evaluations.
- **Wigner's D-function  $D_{mm'}^j(\alpha, \beta, \gamma)$ :** The D-functions are often required for the transformation of wave functions, if either the system or the coordinates are rotated

$$|\Psi_{jm'}(\vartheta', \varphi', \sigma')\rangle = \sum_m |\Psi_{jm}(\vartheta, \varphi, \sigma)\rangle D_{mm'}^j(\alpha, \beta, \gamma).$$

Here  $\vartheta, \varphi$  and  $\vartheta', \varphi'$  are the polar angles in the initial and the rotated system, while  $\sigma(\sigma')$  denote the corresponding spin variables. More general, these functions occur in the transformation of any irreducible spherical tensor of rank  $j$ . Therefore, the D-functions occur very frequently in the treatment of scattering processes from elementary particles up to molecules and clusters, and by including capture, transfer, and emission processes. The Wigner D-functions also fulfill a large number of symmetry properties (Varshalovich *et al.* 1988) and are expressed most readily in terms of the Euler angles and the (so-called) Wigner rotation matrix  $d_{mm'}^j(\beta)$ , see below.

- **Rotation matrix  $d_{mm'}^j(\beta)$ :** This (real) matrix describes the rotation of any spherical tensor by the angle  $\beta$  around a given axis, say, the quantization axis of the system. Several explicit representations of this real function exist in terms of  $\sin(\beta/2)$  or  $\cos(\beta/2)$ , the hypergeometric function, or various other polynomials. In JAC, the rotation matrix  $d_{mm'}^j(\beta)$  is one of the basic data structures in the algebraic manipulation of expressions from Racah's algebra.
- **Spherical harmonics:** The spherical harmonics are applied in many fields of physics. In quantum mechanics, they form an important basis for classifying the one- and many-particle states since they are known to be simultaneous eigenfunctions of one component and of the square of the orbital angular momentum operator  $-\mathbf{i}\mathbf{r} \times \nabla$ . In many-particle physics, the properties of these functions (completeness, orthogonality, ...) are frequently utilized to represent and evaluate the spin-angular part of the corresponding matrix elements analytically.

- **Spherical harmonics**  $Y_{\ell m}(\theta, \phi)$ : These functions form a complete and orthonormal set on the unit sphere, and are therefore widely used in classical and quantum physics. The spherical harmonics frequently appear in the representation of wave functions for a wide range of physical systems, in the evaluation of the corresponding (quantum) matrix elements, and at many places elsewhere. In JAC, these functions are also one of the basic data structures in the algebraic manipulation of expressions from Racah's algebra.

### 15.1.c. Symmetries of the Wigner $3n-j$ symbols, rotation matrices and spherical harmonics

#### Symmetries of the Wigner $3n-j$ symbols:

- **Symmetries of the Wigner  $3-j$  symbols:** This symbol has the following symmetries with regard to a permutation of columns and with regard to a change of signs in the projections of all angular momenta

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} \\ &= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix} \\ \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \end{aligned}$$

- **Classical symmetries:** When combined, these symmetry relations give rise to 12 formally different  $3-j$  symbols with the same absolute value. There are **additional symmetries known due to Regge (1958)** which are most easily explained in terms of Regge symbols (Varshalovich *et al.* 1988).
- A similar distinction between classical symmetries and additional symmetric forms due to Regge can be made also for the  $6-j$  symbols.
- **Number of symmetries of the Wigner  $3n-j$  symbols:** The table below lists the number of classical symmetries vs. the overall number of symmetric forms known for the Wigner symbols. In order to simplify Racah algebra expressions, it is crucial to exploit these symmetries; they are therefore all incorporated in the program as it is explained below.
- For practical purposes, however, the classical symmetries are much more important and the distinction is therefore kept. In our notation, the **classical symmetries are a subset of the Regge symmetries**.

## 15. Symbolic evaluation of expressions from Racah's algebra

- Number of classical symmetries of Wigner 3- $j$  symbols vs. the symmetries known due to Regge (1958)

3- $j$ symbol	classical symmetries	Regge symmetries (Regge 1958)
3- $j$	12	72
6- $j$	24	144
9- $j$	72	—

### Definition and symmetries of the Wigner $D$ -functions and rotation matrices:

- **Wigner  $D$ -functions  $D_{pq}^j(\alpha, \beta, \gamma)$ :** The Wigner  $D$ -functions are defined as the matrix elements of the rotation operator  $\hat{R}(\alpha, \beta, \gamma)$  in  $\mathcal{R}^3$  and are often parametrized in terms of the three Euler angles  $\alpha$ ,  $\beta$ , and  $\gamma$ . In particular, these functions arise not only in the transformation of tensor components under the rotation of the coordinates but also as the eigenfunctions of the spherical top.
- **Definition of the  $D_{pq}^j(\alpha, \beta, \gamma)$  and  $d_{pq}^j(\beta)$  rotation matrices:** The Wigner  $D$ -function is defined as a product of three functions that each depend on just a single Euler angle and with the so-called Wigner rotation matrix  $d_{pq}^j(\beta)$ :

$$D_{pq}^j(\alpha, \beta, \gamma) = e^{-ip\alpha} d_{pq}^j(\beta) e^{-iq\gamma}.$$

- **Euler angles  $(\alpha, \beta, \gamma)$ :** These angle can be utilized to characterize all possible rotations of a given (coordinate) system if the following range of values are considered:

$$0 \leq \alpha \leq 2\pi, \quad 0 \leq \beta \leq \pi, \quad 0 \leq \gamma \leq 2\pi.$$

- **Symmetries of the  $D_{pq}^j$  functions and Wigner rotation matrices  $d_{pq}^j$ :** The Wigner rotation matrix  $d_{pq}^j(\beta)$  satisfies the following basic symmetries (Varshalovich *et al.*, 1988, eq. 4.4.1):

$$\begin{aligned} d_{pq}^j(\beta) &= (-1)^{p-q} d_{-p-q}^j(\beta) &= (-1)^{p-q} d_{qp}^j(\beta) &= d_{-q-p}^j(\beta) \\ &= d_{qp}^j(-\beta) &= (-1)^{q-p} d_{qp}^j(\beta) &= (-1)^{-j-p} d_{-pq}^j(\beta - \pi) &= (-1)^{-j-2p-q} d_{p-q}^j(\beta - \pi) \\ &= (-1)^{-2j} d_{pq}^j(\beta + 2\pi) &= (-1)^{-2j} d_{pq}^j(\beta - 2\pi) &= (-1)^{j-q} d_{p-q}^j(\beta + \pi) &= (-1)^{j-2q-p} d_{-pq}^j(\beta + \pi). \end{aligned}$$

The symmetry properties of the Wigner  $D$ -function are listed by Varshalovich *et al.* (1988, Eq. 4.2.2) and are taken into account since the  $D$ -function are internally handled in terms of the Wigner rotation matrix.

### Symmetries of the spherical harmonics:

➤ **Symmetries:** The spherical harmonics satisfy the following basic symmetries:

$$\begin{aligned} Y_{\ell m}(\vartheta, \varphi) &= (-1)^m e^{2im\varphi} Y_{\ell, -m}(\vartheta, \varphi) = (-1)^m Y_{\ell m}(-\vartheta, \varphi) = e^{2im\varphi} Y_{\ell, -m}(-\vartheta, \varphi) = (-1)^m Y_{\ell, -m}(\vartheta, -\varphi) \\ &= e^{2im\varphi} Y_{\ell m}(\vartheta, -\varphi) = Y_{\ell, -m}(-\vartheta, -\varphi) = (-1)^m e^{2im\varphi} Y_{\ell m}(-\vartheta, -\varphi) . \end{aligned}$$

#### 15.1.d. Expansions of the Wigner $3n-j$ symbols, rotation matrices and spherical harmonics

### Explicit formulas for the computation of the Wigner $3n-j$ symbols:

➤  **$\Delta$  symbol:**

$$\Delta(a, b, c) = \left[ \frac{(a+b-c)! (a-b+c)! (-a+b+c)!}{(a+b+c+1)!} \right]^{1/2} .$$

➤ **Wigner  $3-j$  symbol:** The numerical value of a Wigner  $3-j$  symbol can be calculated by the expression (Racah, 1942) and has a non-zero value only if the arguments of all factorials are non-negative integers

