

Finite Element Approach to Photoemission of Complex Molecules

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Notation:

- \mathbf{r} vector in 3 dimensions
- \mathbb{R} General matrix
- $|\Psi\rangle$ one-particle wave function
- $|\Phi^{\text{DO}}\rangle$ Dyson orbital
- $|\Phi^{\text{el}}\rangle$ Free electron function
- $|\Psi^N\rangle$ N -electron wave function
- \hat{a}/\hat{a}^\dagger annihilation/creation operators:..

Abbreviations:

- CAP complex absorbing potential
- CI configuration interaction
- DO Dyson orbital
- DFT density functional theory
- DVR discrete variable approximation
- ESP electrostatic potential
- eV electron volt
- FD finite difference
- FEF free electron function
- FEM finite element method
- FE-DVR finite element discrete variable approximation
- FV finite volume
- GASCI
- LCAO linear combination of atomic orbitals
- LUMO lowest unoccupied molecular orbital
- RBF radial basis function
- SCF self-consistent field
- SD Slater determinant
- SA sudden approximation
- SE Schrödinger equation
- TDDFT time dependent density functional theory

1 | Introduction

Steady state as well as time-resolved photoelectron spectroscopy have become widely used tools to study the composition of gases and liquids [1–4], the structure of solids [5] as well as chemical reactions such as electron transfer [3]. The process studied by photoelectron spectra is the absorption of a high-energetic photon (usually in the ultra-violet to hard X-ray regime) by an N -electron system which leads to the release of an electron whose kinetic energy is measured. This process is sketched in Figure 1.1 where the bound states are depicted by horizontal bars and the states of the outgoing electron are visualised by the gradient-filled block, indicating that its energy is continuous. Measuring the kinetic energy of the photoelectron yields information on the energy of its previous states due to energy-conservation over the process.

One of the main reasons for the broad success of this particular type of spectroscopy is that these spectra are very sensitive to small changes in the chemical environment and hence yield information not only about the chemical structure of molecules but also about intermolecular interactions as for example solvation effects [1, 6–9]. Furthermore, photoelectron spectroscopy provides a more direct access to the energy levels than optical absorption and emission spectroscopy since the transition energies are obtained with respect to the vacuum level and no “dark” states occur due to different selection rules. Finally the ease of handling charged particles experimentally makes this method appealing and a good temporal resolution can be achieved by varying the path in the time of flight spectrometer. Moreover, besides its capabilities in steady state spectroscopy, photoelectron spectra are the standard tool to study attosecond physics due to the naturally high energy of the short pulses which ionise the systems under

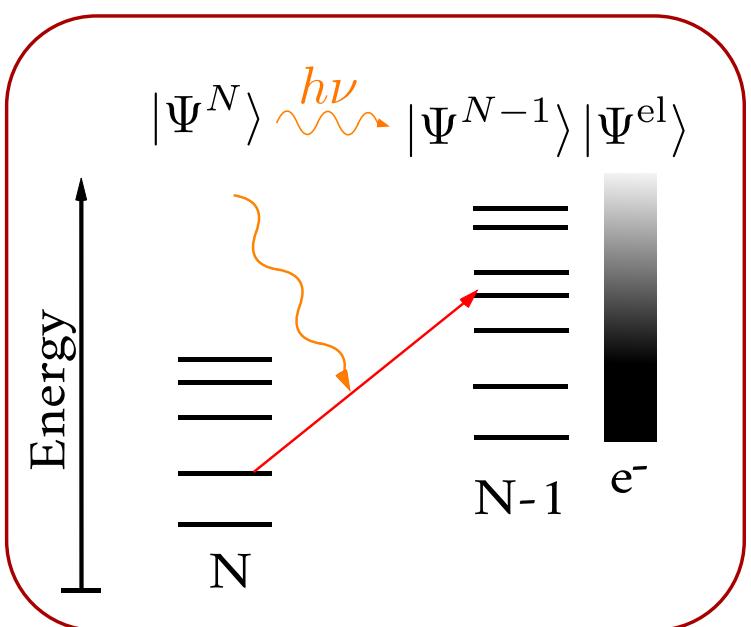


Figure 1.1: Schematic representation of a photoelectron transition : an incoming photon with energy $h\nu$ ionises the N -electron system, transferring it into a free electron in a continuum state and a system of $N - 1$ bound electrons. The bars denote bound states, the color-gradient depicts the energy of the outgoing electron.

study [10–15]. However, a limitation of photoelectron spectroscopy is that the short free-path of electrons in condensed phases limits the probe depth significantly.

Having performed a measurement of a photoelectron spectrum (PES) it is, at least for complex systems, rich of features and hence the interpretation requires theoretical methods. This especially applies to systems with strong electron correlation which manifests itself in the appearance of combination transitions. Over the decades a large variety of methods to calculate photoelectron spectra have been developed at different levels of theory. In literature often the theoretical spectra are estimated on the basis of Koopmans' theorem [16], (or its density functional theory (DFT) counterpart [17],) assuming equal intensities for all transitions [18–21]. Even though this is a quite successful approach for solid states [22, 23] and gives an easy interpretation, it is too simplistic in many cases since it neglects electron relaxation and correlation effects and hence may give an invalid picture as shown by Cederbaum *et al.* even for small systems such as various diatomics [24, 25]. Furthermore in this model no reliable information about intensities can be obtained. To retrieve quantitative transition strengths, more advanced models are needed. Since simulations in time-domain are very demanding they are only applied to small molecules, mainly to study strong-field effects such as high harmonic generation [11, 26–29] which can not be described in frequency-domain. In this thesis however the focus is on complex molecular systems and a wide range of kinetic energies, while more moderate field strengths should be applied. Hence frequency-domain methods derived from a perturbation theory with respect to the irradiating electromagnetic field are applicable here.