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \delta_{m_1+m_2+m_3,0} (-1)^{j_1-j_2-m_3} \Delta(j_1, j_2, j_3) [(j_1-m_1)! (j_1+m_1)! (j_2-m_2)! (j_2+m_2)! (j_3-m_3)! (j_3+m_3)!]^{1/2} \\ &\times \sum_l \left[ \frac{(-1)^l}{l! (j_1+j_2-j_3-l)! (j_1-m_1-l)! (j_2+m_2-l)! (j_3-j_2+m_1+l)! (j_3-j_1-m_2+l)!} \right] . \end{aligned}$$

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➤ **Wigner 6- $j$  symbol:** Edmonds (1957) displays the following expression for the computation of a Wigner 6- $j$  symbol

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{matrix} \right\} = \Delta(j_1, j_2, j_3) \Delta(j_1, l_2, l_3) \Delta(l_1, j_2, l_3) \Delta(l_1, l_2, j_3) \sum_l \left[ \frac{(-1)^l (\ell + 1)!}{(l - j_1 - j_2 - j_3)! (l - j_1 - l_2 - l_3)!} \right. \\ \left. \times \frac{1}{(l - l_1 - j_2 - l_3)! (l - l_1 - l_2 - j_3)! (j_1 + j_2 + l_1 + l_2 - l)! (j_2 + j_3 + l_2 + l_3 - l)! (j_3 + j_1 + l_3 + l_1 - l)!} \right].$$

➤ **Wigner 9- $j$  symbol:** The Wigner 9- $j$  symbol with numeric arguments is usually calculated by the known sum rule over three Wigner 6- $j$  symbols and is **zero unless the arguments in each row and column satisfy the triangular relation**

$$\left\{ \begin{matrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{matrix} \right\} = \sum_j (-1)^{2j} \left\{ \begin{matrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & j \end{matrix} \right\} \left\{ \begin{matrix} j_{12} & j_{22} & j_{32} \\ j_{21} & j & j_{23} \end{matrix} \right\} \left\{ \begin{matrix} j_{13} & j_{23} & j_{33} \\ j & j_{11} & j_{12} \end{matrix} \right\}.$$

### Explicit formulas and expansions of the Wigner rotation matrices $d_{pq}^j(\beta)$ :

➤ Below, we display six explicit expansions of the Wigner rotation matrices in alphabetical order.

➤ **Asymptotic expansion of  $d_{pq}^j$  for  $j \gg 1$ :** There are three asymptotics expansion of Wigner rotation matrices as displayed by Varshalovich *et al.* (1988, Eqs. 4.18.1–4). For  $j \gg 1$ , for instance, the Wigner rotation matrix can be written as

$$d_{pq}^j(\beta) \approx \xi_{pq} \sqrt{\frac{s!(s+\mu+\nu)!}{(s+\mu)!(s+\nu)!}} \sqrt{\frac{2}{\pi s}} \frac{\cos \left[ \left( s + \frac{\mu+\nu+1}{2} \right) \beta - \frac{\pi}{4} (2\mu+1) \right]}{\sqrt{\sin \beta}} + O\left(\frac{1}{J^{\frac{3}{2}}}\right),$$

and where  $\mu$ ,  $\nu$ , and  $s$  are related to  $p$ ,  $q$ , and  $j$  as follows

$$\mu = |p - q|, \quad \nu = |p + q|, \quad s = j - \frac{1}{2}(\mu + \nu), \quad \xi_{pq} = \begin{cases} 1 & \text{if } q \geq p, \\ (-1)^{q-p} & \text{if } q < p. \end{cases}$$

➤ **Asymptotic expansion of  $d_{pq}^j$  for  $J \rightarrow \infty$  and  $\beta \rightarrow 0$ :** A second expansion for  $j\beta < \infty$  is given in terms of the Bessel functions  $J_n(x)$  by

$$d_{pq}^j(\beta) \approx J_{p-q}(j\beta)$$

➤ Asymptotic expansion of  $d_{pq}^j$  for small variations of the rotation axis:

$$d_{pq}^j(\beta) \approx \frac{\xi_{pq}}{\mu!} \sqrt{\frac{(s+\mu+\nu)!(s+\mu)!}{s!(s+\nu)!}} \left(\frac{\beta}{2}\right)^\mu \left\{ 1 - \frac{2s(s+\mu+\nu+1) + \nu(\mu+1)}{2(\mu+1)} \left(\frac{\beta}{2}\right)^2 + \dots \right\}, \quad \beta \rightarrow 0$$

$$d_{pq}^j(\beta) \approx \frac{(-1)^s \xi_{pq}}{\nu!} \sqrt{\frac{(s+\mu+\nu)!(s+\nu)!}{s!(s+\nu)!}} \left(\frac{\pi-\beta}{2}\right)^\mu \left\{ 1 - \frac{2s(s+\mu+\nu+1) + \mu(\nu+1)}{2(\nu+1)} \left(\frac{\pi-\beta}{2}\right)^2 + \dots \right\}, \quad \beta - \pi \rightarrow 0$$

➤ Clebsch-Gordan series expansion of products of two  $d_{pq}^j(\beta)$  with equal arguments: Products of two Wigner rotation matrices with equal angular arguments can be expanded in terms of their uncoupled and coupled representations, i.e. by means of the Clebsch-Gordan coefficient. When expressed in terms of the Wigner 3- $j$  symbols, the product of two Wigner rotation matrices (with equal angular arguments) are given by

$$d_{p_1 q_1}^{j_1}(\beta) d_{p_2 q_2}^{j_2}(\beta) = \sum_{JPQ} (-1)^{-2J+2j_2-p_2-q_2} (2j_2+1) \begin{pmatrix} J & j_2 & j_2 \\ P & p_2 & -p_2 \end{pmatrix} \begin{pmatrix} J & j_2 & j_2 \\ Q & q_2 & -q_2 \end{pmatrix} d_{PQ}^J(\beta)$$

in terms of two Wigner 3- $j$  symbols and one Wigner rotation matrix  $d_{PQ}^J(\beta)$ . For  $\beta = \frac{\pi}{2}$ , in particular, the magnetic quantum numbers can be replaced by  $j_1 = j_2 = j$ ,  $p_1 = p_2 = p$  and  $q_1 = q_2 = q$ , and this gives rise to the expansion

$$\left(d_{pq}^j\left(\frac{\pi}{2}\right)\right)^2 = \sum_{J=0,2,4,\dots} (-1)^{J+2j+2p} (2j+1) \frac{(J-1)!!}{J!!} \begin{pmatrix} J & j & j \\ 0 & p & p \end{pmatrix} \begin{pmatrix} J & j & j \\ 0 & q & q \end{pmatrix}.$$

Such expansion relates the Wigner rotation matrices to the Wigner  $n$ - $j$  symbols. These two expansions are displayed in Varshalovich *et al.* (1988, Eq. 4.6.1 and Eq. 4.16.9), although expressed in terms of Clebsch-Gordan coefficients.

## Expansions of the spherical harmonics:

➤ Varshalovich *et al.* (1988, section 5.2) shows several explicit formulas for computing the spherical harmonic  $Y_{\ell m}(\vartheta, \varphi)$  with given integers  $\ell$  and  $m$ , and where the summation runs over all terms with non-negative factorials.

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➤ Expansion of  $Y_{\ell m}(\vartheta, \varphi)$  in terms of  $\sin \vartheta$ : Varshalovich *et al.* (1988, Eq. 5.2.17)

$$Y_{\ell m}(\vartheta, \varphi) = e^{im\varphi} \sqrt{\frac{2\ell+1}{4\pi(\ell+m)!(\ell-m)!}} \begin{cases} \sum_{s=|m|, |m|+2, \dots}^{\ell} (-1)^{\frac{s+m}{2}} \frac{(\ell+s)!}{(s+m)!!(s-m)!!} \cdot \frac{(\ell+m)!!(\ell-m)!!}{(\ell+s)!!(\ell-s)!!} (\sin \vartheta)^s & \text{if } \ell - m \text{ is even,} \\ \cos \vartheta \sum_{s=|m|, |m|+2, \dots}^{\ell-1} (-1)^{\frac{s+m}{2}} \frac{(\ell+s)!}{(s+m)!!(s-m)!!} \cdot \frac{(\ell+m-1)!!(\ell-m-1)!!}{(\ell+s-1)!!(\ell-s-1)!!} (\sin \vartheta)^s & \text{if } \ell - m \text{ is odd.} \end{cases}$$

➤ Expansion of  $Y_{\ell m}(\vartheta, \varphi)$  in terms of  $\sin \vartheta$  and  $\cos \vartheta$ : Cf. Varshalovich *et al.* (1988, Eq. 5.2.19) with a polynomial in  $\cos \vartheta$

$$Y_{\ell m}(\vartheta, \varphi) = e^{im\varphi} \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} (\sin \vartheta)^m \sum_{\substack{s \\ \ell+m-s \text{ even}}} (-1)^{\frac{\ell+m-s}{2}} \frac{(\ell+m+s-1)!!}{(\ell-m-s)!!} \frac{(\cos \vartheta)^s}{s!}$$



## 15.2. In JAC implemented symbolic evaluations of Racah algebra expressions

### 15.2.a. Strategies in the symbolic evaluation of expressions from Racah's algebra

#### Strategies for simplification:

- For the successful simplification of expressions from Racah's algebra, one need often to exploit the orthogonality relations as well as a variety of important sum rules. The literature about Racah's algebra is therefore devoted to a large extent in order to find and to prove proper relations among the Wigner symbols and/or to compile them in some applicable form.
- **Standard presentation of orthogonality and sum rules:** The standard presentation of the different orthogonality and sum rules, as they are displayed below, gives a first impression how complex expressions can be rewritten in a simpler form. In practice, however, these standard forms are often not of great help since one first need to recognize the equivalence of some part of a Racah algebra expression, for instance with one side of a given sum rule, before this special rule can be applied.
- A numerical evaluation of a Racah expression is of course not possible as long as the input angular momentum quantum numbers are specified numerically. On the other hand, the main strength of using the techniques of Racah's algebra techniques is that such expressions can often be simplified considerably by algebraic transformations.
- Understanding the symmetries and properties of Wigner symbols, three different strategies for the simplification can be derived quite easily:
  - (i) **Use of known special values.** This replaces a Wigner  $3n-j$  symbol by a (much) simpler expression that, in particular, does not contain any implicit summation. For this strategy, each Wigner  $3n-j$  symbol can be analysed and perhaps replaced independently by some special-value rules.
  - (ii) **Use of orthogonality properties.**
  - (iii) **Use of sum rules.**
- The main obstacle in applying the strategies (ii) and (iii) is that these strategies require a careful analysis of the Racah expression as a whole. Since all orthogonality relations and sum rules include summations over formal quantum numbers, all summation variables not only have to be in the correct position in the Wigner  $3n-j$  symbols, but they must also contribute to a correct phase and weight of the overall expression. Moreover, the same variables may not occur in other Wigner symbols of the Racah expression which are not part of the selected rule.
- These difficulties in the simplification process are further enhanced by the large number of equivalent forms of the total Racah expression due to the symmetries of the Wigner  $3n-j$  symbols. Therefore, in order to simplify a Racah expression by a given sum rule, in practice one

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has to start with a certain part of the expression and then try to identify equivalence with some relation by means of the various symmetries of the  $3n-j$  symbols.

- Once the equivalence has been proven, this part of the Racah expression can be replaced by a corresponding simpler term. In this context, **simplification of a Racah expression always means to 'reduce' the number of summation indices and/or the number of Wigner  $3n-j$  symbols.**
- **Aim of symbolic transformations:** The aim of these symbolic transformation is to obtain an *optimum* summation formula in the sense of a minimal number of Wigner  $6-j$  symbols and/or summation variables.
- **Results of the simplification process:** The results of the simplification process will be provided as Racah expressions and may thus immediatly be used for further derivations and calculations within the theory of angular momentum.
- This rather cumbersome procedure of running through all symmetric forms of a Racah expression and of identifying algebraic equivalent parts makes the simplification of such expressions very suitable for symbolic evaluations. An efficient scheme to perform simplifications of Racah expressions by means of the steps (i-iii) is aimed to be realized by the symbolic evaluations of the JAC tools.
- A major difficulty for the simplification of general Racah expressions arise from the large number of symmetric forms of the total expression which is the direct result of the symmetries of the Wigner  $3n-j$  symbols. Apart from the so-called classical symmetries of the Wigner  $n-j$  symbols, there are additional symmetries known due to Regge for the  $3-j$  and  $6-j$  symbols; cf. section 15.1.c. These symmetries need to be exploited in order to simplify general Racah algebra expressions. In JAC, we shall keep the distinction between the classical symmetries and those due to Regge since the classical ones are by far more important for all practical purposes; as mentioned above, we consider the classical symmetries to be a subset of the Regge symmetries.

## 15.3. In JAC partly-implemented symbolic evaluations of Racah algebra expressions

### 15.3.a. Recursive relations for the Wigner $3n-j$ symbols and rotation matrices

#### Recursion relations of the Wigner $3-j$ symbols:

➤ Four recursion relations of the Wigner  $3-j$  symbols are listed by Rotenberg *et al.* (1959, Eqs. 1.45–1.48), and where we use  $J = j_1 + j_2 + j_3$ .

➤ **Half-integer recursion:** This recursion relation decreases two  $j$ -values by  $1/2$

$$\begin{aligned} & [(J+1)(J-2j_1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ &= [(j_2+m_2)(j_3-m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_1 & m_2-1/2 & m_3+1/2 \end{pmatrix} - [(j_2-m_2)(j_3+m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_1 & m_2+1/2 & m_3-1/2 \end{pmatrix}. \end{aligned}$$

➤ **Louck's (1958) half-integer recursion:**

$$\begin{aligned} (j_2+m_2)^{1/2} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_2-m_3 & -m_2 & m_3 \end{pmatrix} &= - [(J-2j_1)(J+1)(j_3+m_3)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3-1/2 \\ m_2-m_3 & -m_2+1/2 & m_3-1/2 \end{pmatrix} \\ &- [(J-2j_3)(J-2j_2+1)(J+1)(j_3-m_3+1)]^{1/2} \begin{pmatrix} j_1 & j_2-1/2 & j_3+1/2 \\ m_2-m_3 & -m_2+1/2 & m_3-1/2 \end{pmatrix}. \end{aligned}$$

➤ **Integer recursion:** A decrease of a single  $j$ -values by 1 is made with

$$\begin{aligned} & [(J+1)(J-2j_1)(J-2j_2)(J-2j_3+1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ &= [(j_2-m_2)(j_2+m_2+1)(j_3+m_3)(j_3+m_3-1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3-1 \\ m_1 & m_2+1 & m_3-1 \end{pmatrix} - 2m_2 [(j_3+m_3)(j_3-m_3)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3-1 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ &- [(j_2+m_2)(j_2-m_2+1)(j_3-m_3)(j_3-m_3-1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3-1 \\ m_1 & m_2-1 & m_3+1 \end{pmatrix}. \end{aligned}$$

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➤ **Magnetic recursion:** A recursion relation with regard to the magnetic quantum numbers reads:

$$\begin{aligned}
 & - [(j_3 + m_1 + m_2 + 1)(j_3 - m_1 - m_2)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 + 1 \end{pmatrix} \\
 & = [(j_1 + m_1 + 1)(j_1 - m_1)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 + 1 & -m_3 \end{pmatrix} + [(j_2 + m_2 + 1)(j_2 - m_2)]^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 + 1 & m_2 & -m_3 \end{pmatrix}.
 \end{aligned}$$

### Recursion relations of the Wigner 6- $j$ symbols:

➤ No explicit recurrence relation has yet been considered for the Wigner 6- $j$  symbols.