In this thesis, the PESs are calculated within the Dyson orbital (DO) formalism which is derived and explained in more detail. This formalism is based on Fermis' Golden Rule [30] and allows a reduction of the dipole moment matrix element from an N -electron integral to effective one-particle quantities. Thereby the initial state and the bound part of the final state are represented by a one-electron quantity denoted as DO. The other wave function entering the dipole moment operator is the free electron function (FEF). In this formalism electron relaxation and correlation effects between bound states of the unionised and ionised systems are included, allowing the description of combination transitions. Per contra, this formalism neglects the correlation of the outgoing electron with the ionic remainder and thus may neglect certain transitions [31].

Since the bound state wave functions can be obtained from standard quantum-chemical tools, the computation of the DO is straightforward even though technically demanding [32]. The computation of the FEF is in general not trivial since analytic solutions are known only for few special cases such as hydrogen-like atoms [33] and general basis sets as they are used for bound states are not available. Among others, three analytic expressions have been suggested, each based on an expansion of spherically symmetric functions in plane waves [34]. One of them is the spherical wave basis which is a set of solutions of the Schrödinger equation (SE) without any potential and hence is especially well-suited for photodetachment from negative ions, leaving systems in an uncharged state [34, 35]. The other two expansions are based on Coulomb waves which assume a Coulomb potential and hence are exact for the ionisation of hydrogen-like atoms [33]. Thereby one of them is an expansion in Coulomb waves for the given momentum vector \mathbf{k} while the other is an asymptotic expression for Coulomb waves with vanishing momentum (Coulomb $|\mathbf{k}| = 0$).

The functions each are expanded in a series of increasing quantum numbers for angular momentum l and its projection m . Since all three functions assume spherical symmetry of the potential, they are expected to give a good approximation to the real FEF for spherically symmetric systems only. Ionisation *e. g.* from a delocalised orbital of a linear molecule have a different symmetry and thus can be expected to be described only crudely by this approach. The effects due to lower molecular symmetry become especially important for low kinetic energies because the interaction with the ionic remainder becomes strong in this case.

To analyse the quality of a given expression for a FEF, it is instructive to study the intensity of a given transition as a function of kinetic energy. Such a study is examined in Figure 1.2, showing the intensity of the photoionisation transition from the highest occupied molecular orbital (HOMO) of water for different kinetic energies of the photo-electron, estimated with the above-mentioned expansions. The comparison shows that all three expansions yield different intensities for most transition energies. Besides leading a wrong wrong symmetry of the FEF, these expansions yiled even in the limit of infinite terms only a plane-wave, neglecting the ionic potential and hence are not asymptotically correct.

To overcome the restrictions in symmetry and kinetic energy of the photoelectron function, an explicit formulation is needed, taking the molecular electrostatic potential experienced by the outgoing electron into account. Assuming that the correlation between the FEF and the bound states of the ion is weak (which is a prerequisite for the DO formalism anyway), one can use the mean-field potential of the molecular remainder. This allows for obtaining the FEF from the one-electron SE with an appropriate potential and thus reduces the complexity compared to the exact case where a coupled N -electron equation needs to be solved, considerably.

In the thesis at hand a good approximation to the FEF is aimed which should be applicable to a wide range of molecules and photon energies. Such a flexible description is possible exploiting the finite element method for solving the SE. In the finite element method, the space of interest is subdivided into small volume elements and solved variationally with stepwise polynomials whose support spans over one or few elements only [36, 37]. The finite element description is especially efficient here since the size of the elements

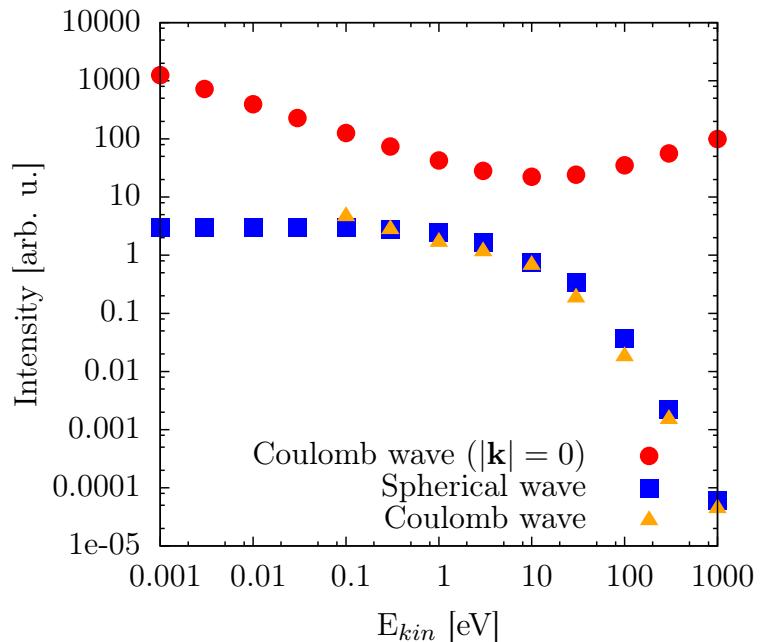


Figure 1.2: The intensity of the lowest-lying transition of water depending on the kinetic energy of the photoelectron. Each expansion is performed up to $l = 10$.

can be locally adapted to reproduce finer structures or broader shapes [36, 38]. Using finite elements, the one-particle SE is formulated a generalised eigenvalue problem with sparse matrices.

An important characteristic of the exact FEF is its spacially infinite extend which can not be handled by the finite element method. To describe the function in a good approximation, the finite elements are extended by infinite elements [39–42] which are volume elements with infinite radial extend that are connected to the outer surface of the finite element region. Thereby the radial function is a polynomial in $\frac{1}{r}$ multiplied by e^{ikr} , resembling the asymptotic behaviour of known analytic solutions and fulfilling the Sommerfeld radiation condition [43].