### Recursion relations of the Wigner 9- $j$ symbols:

➤ A single recursion relation among the Wigner 9- $j$  symbols is shown by Rotenberg *et al.* (1959, Eq. 3.24).

$$\begin{Bmatrix} s & s & 1 \\ l_1 & l_2 & L \\ j_1 & j_2 & L \end{Bmatrix} = \frac{l_1(l_1 + 1) + j_2(j_2 + 1) - j_1(j_1 + 1) - l_2(l_2 + 1)}{2[s(s + 1)(2s + 1)L(L + 1)(2L + 1)]^{1/2}} \begin{Bmatrix} s & s & 0 \\ l_1 & l_2 & L \\ j_1 & j_2 & L \end{Bmatrix}.$$

### Recursion relations of the spherical harmonics:

➤ **Recursion relations:** Cf. Varshalovich *et al.* (1988, Eqs. 5.7.1–2)

$$\begin{aligned}
 \cos \vartheta Y_{\ell m}(\vartheta, \varphi) &= \sqrt{\frac{(\ell - m + 1)(\ell + m + 1)}{(2\ell + 1)(2\ell + 3)}} Y_{\ell+1, m}(\vartheta, \varphi) + \sqrt{\frac{(\ell - m)(\ell + m)}{(2\ell - 1)(2\ell + 1)}} Y_{\ell-1, m}(\vartheta, \varphi) \\
 - 2m \cos \vartheta Y_{\ell m}(\vartheta, \varphi) &= \sqrt{l(\ell + 1) - m(m + 1)} e^{-i\varphi} Y_{\ell, m+1}(\vartheta, \varphi) + \sqrt{l(\ell + 1) - m(m - 1)} e^{i\varphi} Y_{\ell, m-1}(\vartheta, \varphi).
 \end{aligned}$$

### 15.3.b. Special values of the Wigner $3n-j$ symbols and rotation matrices

#### Special values of the Wigner $3-j$ symbols:

➤ Edmonds (1957, appendix 2) lists the following 20 special values for  $3-j$  symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{J/2} \left[ \frac{(j_1 + j_2 - j_3)!(j_1 + j_3 - j_2)!(j_2 + j_3 - j_1)!}{(j_1 + j_2 + j_3 + 1)!} \right]^{1/2} \frac{(J/2)!}{(J/2 - j_1)!(J/2 - j_2)!(J/2 - j_3)!}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = 0 \quad \begin{cases} \text{if } J = j_1 + j_2 + j_3 \text{ is even} \\ \text{if } J = j_1 + j_2 + j_3 \text{ is odd} \end{cases}$$

$$\begin{pmatrix} J + 1/2 & J & 1/2 \\ M & -M - 1/2 & 1/2 \end{pmatrix} = (-1)^{J-M-1/2} \left[ \frac{J - M + 1/2}{(2J + 2)(2J + 1)} \right]^{1/2}$$

$$\begin{pmatrix} J + 1 & J & 1 \\ M & -M - 1 & 1 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{(J - M)(J - M + 1)}{(2J + 3)(2J + 2)(2J + 1)} \right]^{1/2}$$

$$\begin{pmatrix} J + 1 & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{2(J + M + 1)(J - M + 1)}{(2J + 3)(2J + 2)(2J + 1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M - 1 & 1 \end{pmatrix} = (-1)^{J-M} \left[ \frac{2(J - M)(J + M + 1)}{(2J + 2)(2J + 1)(2J)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{M}{[(2J + 1)(J + 1)J]^{1/2}}$$

$$\begin{pmatrix} J + 3/2 & J & 3/2 \\ M & -M - 3/2 & 3/2 \end{pmatrix} = (-1)^{J-M+1/2} \left[ \frac{(J - M - 1/2)(J - M + 1/2)(J - M + 3/2)}{(2J + 4)(2J + 3)(2J + 2)(2J + 1)} \right]^{1/2}$$

$$\begin{pmatrix} J + 3/2 & J & 3/2 \\ M & -M - 1/2 & 1/2 \end{pmatrix} = (-1)^{J-M+1/2} \left[ \frac{3(J - M + 1/2)(J - M + 3/2)(J + M + 3/2)}{(2J + 4)(2J + 3)(2J + 2)(2J + 1)} \right]^{1/2}$$

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$$\begin{aligned}
 \begin{pmatrix} J+1/2 & J & 3/2 \\ M & -M-3/2 & 3/2 \end{pmatrix} &= (-1)^{J-M-1/2} \left[ \frac{3(J-M-1/2)(J-M+1/2)(J+M+3/2)}{(2J+3)(2J+2)(2J+1)(2J)} \right]^{1/2} \\
 \begin{pmatrix} J+1/2 & J & 3/2 \\ M & -M-1/2 & 1/2 \end{pmatrix} &= (-1)^{J-M-1/2} \left[ \frac{(J-M+1/2)}{(2J+3)(2J+2)(2J+1)(2J)} \right]^{1/2} (J+3M+3/2) \\
 \begin{pmatrix} J+2 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} &= (-1)^{J-M} \left[ \frac{(J-M-1)(J-M)(J-M+1)(J-M+2)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2} \\
 \begin{pmatrix} J+2 & J & 2 \\ M & -M-1 & 1 \end{pmatrix} &= (-1)^{J-M} 2 \left[ \frac{(J+M+2)(J-M+2)(J-M+1)(J-M)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2} \\
 \begin{pmatrix} J+2 & J & 2 \\ M & -M & 0 \end{pmatrix} &= (-1)^{J-M} \left[ \frac{6(J+M+2)(J+M+1)(J-M+2)(J-M+1)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2} \\
 \begin{pmatrix} J+1 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} &= (-1)^{J-M+1} 2 \left[ \frac{(J-M-1)(J-M)(J-M+1)(J+M+2)}{(2J+4)(2J+3)(2J+2)(2J+1)(2J)} \right]^{1/2} \\
 \begin{pmatrix} J+1 & J & 2 \\ M & -M-1 & 1 \end{pmatrix} &= (-1)^{J-M+1} 2 (J+2M+2) \left[ \frac{(J-M+1)(J-M)}{(2J+4)(2J+3)(2J+2)(2J+1)(2J)} \right]^{1/2} \\
 \begin{pmatrix} J+1 & J & 2 \\ M & -M & 0 \end{pmatrix} &= (-1)^{J-M+1} 2M \left[ \frac{6(J+M+1)(J-M+1)}{(2J+4)(2J+3)(2J+2)(2J+1)(2J)} \right]^{1/2} \\
 \begin{pmatrix} J & J & 2 \\ M & -M-2 & 2 \end{pmatrix} &= (-1)^{J-M} \left[ \frac{6(J-M-1)(J-M)(J+M+1)(J+M+2)}{(2J+3)(2J+2)(2J+1)(2J)(2J-1)} \right]^{1/2} \\
 \begin{pmatrix} J & J & 2 \\ M & -M-1 & 1 \end{pmatrix} &= (-1)^{J-M} (1+2M) \left[ \frac{6(J+M+1)(J-M)}{(2J+3)(2J+2)(2J+1)(2J)(2J-1)} \right]^{1/2} \\
 \begin{pmatrix} J & J & 2 \\ M & -M & 0 \end{pmatrix} &= (-1)^{J-M} \frac{2[3M^2 - J(J+1)]}{[(2J+3)(2J+2)(2J+1)(2J)(2J-1)]^{1/2}}
 \end{aligned}$$

### Special values of the Wigner 6- $j$ symbols:

➤ Edmonds (1957, appendix 2, table 5) displays the following 19 special values for 6- $j$  symbols; in this list, moreover, we use  $s = a + b + c$ .