The bound states can be obtained on the level of density functional theory (DFT) which is a formally exact method based on the Hohenberg-Kohn theorem [44], stating that the total electron density determines all system properties such as electronic binding energies. However, the correct form of the exchange potential as well as the kinetic energy are not known as functionals of the electron density and hence approximate functionals need to be used. While the kinetic energy can be estimated reasonably by the Kohn-Sham scheme [45], the expressions used for the exchange-correlation potential yield electron densities that have a wrong long-range asymptotic decay which affects the observables of these systems [19, 20, 46]. To reduce this error, range-separated hybrid functionals are used where the usual DFT exchange functionals are used at small distances while a Hartree-Fock exact exchange ensures the correct behaviour at larger distances. The interchange between these contributions is modelled via an error function with a characteristic distance that is optimized for each system separately. This procedure has been observed to enhance the accuracy of the predicted properties such as the orbital energies [46–49].

While the schemes described above are well established, their combination is only rarely used. Especially the FEF is found in literature to be approximated only crudely as plane-wave functions [50] or in some expansion as described above [32, 34, 47]. The goal of this thesis is to use the DO formalism with bound states being described by DFT using the above-mentioned optimized range-separated hybrid (OTRSH) functionals to obtain accurate orbital energies and complement it with a FEF that accounts the molecular electrostatic potential explicitly using the finite and infinite element methods which have been applied only to very few quantum mechanical problems [51, 52].

In the protocol used the DFT and time-dependent DFT calculations for excited states are done using a locally modified version of **NWChem** [53] and the **Gaussian 09** package [54]. From those, the DO is calculated with the in-house code **DYSON** developed previously [32]. A self-written interface extracts the required data as *e.g.* the molecular orbital coefficients and overlap matrix of atomic orbitals from the output of these programs. For the computation of the FEF, the program **FreeWilly** [55] is developed using the finite element library **Libmesh** [56]. **Libmesh** is an open source library that provides a broad range of capabilities and interfaces to several high-performance linear algebra libraries [57–59]. Moreover, it supports MPI parallelisation and implements a recent formulation of the above-mentioned infinite elements [42]. Especially the latter is to the best of my knowledge a unique option. Furthermore it has an automated procedure to adaptively refine or coarsen the elements according to local error estimates.

The goal of this thesis is to find a systematic way to setup the finite element mesh

for any given molecule to describe the photoelectron with a reasonable accuracy that goes beyond the capabilities of existing programs in this field. This procedure will be tested on different model systems.

- Lithium: light atomic system, many experimental and experimental reference data available, the `ezDyson` calculations are expected to give a good approximation.
- CO₂: linear easy molecule with some reference data available, used to test some further properties
- Benzene (?): More complex molecule with reference data, well investigated
- Some other system(s) for which `ezDyson` gives poor results (?)

2 | Calculation of Photoelectron spectra

The large variety of systems and effects studied with photoelectron spectroscopy led to the existence of diverse methods for theoretical modelling of the spectra [60, 61]. In this work, the focus is put on steady-state photoelectron spectra of molecular systems with a size up to some tens of atoms. As light source, here a classical ultra-violet or soft X-ray source with a discrete spectrum such as a gas discharge lamp or a laser is assumed where the strength of the applied electromagnetic field is weak and the kinetic energy of the outgoing electrons reaches at most tens of electronvolt but may become arbitrarily small.

A summary of methods that can be used to describe the most important scenarios arising in photoelectron spectroscopy is given in the Table 2.1 and some of them are described in more detail in the following sections. The main classification of these methods can be done dividing them into time and frequency domain. These domains are related to each other via the Fourier transform but provide different pictures and properties. Using a frequency-domain method, the Hamiltonian has to be diagonalised to obtain the states' energies and wave functions. In contrast to this, in time domain the Hamiltonian is applied to an initial state to propagate the system in time. Usually such a simulation needs several thousands of propagation steps to obtain reasonable accuracy. Moreover, the joint treatment of bound and continuum states demands a large and flexible basis which makes time domain methods usually computationally very demanding and restricts their applicability to small systems as shown in the Table 2.1. On the other hand, in frequency-domain the nonlinear response properties are neglected so that strong-field effects such as multiphoton ionisation and high harmonic generation (HHG) can not be treated. Due to the different treatment of the system in both domains, they each have a set of methods that can be used and which are more or less specific to the domain as shown in the third column of Table 2.1. The same holds for the quantum chemical methods available to treat the system.

	Field Str.	Method	System Size	Typical Problems	QC ^(a)
Time-domain	weak to strong	TDDO [62] SE Green's function	atoms [63], diatomics [26, 64, 65] triatomics [66]	HHG [27–29], Multiph. ionisation attosec. dynam.[10–15]	(TD)DFT, GASCI [63], EOM-CC [67], CASSCF
Frequency-domain	weak	R-Matrix [68–72] DO [35, 50] Green's Function [73, 74] Koopmans'[17, 75, 76]	up to biomolecules [77], solid state [22, 23]	steady-state, angle-res. PES time-res. PES	RASSCF [32, 47], TD-DFT

Table 2.1: Overview of time- and frequency-domain methods and theyr typical applications.

^(a)QC: quantum chemical; GASCI: generalised active space configuration interaction; CASSCF: complete active space self-consistent field; EOM-CC: equation of motion- coupled cluster; RASSCF: restricted active space self-consistent field.

Besides the distinction according to the domain, the methods can be also categorised according to the partitioning of the system they use which is sketched in Figure 2.1. The simplest and crudest method is an approach derived from Koopman's theorem where only the ground state of the un-ionised state is considered which is visualised in Figure 2.1 by the fact that the box for this method is only at the N -electron system. Similarly, also the Green's function approach treats only the initial state but accounts for electron relaxation and thus correlation effects during ionisation due to its quasi-particle picture. In the DO formalism, in contrast, the final state is treated explicitly, using a partitioning into the bound $N - 1$ -electron state $|\Psi^{N-1}\rangle$ and the FEF $|\Psi^{\text{el}}\rangle$. Finally a large class of methods treat the system uniformly, using a joint treatment for the bound and continuum states as indicated by the single box in Figure 2.1.

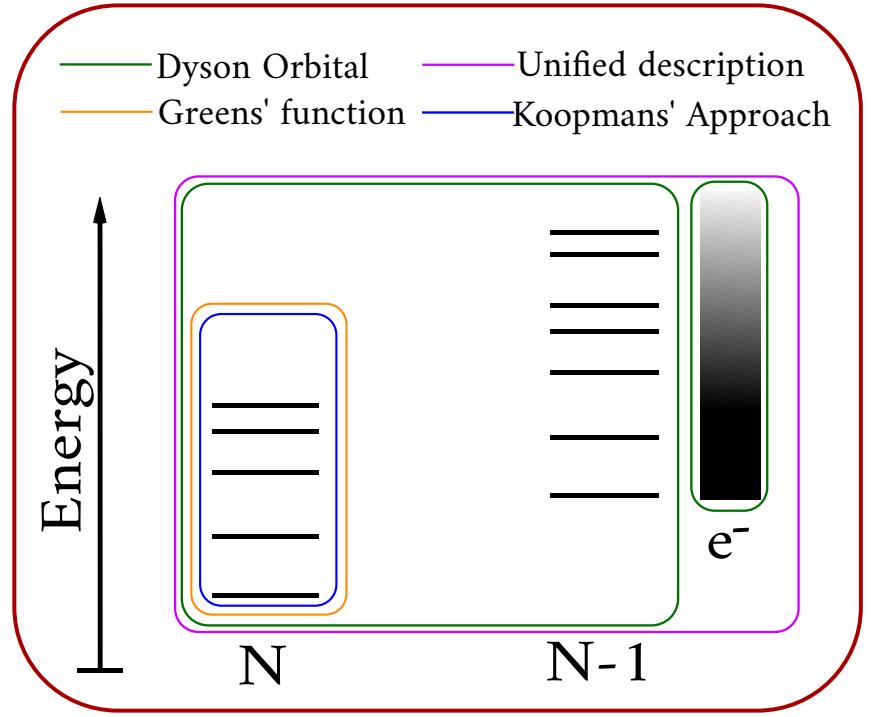


Figure 2.1: Scheme of the system-representation used in the different methods.

The Koopmans' approach is, at least among the frequency domain methods, the most prominent representative [19, 75, 76, 78]. In this scheme, the systems ground state is computed with a self-consistent field quantum mechanical method to obtain the one-electron binding energies. The photoelectron spectrum is than estimated using the orbital energies as the transition energies and using uniform intensities. Although this method has shown to be in qualitative agreement with experiments for different systems [19, 20, 78–80], it breaks down in case of strong electron correlation [24, 74] due to relaxation of the orbitals upon ionisation. This method is characterised by its low computational costs and robustness and, thus, is well-suited for very large systems such as solid state problems where calculations beyond ground-state DFT are very demanding or not feasible at all.

In the following sections, the most important methods will be briefly introduced according to their affiliation to the groups distiguished in Figure 2.1. First, in section 2.1 the working equations of the Green's function approach are introduced to give a fundamental understanding of this group of methods. Thereafter, in section 2.2 several approaches both in time- and frequency-domain are described that use a unified description of the complete N -electron system. Finally the DO formalism is derived in more detail, since it is the method of choise in this work, in section 2.3.

2.1 The Green's Function Approach

From a formal point of view, the computation of photoelectron spectra using the Green's function approach is similar to the use of Koopmans' approach since in both methods only the ground state of the unionised system is considered. However, the level of theory achievable when using Green's functions is much higher.

In contrast to most other quantum-chemical methods, in the Greens' function approach expectation values for a given operator \hat{O} are not computed as a scalar product $\langle \Psi^N | \hat{O} | \Psi^N \rangle$ with the wave function $|\Psi^N\rangle$ of the N electron state of interest, but by contour integrals with the Greens' function [81, 82]. Thereby the (one particle) Greens' function is a matrix \mathbb{G} whose elements are defined as

$$G_{i,j}(t, t') = -i\langle \Psi^N | \hat{T} \left(\hat{a}_i(t) \hat{a}_j^\dagger(t') \right) | \Psi^N \rangle \quad (2.1)$$

with the creation operator $\hat{a}_j^\dagger(t) = e^{i\hat{H}t} \hat{a}_j e^{-i\hat{H}t}$ of an electron in state j at time t in Heisenberg picture and the annihilation operator $\hat{a}(t) = e^{-i\hat{H}t} \hat{a}_j e^{i\hat{H}t}$ respectively. \hat{T} is the Dyson time ordering operator that orders the operators \hat{a} and \hat{a}^\dagger by their time arguments to ensure that the operator with smaller time argument acts first [81]. Hence, the Greens' function can be interpreted as an additional electron (or hole, depending on the time ordering) propagating from t' to t in a system described by the Hamiltonian \hat{H} [81].

To find an expression of the Green's function (2.1) from which the transition energies and intensities can be extracted, it needs to be reformulated. In the first step, the time ordering operator is written explicitly which results in

$$G_{i,j}(t, t') = i\langle \Psi^N | \hat{a}_j(t) \hat{a}_i^\dagger(t') | \Psi^N \rangle \Theta(t - t') - i\langle \Psi^N | \hat{a}_i^\dagger(t') \hat{a}_j(t) | \Psi^N \rangle \Theta(t' - t). \quad (2.2)$$

Inserting the closure relation $\hat{1} = \sum_k |\Psi_k^M\rangle \langle \Psi_k^M|$, where $M = N \pm 1$ and $|\Psi_k^M\rangle$ describes a bound state, between the operators in both terms of (2.2), the Lehmann representation [81] is obtained whose Fourier transform is

$$G_{i,j}(\omega) = i \sum_k \frac{\left| \langle \Psi^N | \hat{a}_j | \Psi_k^{N+1} \rangle \right|^2}{\omega - (E_k^{N+1} - E^N) + i\nu} - i \sum_k \frac{\left| \langle \Psi^N | \hat{a}_i^\dagger | \Psi_k^{N-1} \rangle \right|^2}{\omega + (E_k^{N-1} - E^N) - i\nu}, \quad (2.3)$$

where ν is a small parameter arising from calculation of principal value and ω denotes the argument of the Fourier transform while E^N and E_k^M are the energies of the N -electron ground state $|\Psi^N\rangle$ and of the k -th M -electron state $|\Psi_k^M\rangle$, respectively. In this form, the second sum corresponds to transitions in the PES: the nodes of the denominator (poles of the Greens' function) can be easily assigned to the ionisation potentials and, thus, the transition energies in photoelectron spectra. Further, the integrals in the nominator are equivalent to the sudden approximation derived in chapter 2.3.3 and hence provide a good approximation to the transition strengths. The terms in the first sum correspond to the respective quantities of electron detachment [82].