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b-1 \end{matrix} \right\} = (-1)^s \left[ \frac{s(s+1)(s-2a-1)(s-2a)}{(2b-1)2b(2b+1)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b \end{matrix} \right\} = (-1)^s \left[ \frac{2(s+1)(s-2a)(s-2b)(s-2c+1)}{2b(2b+1)(2b+2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b+1 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)}{(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c & b \end{matrix} \right\} = (-1)^{s+1} \frac{2[b(b+1) + c(c+1) - a(a+1)]}{[2b(2b+1)(2b+2)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{matrix} a & b & c \\ 3/2 & c-3/2 & b-3/2 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-1)s(s+1)(s-2a-2)(s-2a-1)(s-2a)}{(2b-2)(2b-1)2b(2b+1)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 3/2 & c-3/2 & b-1/2 \end{matrix} \right\} = (-1)^s \left[ \frac{3s(s+1)(s-2a-1)(s-2a)(s-2b)(s-2c+1)}{(2b-1)2b(2b+1)(2b+2)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 3/2 & c-3/2 & b+1/2 \end{matrix} \right\} = (-1)^s \left[ \frac{3(s+1)(s-2a)(s-2b-1)(s-2b)}{2b(2b+1)(2b+2)(2b+3)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)}{(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 3/2 & c-3/2 & b+3/2 \end{matrix} \right\} = (-1)^s \left[ \frac{(s-2b-2)(s-2b-1)(s-2b)}{(2b+1)(2b+2)(2b+3)(2b+4)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)(s-2c+3)}{(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 3/2 & c-1/2 & b-1/2 \end{matrix} \right\} = (-1)^s \frac{[2(s-2b)(s-2c) - (s+2)(s-2a-1)] [(s+1)(s-2a)]^{1/2}}{[(2b-1)(2b)(2b+1)(2b+2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

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$$\begin{aligned}
\left\{ \begin{matrix} a & b & c \\ 3/2 & c-1/2 & b+1/2 \end{matrix} \right\} &= (-1)^s \frac{[(s-2b-1)(s-2c)-2(s+2)(s-2a)]}{[2b(2b+1)(2b+2)(2b+3)]^{1/2}} \frac{[(s-2b)(s-2c+1)]^{1/2}}{[2c(2c+1)(2c+2)(2c-1)]^{1/2}} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-2 \end{matrix} \right\} &= (-1)^s \left[ \frac{(s-2)(s-1)s(s+1)(s-2a-3)}{(2b-3)(2b-2)(2b-1)2b(2b+1)} \right]^{1/2} \left[ \frac{(s-2a-2)(s-2a-1)(s-2a)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-1 \end{matrix} \right\} &= (-1)^s 2 \left[ \frac{(s-1)s(s+1)(s-2a-2)(s-2a-1)}{(2b-2)(2b-1)2b(2b+1)(2b+2)} \right]^{1/2} \left[ \frac{(s-2a)(s-2b)(s-2c+1)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b \end{matrix} \right\} &= (-1)^s \left[ \frac{6s(s+1)(s-2a-1)(s-2b-1)(s-2a)(s-2b)}{(2b-1)2b(2b+1)(2b+2)(2b+3)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b+1 \end{matrix} \right\} &= (-1)^s 2 \left[ \frac{(s+1)(s-2a)(s-2b-2)(s-2b-1)(s-2b)}{2b(2b+1)(2b+2)(2b+3)(2b+4)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)(s-2c+3)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b+2 \end{matrix} \right\} &= (-1)^s \left[ \frac{(s-2b-3)(s-2b-2)(s-2b-1)(s-2b)}{(2b+1)(2b+2)(2b+3)(2b+4)(2b+5)} \right]^{1/2} \left[ \frac{(s-2c+1)(s-2c+2)(s-2c+3)(s-2c+4)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-1 & b-1 \end{matrix} \right\} &= (-1)^s 4 \frac{[(a+b)(a-b+1)-(c-1)(c-b+1)]}{[(2b-2)(2b-1)2b(2b+1)(2b+2)]^{1/2}} \left[ \frac{s(s+1)(s-2a-1)(s-2a)}{(2c-2)(2c-1)2c(2c+1)(2c+2)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-1 & b \end{matrix} \right\} &= (-1)^s 2 \frac{[(a+b+1)(a-b)-c^2+1]}{[(2b-1)2b(2b+1)(2b+2)(2b+3)]^{1/2}} \left[ \frac{6(s+1)(s-2a)(s-2b)(s-2c+1)}{(2c-2)(2c-1)2c(2c+1)(2c+2)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c-1 & b+1 \end{matrix} \right\} &= (-1)^s 4 \frac{[(a+b+2)(a-b-1)-(c-1)(b+c+2)]}{[2b(2b+1)(2b+2)(2b+3)(2b+4)]^{1/2}} \left[ \frac{(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)}{(2c-2)(2c-1)2c(2c+1)(2c+2)} \right]^{1/2} \\
\left\{ \begin{matrix} a & b & c \\ 2 & c & b \end{matrix} \right\} &= (-1)^s \frac{2}{[(2b-1)2b(2b+1)(2b+2)(2b+3)]^{1/2}} \frac{[3X(X-1)-4b(b+1)c(c+1)]}{[(2c-1)2c(2c+1)(2c+2)(2c+3)]^{1/2}}
\end{aligned}$$

and where we use  $s = a + b + c$  and  $X = b(b+1) + c(c+1) - a(a+1)$  in the last relation.



**Special values of the Wigner 9- $j$  symbols:**

➤ One special value for a Wigner 9- $j$  symbol reads as

$$\begin{Bmatrix} a & b & 0 \\ c & d & 0 \\ e & f & 0 \end{Bmatrix} = \delta_{ab} \delta_{cd} \delta_{ef} \frac{\delta(a, c, e)}{[a, c, e]^{1/2}}.$$

➤ Another special value for the Wigner 9- $j$  symbols is given by Varshalovich *et al.* (1988, Eq. 10.9.1)

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & 0 \end{Bmatrix} = \delta_{cf} \delta_{gh} \frac{(-1)^{b+c+e+f}}{[c, g]^{1/2}} \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix}.$$

**15.3.c. Orthogonality and sum rules of the Wigner 3- $n$ - $j$  symbols****Remarks:**

- A rather comprehensive set of sum rules for the Wigner  $n$ - $j$  symbols is given by Varshalovich *et al.* (1988, chapter 12). These rules are most easily be ordered by the number of Wigner  $n$ - $j$  symbols that contribute to a given rule. For the case of an equal numbers of such symbols, we further classify these rules by the type of the Wigner symbols.
- **Orthogonality relations:** The Wigner  $n$ - $j$  symbols fulfill a variety of orthogonality relations. Two such relations are known for the Wigner 3- $j$  symbols as well as one orthogonality relation for each, the Wigner 6- $j$  and 9- $j$  symbols. Because these orthogonalities have formally the same structure like all other sum rules of the Wigner  $n$ - $j$  symbols, they are all treated together in the JAC program.

### Sum rules with one Wigner 3- $j$ , 6- $j$ or 9- $j$ symbol:

- **Sum rules with one 3- $j$  symbol:** Varshalovich *et al.* (1988, Eq. 12.1.2) shows one sum rule with one 3- $j$  symbol

$$\sum_m (-1)^{j-m} \begin{pmatrix} j & j & j' \\ m & -m & m' \end{pmatrix} = [j]^{1/2} \delta_{m'0} \delta_{j'0}.$$

- **Sum rules with one 6- $j$  symbol:** Rotenberg *et al.* (1959, Eqs. 2.9–10) show sum rules with one 6- $j$  symbol. A more general form is given by Varshalovich *et al.* (1988, Eqs. 12.2.3–4)

$$\sum_X [X] \begin{Bmatrix} a & b & X \\ a & b & c \end{Bmatrix} = (-1)^{2c} \delta(a, b, c)$$

$$\sum_X (-1)^{a+b+X} [X] \begin{Bmatrix} a & b & X \\ b & a & c \end{Bmatrix} = [a, b]^{1/2} \delta_{c0}.$$

- **Sum rules with one 9- $j$  symbol:** Varshalovich *et al.* (1988, Eqs. 12.2.5–6) give two sum rules with one 9- $j$  symbol

$$\sum_X [X] \begin{Bmatrix} a & b & e \\ c & d & f \\ e & f & X \end{Bmatrix} = \frac{\delta_{bc}}{[b]} \delta(a, b, e) \delta(b, d, f)$$

$$\sum_X (-1)^{a+b+c+d-X} [X] \begin{Bmatrix} a & b & e \\ c & d & f \\ f & e & X \end{Bmatrix} = \frac{\delta_{ad}}{[a]} \delta(d, b, e) \delta(a, c, f).$$

### Sum rules with two 3- $j$ , 6- $j$ and/or 9- $j$ symbols:

- **Orthogonality of two 3- $j$  symbols:** Two orthogonality relations for 3- $j$  symbols are given by Rotenberg *et al.* (1959, Eqs. 1.13–14) as well as by Varshalovich *et al.* (1988, Eqs. 12.1.3–4)

$$\sum_{j_3 m_3} (2j_3 + 1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta(m_1, m'_1) \delta(m_2, m'_2)$$

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{\delta(j_3, j'_3) \delta(m_3, m'_3)}{(2j_3 + 1)} \delta(j_1, j_2, j_3).$$