However, computing the Greens' function is a demanding task which is of similar complexity as the computation of a solution to the SE. Over the years several approaches were developed of which the algebraic diagrammatic construction [82] and the equation

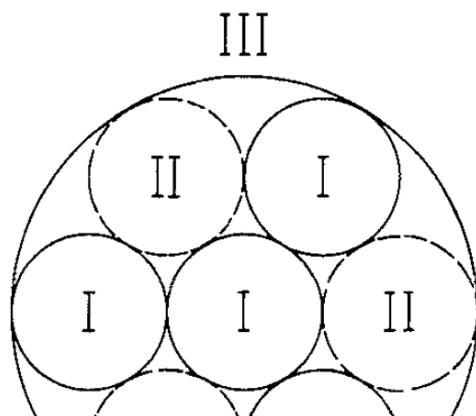
of motion [78, 82] are the most prominent. In the diagrammatic construction one starts with an initial zeroth order Greens' function $\mathbb{G}^0(\omega)$ constructed in a Hartree-Fock basis and corrects it iteratively by the term $\mathbb{G}^0(\omega)\Sigma(\omega)\mathbb{G}(\omega)$, where $\Sigma(\omega)$ is the self-energy, an effective potential that is used to recover electron correlation and relaxation effects [73]. The self-energy usually is expanded in a perturbation series with respect to Feynman diagrams with increasing number of vertices and is exact in the limit of infinite terms [81, 83]. The one-particle energies, Coulomb matrix elements and overlap integrals are obtained from self-consistent field (SCF) calculations [82] *e.g.* on the HF-level [73] but (TD)DFT or any other quantum chemical method can be used as well via the GW-approach [84, 85]. Being much easier to compute, the Hartree-Fock basis has the disadvantage that only single configurational electronic states can be treated.

On the other hand, an important advantage of the Greens' function method is that the transition energies are computed directly whereas in most other methods they are calculated as the difference of the initial and final state energies. The latter approach however can lead to errors in the electronvolt range when the difference in the correlation energy is badly estimated [82].

2.2 Combined Bound and Continuum State Representation

In contrast to the Greens' function method, in which the explicit description of the FEF omitted, a large group of methods describes the full N -electron system before and after the ionisation, respectively (see Figure 2.1). In this section a selection of such methods is presented. The treatment of bound and continuum states, however, requires a very flexible formalism whose large computational costs restrict its applicability to small systems that often fulfil certain symmetry-requirements and have a small amount of electrons.

The most prominent representative of this class in frequency domain is the R-matrix method [70, 71, 86]. Its general idea is to conduct a partition of space into regions which are treated differently and connected by explicit boundary conditions to ensure smoothness of the wave function. These regions are constructed with concentric spheres, restricting the symmetry of wave functions in this scheme. Nonetheless it is found to be applied not only to atoms [68, 69, 87] but also to small molecules [72, 88]. In the R-matrix formalism the inner region is chosen large enough to contain the bound part of the N -electron function that is usually represented by a configuration interaction (CI) expansion of Slater determinants (SDs), using a linear combination of atomic orbitals (LCAO) basis or a grid representation [70]. The FEF is commonly described by a linear combination of bound orbital type functions and continuum functions such as Coulomb waves [71, 86]. In the outer region, an expansion in Coulomb waves is used to ensure the asymptotically correct behaviour. In addition to the inner region and the asymptotic outer region further intermediate regions can be added where the FEF is represented by a multipole-radiation expansion which is a polynomial of



inverse powers of the distance to the centre [70].

A generalisation to non-spherical systems is employed, *e.g.*, by Johnson [89] who used different kinds of non-concentric spheres. One set spheres is centred at atoms while others are placed in the interatomic regions such that the space is filled as dense as possible as shown in Figure 2.2 for a molecule with four atoms. Each atom is located in the centre of a circle denoted as I while the circles II fill the interatomic space. An outer sphere surrounds the molecule to account for the asymptotic region similar to the asymptotic region in R-matrix theory. In this scheme, the exchange-correlation is treated on an approximate level [90] and is spherically averaged, resulting in a description that is equivalent to the muffin-tin potential which is a well-known model in solid state physics [91, 92]. The continuity of the wave-functions as well as their derivatives is ensured over the regions via multiple-scattered-wave theory [89]. The wave-functions are chosen in each region as a one-centre expansion in spherical coordinates of the form

$$\Psi(r, \theta, \phi) = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l c_{l,m} R_l(r) Y_l^m(\theta, \phi) \quad (2.4)$$

where r, θ, ϕ are the spherical coordinates and $Y_l^m(\theta, \phi)$ are the spherical Harmonics [33] and the radial function $R_l(r)$ is a solution of the radial SE

$$\frac{\partial^2 R(r)}{\partial r^2} + \left(E - V(r) + \frac{l(l+1)}{r^2} \right) R(r) = 0 \quad (2.5)$$

with the respective spherically averaged potential $V(r)$ [89].

An approach applied by DeCleva *et al.* to H_2^+ [26] and benzene [93] refrains from the use of spheres, allowing for more general boundaries between the inner and outer regions. Here the FEFs are globally represented as the one-centre expansion (2.4) where $R(r)$ is expressed by a B-spline basis. An advantage of the spline-based description is that smoothness at the interface between the regions is ensured intrinsically.

Another scheme in frequency domain is used by Richards and Larkins [94] with a hybrid ansatz: The bound states of the H_2 molecule are described in the common LCAO scheme and the FEF is described by the product ansatz $\Psi(\mathbf{r}) = R(r, \theta) e^{im\phi}$, which is a generalisation of (2.4), where $R(r, \theta)$ is obtained from a two-dimensional SE on a regular grid using a finite difference (FD) scheme. In contrast to the previously described methods, here no partition of space is performed but instead a finite box with Dirichlet boundary conditions is used. Moreover, the FEF is treated on the HF-level, neglecting correlation effects [94].

Similar descriptions are used in time domain by several authors [63, 67, 95]. Even though they are much more demanding than calculations in frequency domain, time do-

main methods can predict strong-field effects and are used to simulate attosecond dynamic which is both not achievable using frequency-domain methods.

An important difference between time- and frequency-domain methods of practical use is that in time-domain unbound particles are described by a wave packet and hence as a localised function. Moreover, at short times after ionisation the continuum states often can be assumed to be of similar spacial extend as bound states, allowing the basis to be a linear combination of bound state functions but having a complex energy whose real part introduces oscillations and the imaginary part damps the wave function, leading to a finite lifetime of the function [67]. Moreover a complex absorbing potential (CAP) (discussed in chapter 4.4.1 in more detail) is most often applied, ensuring that the continuum states can be described by bound-state functions by cutting off that part of the wave function which is not localised at the molecule anymore. Due to these considerations the LCAO basis can be used for the description of the free particles as well, see *e.g.* Jagau *et al.* [67]. In other simulations, grid-based descriptions are chosen using symmetry-adapted coordinate systems [66, 95–97], allowing for a product ansatz similar to (2.4) and hence a reduction in dimensionality. On the remaining one-dimensional grids often a discrete variable representation (DVR) (described in section 3.3 of this thesis) is chosen. As an example, Yip *et al.* [98] simulate double ionisation of atomic beryllium in spherical coordinates, using the expansion (2.4) where $R(r)$ is separated into two regions in which a DVR and a finite element DVR (FE-DVR) scheme are used respectively. As other examples, Tao *et al.* [95] as well as Bauch *et al.* [63, 64] use the FE-DVR basis in spheroidal coordinates.

The examples introduced above represent only a small fraction of the methods used to describe photoionisation in frequency and time domain. But a drawback that is common to these methods is that a large number of continuum functions is required which are correlated with the bound electrons and thus lead to a computationally expensive description of the system. To overcome this drawback, in the DO formalism that is presented in the coming section the description of bound and continuum states is separated into separate problems.

2.3 The Dyson Orbital Formalism

The Dyson orbital (DO) formalism can be considered as an approximation to the methods described above. Here the free and bound states are described separately, see Figure 2.1, using a product ansatz. Using such a separation leads to a neglect of correlation effects between the outgoing electron and the bound states and is often denoted as sudden ionisation limit [32, 34]. Moreover, non-linear effects as well as recombination transitions are not considered within DO theory. An important advantage, however, is that the overlap between the initial state and the bound part of the final state is formulated as a one-electron quantity, called DO which can be used to simplify the description of the photoionisation process. Usually the DO scheme is considered in the frequency domain, but a time domain formulation exists as well and is described in the following section [62].

2.3.1 Time-dependent Dyson Orbitals

A good starting point for the DO formalism is an expansion of the time-dependent N -electron function $|\Psi^N(t)\rangle$ (omitting the spacial coordinates for brevity) in the form

$$|\Psi^N(t)\rangle = \frac{1}{\sqrt{N}} \sum_k |\Psi_k^{DO}(t)\rangle |\Psi_k^{N-1}\rangle e^{iE_k^{N-1}t} \quad (2.6)$$

where E_k^{N-1} are the energies of the $N - 1$ -electron bound states described by the time-independent wave functions $|\Psi_k^{N-1}\rangle$ that are complete in the space of $N - 1$ -electron wavefunctions. The expansion coefficients $|\Psi_k^{DO}(t)\rangle$ have the dimensionality of a one-particle function and are denoted as time-dependent DO (TDDO). An important feature of the expansion (2.6) is that the dynamics of the N -electron system is reduced to a system of one-electron quantities $|\Psi_k^{DO}(t)\rangle$, propagated according to the electronic SE [62]. In this approach the interaction of the DO with the bound states is approximated by the mean-field electrostatic potential (ESP) [62], neglecting exchange and correlation.

The physical interpretation of the TDDO becomes clear when regarding its definition, given by the $N - 1$ -electron integral

$$|\Psi_k^{DO}(t)\rangle = e^{iE_k^{N-1}t} \sqrt{N} \langle \Psi_k^{N-1} | \Psi^N(t) \rangle_{N-1}. \quad (2.7)$$

The remaining coordinate (2.7) belongs to the photoelectron since $|\Psi^N(t)\rangle$ is restricted to the description of bound states. Considering eq. 2.7 in a frozen orbital approximation, *i.e.* one-electron ionisation, the TDDO corresponds to the photoelectron. However, relaxation effects lead to non-orthogonal orbitals of the N - and $N - 1$ -electron systems and thus lead to additional contributions to the TDDO. Therefore, when considering relaxation effects, the TDDO is a quasi-particle describing the electron that is ionised, including relaxation and correlation effects [34, 62].

2.3.2 Time-independent Dyson Orbitals

Working in frequency domain, no propagation needs to be considered. Instead, the quantity of interest here is the stationary DO which corresponds to the TDDO at $t = 0$. From eq. 2.7 the DO can be interpreted as quasi-particle that is ejected by the irradiating light [34].

While for the TDDO only the general expressions were shown, in this section, since the time-independent DO formalism is used within this work, a more detailed derivation of the expressions is done.