- **Orthogonality of two 6- $j$  symbols:** An orthogonality relation for the Wigner 6- $j$  symbols is given by Rotenberg *et al.* (1959, Eq. 2.6) as well as by Varshalovich *et al.* (1988, Eq. 12.2.7)

$$\sum_X [X] \begin{Bmatrix} a & b & X \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & X \\ a & b & q \end{Bmatrix} = \frac{\delta_{pq}}{[p]} \delta(a, d, p) \delta(b, c, p).$$

- **Sum rules with two 6- $j$  symbols:** Rotenberg *et al.* (1959, Eq. 2.7) as well as Varshalovich *et al.* (1988, Eq. 12.2.8) gives a sum rule for two 6- $j$  symbols

$$\sum_X (-1)^{p+q+X} [X] \begin{Bmatrix} a & b & X \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & X \\ b & a & q \end{Bmatrix} = \begin{Bmatrix} c & a & q \\ d & b & p \end{Bmatrix}.$$

- **Sum rules with two 6- $j$  symbols:** Varshalovich *et al.* (1988, Eq. 12.2.15) show a sum rule including a triple summation over a 6- $j$  symbol

$$\sum_{XYZ} [X, Y, Z] \begin{Bmatrix} X & Y & Z \\ a & b & c \end{Bmatrix} \begin{Bmatrix} X & Y & Z \\ a & b & c \end{Bmatrix} = [a, b, c].$$

- **Sum rules with one 6- $j$  and one 9- $j$  symbol:** Varshalovich *et al.* (1988, Eqs. 12.2.9–10) show two sum rules for one 6- $j$  symbol and one

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9- $j$  symbol, and with  $R = a + b + c + d + e + f + p + q$

$$\sum_X [X] \begin{Bmatrix} a & f & X \\ d & q & e \\ p & c & b \end{Bmatrix} \begin{Bmatrix} a & f & X \\ e & b & s \end{Bmatrix} = (-1)^{2s} \begin{Bmatrix} a & b & s \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & s \\ e & f & q \end{Bmatrix}$$

$$\sum_X (-1)^{R+X} [X] \begin{Bmatrix} a & f & X \\ d & q & e \\ p & c & b \end{Bmatrix} \begin{Bmatrix} a & f & X \\ b & e & s \end{Bmatrix} = (-1)^{2s} \begin{Bmatrix} p & q & s \\ e & a & d \end{Bmatrix} \begin{Bmatrix} p & q & s \\ f & b & c \end{Bmatrix}.$$

Sum rules for three Wigner 3- $j$ , 6- $j$  and/or 9- $j$  symbols:

- **Sum rules with three 3- $j$  symbols:** One such rule is given by Rotenberg *et al.* (1959, Eq. 2.20) as well as by Varshalovich *et al.* (1988, Eq. 2.1.6), and with  $S = l_1 + l_2 + l_3 + n_1 + n_2 + n_3$

$$\sum_{n_1 n_2 n_3} (-1)^S \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & -n_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}.$$

- **Sum rules with two 3- $j$  symbols and one 6- $j$  symbol:** One such rule is given by Rotenberg *et al.* (1959, Eq. 2.19) as well as by Varshalovich *et al.* (1988, Eq. 12.1.5)

$$\sum_{l_3 n_3} (-1)^{j_3+l_3+m_1+n_1} [l_3] \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} = \sum_{m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & n_2 & -m_3 \end{pmatrix}.$$

- **Sum rules with three 6- $j$  symbols:** There is a sum rule for three 6- $j$  symbols from Biedenharn and Elliot; see also Rotenberg *et al.* (1959, Eq. 2.8) or Varshalovich *et al.* (1988, Eq. 12.2.18), and with  $R = a + b + c + d + e + f + p + q + r$

$$\sum_X (-1)^{R+X} [X] \begin{Bmatrix} a & b & X \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & X \\ e & f & q \end{Bmatrix} \begin{Bmatrix} e & f & X \\ b & a & r \end{Bmatrix} = \begin{Bmatrix} p & q & r \\ e & a & d \end{Bmatrix} \begin{Bmatrix} p & q & r \\ f & b & c \end{Bmatrix}.$$

- **Sum rules with three 6- $j$  symbols:** Another sum rules corresponds to the representation of the 9- $j$  symbol in terms of 6- $j$  symbols; see Rotenberg *et al.* (1959, Eq. 3.1) and Varshalovich *et al.* (1988, Eq. 12.2.19)

$$\sum_X (-1)^{2X} [X] \begin{Bmatrix} a & b & X \\ c & d & p \end{Bmatrix} \begin{Bmatrix} c & d & X \\ e & f & q \end{Bmatrix} \begin{Bmatrix} e & f & X \\ a & b & r \end{Bmatrix} = \begin{Bmatrix} a & f & r \\ d & q & e \\ p & c & b \end{Bmatrix}.$$

### Sum rules with four Wigner 3- $j$ , 6- $j$ and/or 9- $j$ symbols:

- **Sum rules with three 3- $j$  symbols:** Rotenberg *et al.* (1959, Eq. 2.18) as well as Varshalovich *et al.* (1988, Eq. 12.1.8) display the representation of a 6- $j$  symbol in terms of four 3- $j$  symbols, and with  $S = l_1 + l_2 + l_3 + n_1 + n_2 + n_3$

$$\begin{aligned} \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} &= \sum_{m_1 m_2 m_3 n_1 n_2 n_3} (-1)^S \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & -n_2 & m_3 \end{pmatrix} \\ &= \sum_{m_1 m_2 n_1 n_2 n_3} (-1)^S [j_3] \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & -n_2 & m_3 \end{pmatrix}. \end{aligned}$$

- Another sum rule for four 3- $j$  symbols is given by Varshalovich *et al.* (1988, Eq. 12.1.9).

$$\begin{aligned} \sum_{n_r n_p n_q n_s} (-1)^{p-n_p+q-n_q+r-n_r+s-n_s} \begin{pmatrix} p & a & q \\ n_p & n_a & -n_q \end{pmatrix} \begin{pmatrix} q & b & r \\ n_q & n_b & -n_r \end{pmatrix} \begin{pmatrix} r & s & p \\ n_r & n_s & -n_p \end{pmatrix} \begin{pmatrix} s & c & d \\ -n_s & n_c & n_d \end{pmatrix} \\ = \begin{Bmatrix} a & b & s \\ r & p & q \end{Bmatrix} \sum_{n_s} \begin{pmatrix} a & s & b \\ n_a & n_s & n_b \end{pmatrix} \begin{pmatrix} d & s & c \\ n_d & -n_s & n_c \end{pmatrix}. \end{aligned}$$

- A useful relation between 3- $j$  and 9- $j$  symbols is due to de-Shalit; cf. Rotenberg *et al.* (1959, Eq. 3.21) as well as Varshalovich *et al.* (1988, Eq. 12.1.11)

$$\sum_{MNRS} \begin{pmatrix} a & e & g \\ n_a & M & N \end{pmatrix} \begin{pmatrix} b & f & h \\ n_b & R & S \end{pmatrix} \begin{pmatrix} e & f & c \\ M & R & n_e \end{pmatrix} \begin{pmatrix} g & h & d \\ N & S & n_x \end{pmatrix} = \sum_{XY} [X] \begin{pmatrix} a & b & X \\ n_a & n_b & Y \end{pmatrix} \begin{pmatrix} X & c & d \\ Y & n_e & n_x \end{pmatrix} \begin{Bmatrix} a & b & X \\ e & f & c \\ g & h & d \end{Bmatrix}.$$

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Only this (last) sum rule for four Wigner 3- $j$  symbols need to be implemented explicitly because the other two above can be simplified in a two-step evaluation using other sum rules.