The main advantage of this formalism in frequency-domain becomes clear when the photoelectron cross-section is considered. In the Fermis' Golden Rule [30] formulation, which assumes the wavelength to be much larger than the characteristic size of the system under study and weak irradiating light-field, the cross-section for the transition between an initial i and final k states is in atomic units [32, 94]

$$\sigma(\epsilon) = \frac{2}{3} \sum_k (\epsilon + E_k - E_i) \left| \langle \Psi_i^N | \hat{\mathbf{d}} | \Psi_k^N \rangle \rho(\epsilon) \right|^2 \propto \sum_k |\mathbf{D}_k|^2 \quad (2.8)$$

where $\epsilon = h\nu - (E_k - E_i)$ is the kinetic energy of the photoelectron that is determined by the photon energy $h\nu$ and the energies E_α of the initial unionised state $|\Psi_i^N\rangle$ and the final ionised state $|\Psi_k^N\rangle$ which includes all electrons, further $\mathbf{D}_k = \langle \Psi_i^N | \hat{\mathbf{d}} | \Psi_k^N \rangle$ is the transition dipole moment and $\rho(\epsilon)$ is the density of final states which is in the following assumed to be a delta function. Writing the initial and final states each as SDs

$$|\Psi_i^N\rangle = \hat{A}_N |\Phi_{i,1} \dots \Phi_{i,N}\rangle \quad (2.9a)$$

$$|\Psi_k^N\rangle = \hat{A}_N |\Phi_{k,1} \dots \Phi_{k,N-1} \Psi_k^{\text{el}}\rangle \quad (2.9b)$$

where \hat{A}_N is an N -electron antisymmetrisation operator, $|\Phi_{k,j}\rangle$ are the j -th (Kohn-Sham) orbitals and Ψ_k^{el} is the FEF. The index k enumerates the final states which can have an arbitrary electron configuration here. The dipole operator $\hat{\mathbf{d}}$ is a one-electron operator that can be written as $\hat{\mathbf{d}} = \sum_{j=1}^N \hat{\mathbf{d}}_j$ where $\hat{\mathbf{d}}_j = \mathbf{r}_j$ in length gauge or $\hat{\mathbf{d}}_j = \nabla_j / (\epsilon + E_k - E_i)$ in velocity gauge respectively [94].

Using the SD representations (2.9), the integral \mathbf{D}_k in eq. (2.8) can be written as

$$\mathbf{D}_k = \langle \Phi_{i,1} \dots \Phi_{i,N} | \hat{A}_N \sum_{j=1}^N \hat{\mathbf{d}}_j \hat{A}_N | \Phi_{k,1} \dots \Phi_{k,N-1} \Psi_{\text{el}} \rangle, \quad (2.10)$$

where hermiticity of the antisymmetrisation operator is used. The expression (2.10) can be further expanded taking into account that \hat{A}_N commutes with the dipole operator and making use of the relation $\hat{A}_N \hat{A}_N = \sqrt{N!} \hat{A}_N = \sum_P (-1)^p \hat{P}$ where the sum goes over all permutations \hat{P} of electron indices with parity p

$$\mathbf{D}_k = \sqrt{N!} \sum_P (-1)^p \sum_{j=1}^N \langle \Phi_{i,P(1)} \dots \Phi_{i,P(N)} | \hat{\mathbf{d}}_j | \Phi_{k,1} \dots \Phi_{k,N-1} \Psi_{\text{el}} \rangle \quad (2.11)$$

$$= \sqrt{N!} \sum_P (-1)^p \sum_{j=1}^N \langle \Phi_{i,P(j)} | \hat{\mathbf{d}}_j | \Phi_{k,j} \rangle \langle \Phi_{i,P(1)} | \Phi_{k,1} \rangle \dots \langle \Phi_{i,P(j-1)} | \Phi_{k,j-1} \rangle \quad (2.12)$$

$$\times \langle \Phi_{i,P(j+1)} | \Phi_{k,j+1} \rangle \langle \Phi_{i,P(N-1)} | \Phi_{k,N-1} \rangle \dots \langle \Phi_{i,P(N)} | \Psi_{\text{el}} \rangle \quad (2.13)$$

where $P(j)$ is a permutation of the j -th orbital. Thereby the term $j = N$ differs qualitatively from the others since the dipole operator acts on the FEF. Hence the sum can be reordered to obtain

$$\begin{aligned} \mathbf{D}_k &= \underbrace{\sqrt{N!} \sum_P (-1)^p \langle \Phi_{i,P(1)} | \Phi_{k,1} \rangle \dots \langle \Phi_{i,P(N-1)} | \Phi_{k,N-1} \rangle \langle \Phi_{i,P(N)} | \hat{\mathbf{d}}_j | \Psi_{\text{el}} \rangle}_{\langle \Psi_k^{\text{DO}} |} + \\ &\quad \underbrace{\sqrt{N!} \sum_P (-1)^p \sum_{j=1}^{N-1} \langle \Phi_{i,P(1)} | \Phi_{k,1} \rangle \dots \langle \Phi_{i,P(j-1)} | \Phi_{k,j-1} \rangle \langle \Phi_{i,P(j)} | \hat{\mathbf{d}}_j | \Phi_{k,j} \rangle \times} \\ &\quad \langle \Phi_{i,P(j+1)} | \Phi_{k,j+1} \rangle \dots \langle \Phi_{i,P(N-1)} | \Phi_{k,N-1} \rangle \langle \Phi_{i,P(N)} | \Psi_k^{\text{el}} \rangle \end{aligned} \quad (2.14)$$

where the first sum is denoted as DO and the second as conjugate DO respectively [65]. To reduce the large amount of integrals therein, the strong orthogonality approximation

is applied under the assumption that the overlap

$$\langle \Phi_{i,j} | \Psi_{\text{el}} \rangle = 0 \quad \forall j = 1, \dots, N \quad (2.15)$$