### Sum rules with five Wigner 3- $j$ , 6- $j$ and/or 9- $j$ symbols:

➤ **Sum rules with five 3- $j$  symbols:** Varshalovich *et al.* (1988, Eqs. 12.1.12–14) give three sum rules involving products of five 3- $j$  symbols.

$$\begin{aligned}
 & \sum_{n_p n_q n_r n_s n_t n_u n_v} (-1)^{p-n_p+q-n_q+r-n_r+s-n_s+t-n_t+u-n_u+v-n_v} \begin{pmatrix} r & t & q \\ n_r & n_t & -n_q \end{pmatrix} \begin{pmatrix} q & p & u \\ n_q & n_p & -n_u \end{pmatrix} \begin{pmatrix} u & a & v \\ n_u & n_a & -n_v \end{pmatrix} \begin{pmatrix} v & s & r \\ n_v & n_s & -n_r \end{pmatrix} \begin{pmatrix} s & p & t \\ -n_s & -n_p & -n_t \end{pmatrix} \\
 &= (-1)^{2u} \frac{\delta_{uv} \delta_{a0} \delta_{na0}}{[u]^{1/2}} \left\{ \begin{matrix} q & p & u \\ s & r & t \end{matrix} \right\} \\
 & \sum_{n_p n_q n_r n_s n_t n_u} (-1)^{p-n_p+q-n_q+r-n_r+s-n_s+t-n_t+u-n_u} \begin{pmatrix} p & a & q \\ n_p & n_a & -n_q \end{pmatrix} \begin{pmatrix} q & r & t \\ n_q & n_r & -n_t \end{pmatrix} \begin{pmatrix} t & s & p \\ n_t & -n_s & -n_p \end{pmatrix} \begin{pmatrix} s & c & u \\ n_s & n_c & -n_u \end{pmatrix} \begin{pmatrix} u & b & r \\ n_u & n_b & -n_r \end{pmatrix} \\
 &= \begin{pmatrix} a & b & c \\ n_a & n_b & n_c \end{pmatrix} \left\{ \begin{matrix} a & b & c \\ u & s & r \end{matrix} \right\} \left\{ \begin{matrix} a & p & q \\ t & r & s \end{matrix} \right\} \\
 & \sum_{n_p n_q n_r n_s n_t n_u} (-1)^{p-n_p+q-n_q+r-n_r+s-n_s+t-n_t+u-n_u} \begin{pmatrix} p & a & q \\ n_p & n_a & n_q \end{pmatrix} \begin{pmatrix} p & a & q \\ n_p & n_a & n_q \end{pmatrix} \begin{pmatrix} q & t & r \\ -n_q & -n_t & -n_r \end{pmatrix} \begin{pmatrix} r & b & s \\ n_r & n_b & n_s \end{pmatrix} \\
 & \times \begin{pmatrix} s & p & u \\ -n_s & -n_p & -n_u \end{pmatrix} \begin{pmatrix} u & c & t \\ n_u & n_c & n_t \end{pmatrix} = (-1)^{r+b+s} \begin{pmatrix} a & b & c \\ -n_a & -n_b & -n_c \end{pmatrix} \left\{ \begin{matrix} a & b & c \\ p & s & u \\ q & r & t \end{matrix} \right\}
 \end{aligned}$$

### Sum rules with six Wigner 3- $j$ , 6- $j$ and/or 9- $j$ symbols:

- **Sum rules with six 3- $j$  symbols:** A sum rule corresponds to the representation of the 9- $j$  symbol in terms of six 3- $j$  symbols; see Rotenberg *et al.* (1959, Eq. 3.1).

$$\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & j \end{pmatrix} = \sum_{ABCDEFGHIJ} \begin{pmatrix} a & b & c \\ A & B & C \end{pmatrix} \begin{pmatrix} d & e & f \\ D & E & F \end{pmatrix} \begin{pmatrix} g & h & j \\ G & H & J \end{pmatrix} \begin{pmatrix} a & d & g \\ A & D & G \end{pmatrix} \begin{pmatrix} b & e & h \\ B & E & H \end{pmatrix} \begin{pmatrix} c & f & j \\ C & F & J \end{pmatrix}.$$

### Graphical loop rules for the Wigner 3- $j$ symbols:

- **Loop rules for one Wigner 3- $j$  symbol:** Several loop rules ( $n$ -loops) can be implemented separately for algebraic evaluations. A loop for one Wigner 3- $j$  symbol is given by Varshalovich *et al.* (1988, Eq. 12.1.2)

$$\sum_m (-1)^m \begin{pmatrix} j & j & J \\ m & -m & M \end{pmatrix} = (-1)^j [j] \delta_{J0} \delta_{M0}.$$

- **Loop rules for two Wigner 3- $j$  symbol:** Varshalovich *et al.* (1988, Eq. 12.1.3) also displays a loop for two Wigner 3- $j$  symbols

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{1}{2j_3 + 1} \delta_{j_3, j'_3} \delta_{m_3, m'_3} \delta(j_1, j_2, j_3).$$

- **Loop rules for three Wigner 3- $j$  symbol:** Varshalovich *et al.* (1988, Eq. 12.1.6) also displays a loop for three Wigner 3- $j$  symbols.

$$\begin{aligned} \sum_{m_1, m_2, m_3} (-1)^{-m_1 - m_2 - m_3} \begin{pmatrix} j_1 & j_4 & j_2 \\ m_1 & m_4 & -m_2 \end{pmatrix} \begin{pmatrix} j_2 & j_5 & j_3 \\ m_2 & m_5 & -m_3 \end{pmatrix} \begin{pmatrix} j_3 & j_6 & j_1 \\ m_3 & m_6 & -m_1 \end{pmatrix} \\ = (-1)^{-j_1 - j_2 - j_3 + j_4 + j_5 + j_6} \begin{pmatrix} j_4 & j_5 & j_6 \\ m_4 & m_5 & m_6 \end{pmatrix} \begin{Bmatrix} j_4 & j_5 & j_6 \\ j_3 & j_1 & j_2 \end{Bmatrix}. \end{aligned}$$

## 15.4. Symbolic evaluations of Racah algebra expressions not yet considered in JAC

### 15.4.a. Orthogonality, completeness and integral representation of the Wigner rotation matrices:

#### Unitarity and completeness of the rotation matrices:

- **Unitarity condition:** This condition for the Wigner rotation matrices can be written either in terms of the Wigner  $D$ -function (Varshalovich *et al.*, 1988, Eqs. 4.1.6) or, equivalently, by means of the Wigner rotation matrices

$$\sum_{p=-j}^j d_{pq}^j(\beta) d_{pr}^j(\beta) = \delta_{qr}, \quad \sum_{q=-j}^j d_{pq}^j(\beta) d_{rq}^j(\beta) = \delta_{pr}.$$

- **Orthogonality and normalization condition for the rotation matrices:** The orthogonality and normalization condition in terms of  $d_{pq}^j(\beta)$  is shown by Varshalovich *et al.* (1988, Eqs. 4.10.6 and 4.11.7)

$$\int_0^{2\pi} d\beta \sin \beta d_{pq}^j(\beta) d_{pq}^k(\beta) = \frac{2}{2j+1} \delta_{jk}$$

$$\int_0^{2\pi} d\alpha e^{-i(p_1-p_2)\alpha} \int_0^{2\pi} d\gamma e^{-i(q_1-q_2)\gamma} \int_0^\pi d\beta \sin \beta d_{p_1 q_1}^{j_1}(\beta) d_{p_2 q_2}^{j_2}(\beta) = \frac{8\pi^2}{2j_2+1} \delta_{j_1 j_2} \delta_{p_1 p_2} \delta_{q_1 q_2}.$$

- **Completeness condition of the rotation matrices:** cf. Varshalovich *et al.* (1988, Eq. 4.10.7) with double domain proportional to  $16\pi^2$

$$\sum_{j=0, \frac{1}{2}, 1, \dots}^{\infty} \sum_{p=-j}^{+j} \sum_{q=-j}^{+j} (2j+1) e^{+i[(\alpha_1-\alpha_2)p+(\gamma_1-\gamma_2)q]} d_{pq}^j(\beta_1) d_{pq}^j(\beta_2) = 16\pi^2 \delta(\alpha_1 - \alpha_2) \delta(\cos \beta_1 - \cos \beta_2) \delta(\gamma_1 - \gamma_2).$$



### Integrals involving Wigner $D_{pq}^j$ functions or rotation matrices $d_{pq}^j$ :

- The Wigner rotation matrices fulfill various integration rules as well as integration with invariant summation rules, and where some of these integrals involve products of more than one Wigner  $D$ -function. Whenever possible, we express the Clebsch-Gordan series as a product of two Wigner 3- $j$  symbols. Most of the following integration rules require solid angle integration either over the standard domain

$$\int d\Omega \equiv \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin(\beta)$$

or over an extended domain with

$$\int d\Omega \equiv \int_0^{4\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin(\beta) \quad \text{or} \quad \int d\Omega \equiv \int_0^{2\pi} d\alpha \int_0^{4\pi} d\gamma \int_0^\pi d\beta \sin(\beta) .$$

$$0 \leq \alpha \leq 4\pi, \quad 0 \leq \beta \leq \pi, \quad 0 \leq \gamma \leq 2\pi, \quad \text{or} \quad 0 \leq \alpha \leq 2\pi, \quad 0 \leq \beta \leq \pi, \quad 0 \leq \gamma \leq 4\pi,$$

For this redefinition of the domain of integration, the factors  $8\pi^2$  must typically be replaced by  $16\pi^2$ .

- **Integrals with one  $D_{pq}^j(\alpha, \beta, \gamma)$ :** Varshalovich *et al.* (1988, Eqs. 4.11.1 and 4.11.6) displays the following normalization integral as well as the corresponding special case for  $\alpha = \gamma = 0$  and/or  $p = q = 0$

$$\int d\Omega D_{pq}^j(\alpha, \beta, \gamma) = \int d\Omega e^{-i(p\alpha + q\gamma)} d_{pq}^j(\beta) = 8\pi^2 \delta_{j0} \delta_{p0} \delta_{q0}, \quad \text{if } j \text{ is integer}$$

$$\int_0^\pi d\beta \sin \beta d_{00}^j(\beta) = 2 \delta_{j0}.$$

### 15.4.b. Sum rules for spherical harmonics

#### Products of two and more spherical harmonics:

➤ Sum rules for two spherical harmonics:

$$\sum_{m=-\ell}^{\ell} (-1)^m Y_{\ell m}(\vartheta, \varphi) Y_{\ell, -m}(\vartheta, \varphi) = \sum_{m=-\ell}^{\ell} |Y_{\ell m}(\vartheta, \varphi)|^2 = \frac{2\ell + 1}{4\pi}$$

$$\sum_{l=0}^{\infty} \sum_{m=-\ell}^{\ell} (-1)^m m Y_{\ell, -m}(\vartheta, \varphi) Y_{\ell m}(\vartheta, \varphi) = 0$$

$$\sum_{l=0}^{\infty} \sum_{m=-\ell}^{\ell} (-1)^m m^2 Y_{\ell, -m}(\vartheta, \varphi) Y_{\ell m}(\vartheta, \varphi) = \frac{l(l+1)(2\ell+1)}{8\pi} \sin^2 \vartheta$$

$$\sum_{l=0}^{\infty} \sum_{m=-\ell}^{\ell} (-1)^m Y_{\ell, -m}(\vartheta, \varphi) Y_{\ell m}(\vartheta', \varphi') = \delta(\varphi - \varphi') \delta(\cos \vartheta - \cos \vartheta') = \delta(\varphi - \varphi') \frac{\delta(\vartheta - \vartheta')}{|\sin \vartheta|}.$$

➤ The Clebsch-Gordan expansion of two spherical harmonics: A product of two spherical harmonics with the same angles can be written as shown by Varshalovich *et al.* (1988, Eq. 5.6.9)

$$Y_{\ell_1 m_1}(\vartheta, \varphi) Y_{\ell_2 m_2}(\vartheta, \varphi) = \sum_{L, M} \left[ \frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2L + 1)} \right]^{1/2} \langle \ell_1 0, \ell_2 0 | L 0 \rangle \langle \ell_1 m_1, \ell_2 m_2 | L M \rangle Y_{LM}(\vartheta, \varphi)$$

➤ The Clebsch-Gordan expansion of  $n$  spherical harmonics: Using this relation  $n - 1$  times, one can easily derive a more general expression

$$\prod_{i=1}^n Y_{\ell_i m_i}(\vartheta, \varphi) = \sum_{L_n} B_{L_n} Y_{L_n M_n}(\vartheta, \varphi)$$

$$B_{L_n} = \frac{1}{\sqrt{(4\pi)^{n-1}(2L_n + 1)}} \sum_{\substack{L_1, L_2, \dots, L_n \\ M_1, M_2, \dots, M_n}} \prod_{i=1}^n \sqrt{2\ell_i + 1} \langle L_{i-1} 0, \ell_i 0 | L_i 0 \rangle \langle L_{i-1} M_{i-1}, \ell_i m_i | L_i M_i \rangle.$$

- **Irreducible tensor product of two spherical harmonics:** An irreducible tensor product of two spherical harmonics with the same angles can be written as (Varshalovich *et al.* 1988, Eq. 5.6.14)

$$\{Y_{\ell_1}(\vartheta, \varphi) \otimes Y_{\ell_2}(\vartheta, \varphi)\}_{LM} = \left[ \frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2L + 1)} \right]^{1/2} \langle \ell_1 0, \ell_2 0 | L 0 \rangle Y_{LM}(\vartheta, \varphi)$$

- **Irreducible tensor product of  $n$  spherical harmonics:** Using this relation  $n - 1$  times, one finds a more general expression (Varshalovich *et al.* 1988, Eq. 5.6.16):

$$\left\{ \cdot \left\{ \{Y_{\ell_1}(\vartheta, \varphi) \otimes Y_{\ell_2}(\vartheta, \varphi)\}_{L_2} \otimes Y_{\ell_3}(\vartheta, \varphi) \right\}_{L_3} \cdot \otimes Y_{\ell_n}(\vartheta, \varphi) \right\}_{L_n M_n} = \frac{1}{\sqrt{(4\pi)^{n-1}(2L_n + 1)}} \prod_{i=1}^n \left[ \sqrt{2\ell_i + 1} \langle L_{i-1} 0, \ell_i 0 | L_i 0 \rangle \right] Y_{L_n M_n}(\vartheta, \varphi).$$

- **Multipole expansions by using spherical harmonics:** The spherical harmonics are not only orthonormal to each other but they also form a complete set of functions for the expansion of any function  $f(\Theta, \Phi)$  that satisfies the given condition:

$$\int_0^{2\pi} d\Phi \int_0^\pi d\Theta \sin \Theta |f(\Theta, \Phi)|^2 < \infty : \quad f(\Theta, \Phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \tilde{f}_{lm} Y_{lm}(\Theta, \Phi), \quad \tilde{f}_{lm} \equiv \int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{lm}^*(\vartheta, \varphi) f(\vartheta, \varphi).$$

### 15.4.c. Integrals involving spherical harmonics

#### Integrals involving spherical harmonics:

- **Orthonormality of the spherical harmonics:**

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{\ell m}^*(\vartheta, \varphi) Y_{\ell' m'}(\vartheta, \varphi) = \delta_{\ell \ell'} \delta_{m m'}.$$

## 15. Symbolic evaluation of expressions from Racah's algebra

➤ **Further integrals over  $4\pi$ :** Cf. Varshalovich *et al.* (1988, Eqs. 5.9.1 and 5.9.5):

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{\ell m}(\vartheta, \varphi) = \sqrt{4\pi} \delta_{\ell 0} \delta_{m 0}$$

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{\ell_1 m_1}(\vartheta, \varphi) Y_{\ell_2 m_2}(\vartheta, \varphi) Y_{\ell_3 m_3}(\vartheta, \varphi) = \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

## Derivatives of spherical harmonics:

➤ **Derivatives of spherical harmonics:** Cf. Varshalovich *et al.* (1988, Eq. 5.8.5) and with the associated Legendre polynomials  $P_l^m(\cos \vartheta)$

$$\frac{d}{dx} \int_{g(x)}^{h(x)} dy f(y) = \frac{dh(x)}{dx} f(h(x)) - \frac{dg(x)}{dx} f(g(x)) \quad \text{chain rule}$$

$$\frac{d}{d\vartheta} Y_{\ell m}(\vartheta, \varphi) = \frac{1}{2} \sqrt{\ell(\ell+1) - m(m+1)} Y_{\ell, m+1}(\vartheta, \varphi) e^{-i\varphi} - \frac{1}{2} \sqrt{\ell(\ell+1) - m(m-1)} Y_{\ell, m-1}(\vartheta, \varphi) e^{i\varphi}.$$

$$\frac{d}{d\varphi} Y_{\ell m}(\vartheta, \varphi) = i m Y_{\ell m}(\vartheta, \varphi).$$

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