of the FEF with all bound states vanishes. This is strictly valid if $|\Phi_{i,j}\rangle$ and $|\Psi^{\text{el}}\rangle$ would correspond to the same Hamiltonian. But in most cases the relaxation of the orbital $|\Phi_{i,j}\rangle$ is small, leading to a small but non-zero overlap with the FEF [47, 65]. Applying the strong orthogonality condition leads to the drop out of the second sum in eq. 2.14 and the transition dipole moment simplifies to

$$\begin{aligned} \mathbf{D}_k &= \sum_p (-1)^P \langle \Phi_{i,P(1)} | \Phi_{k,1} \rangle \dots \langle \Phi_{i,P(N-1)} | \Phi_{k,N-1} \rangle \langle \Phi_{i,P(N)} | \hat{\mathbf{d}}_j | \Psi_k^{\text{el}} \rangle \\ &= \langle \Psi_k^{\text{DO}} | \hat{\mathbf{d}}_j | \Psi_k^{\text{el}} \rangle \end{aligned} \quad (2.16)$$

which corresponds to the definition of the TDDO in eq. (2.7) for $t = 0$ as mentioned above. The expression for the PES cross-section in the DO formalism simplifies to

$$\sigma(\epsilon) = \frac{2}{3} \sum_k (\epsilon + E_k - E_i) \left| \langle \Psi_k^{\text{DO}} | \hat{\mathbf{d}} | \Psi_{\text{el}} \rangle \right|^2. \quad (2.17)$$

In the derivation given above, it is assumed that initial and final states can be represented by single SD. In practice, states often are described by a linear combination of SDs with different electronic configurations. A respective generalisation of the DO is straight forward but introduces additional summations and thus leads to more complex terms [47].

2.3.3 Sudden Approximation

Further simplification of the DO formalism can be obtained by applying the so-called sudden approximation (SA) where the computation of the FEF is omitted. In the SA it is assumed that the transition to the continuum with corresponding energy has a constant probability [99]. This can be justified for high kinetic energies where the oscillations of the FEF are much stiffer than the structures of bound states so that small changes in the energy of the FEF do not play an important role. Thus, the transition dipole moment (2.14) reduces to the scalar

$$D_k = \sum_p (-1)^P \langle \Phi_{i,P(1)} | \Phi_{k,1} \rangle \dots \langle \Phi_{i,P(N-1)} | \Phi_{k,N-1} \rangle \quad (2.18)$$

which involves only the bound $N - 1$ -electron system [100]. With this assumption the kinetic energy of the free electron dependence of the PES is neglected, assuming error introduced is a similar factor for all transitions. This has shown to be a valid assumption if the nature and spacial extend of the Dyson orbitals is similar for different transitions. Note that the expression (2.18) corresponds to the nominator of the Greens' function in (2.3) and thus is the level of theory at which the Greens' function PES transitions are computed.

Finally, the expression (2.18) can be further simplified to get the approach described in the introduction to this chapter, based on Koopmans' theorem. Therefore the electron

relaxation is neglected and thus the $N - 1$ -electron state can be written as $|\Psi_k^{N-1}\rangle = \hat{a}_k |\Psi_i^N\rangle$. Thus, the sum over all permutations \hat{P} in (2.18) reduces to the case $\delta_{P(j),j}$ due to orthogonality of the orbitals. Moreover, due to the normalisation of the orbital functions, all transitions have a probability of one and thus corresponds to the scheme described earlier.

3 | Description of Free Particles

The description of unbound particles has several complications of conceptual and technical kind. In this chapter, different numerical methods are introduced that can be used to solve the one-electron SE in particular for FEFs. In section 3.1, the conceptual differences between bound and continuum states as well as the numerical treatment of the latter in a finite basis are discussed. Thereafter, in the sections 3.2 - 3.6, different numerical methods are introduced that can be used to solve the one-particle SE on a molecular domain.

3.1 Continuum Waves

Continuum waves are discussed only sparsely in lectures on quantum mechanics, even though their fundamental differences compared to bound states makes them an interesting object to study. The states considered here have a spatial infinite extend as it is well-known for plane waves

$$\Psi_{\mathbf{k}}^{\text{plan}}(\mathbf{r}) = \sqrt{\frac{|\mathbf{k}|}{(2\pi)^3}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (3.1)$$

with \mathbf{k} being the wave-vector as well as for spherical waves. Moreover, continuum wave functions are not square integrable and hence can not be normalised according to $\int \Psi_{\mathbf{k}}^{\dagger}(\mathbf{r}) \Psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r} = 1$ and thus the probability interpretation is invalid [101]. Instead, these functions are sharp in a continuous variable (namely the momentum) and hence should rather be interpreted as probability densities, suggesting the normalisation $\int \Psi^{\dagger}(\mathbf{r}) \Psi(\mathbf{r}') d\mathbf{r} = \delta(\mathbf{k} - \mathbf{k}')$ where $\delta(\mathbf{k})$ is the Dirac delta distribution [101, 102]. This property distinguishes the analytical FEF from those obtained with numerical methods that often have a finite support and are obtained from an approximate Hamiltonian matrix which has no continuous spectrum due to finiteness of its basis. Especially the difference in the normalisation of wave functions and by this in the dimensionality of overlap integrals also affects the integral evaluated when calculating the transition dipole matrix elements [103]. However, the Stieltjes imaging approach described in section 3.1.1 gives a formal verification for the use of square-integrable function for the approximation of a continuum state. Moreover, it provides a formalism to enhance the quality of spectra obtained with numerical methods.

A further aspect of numerical treatment of continuum functions that is only sparsely discussed in literature concerns the question of the physical interpretation of the numerical solution **Can one expect some theory about it?**. When dealing with approximate continuum functions, it is often assumed that the analytic function of interest $|\Psi_a(\mathbf{k})\rangle$ is approximated by that particular numeric solution $|\Psi_n(\mathbf{k}')\rangle$ which is closest in energy to the desired one [26] **more sources: ideas?**. An alternative interpretation would be to assume that the

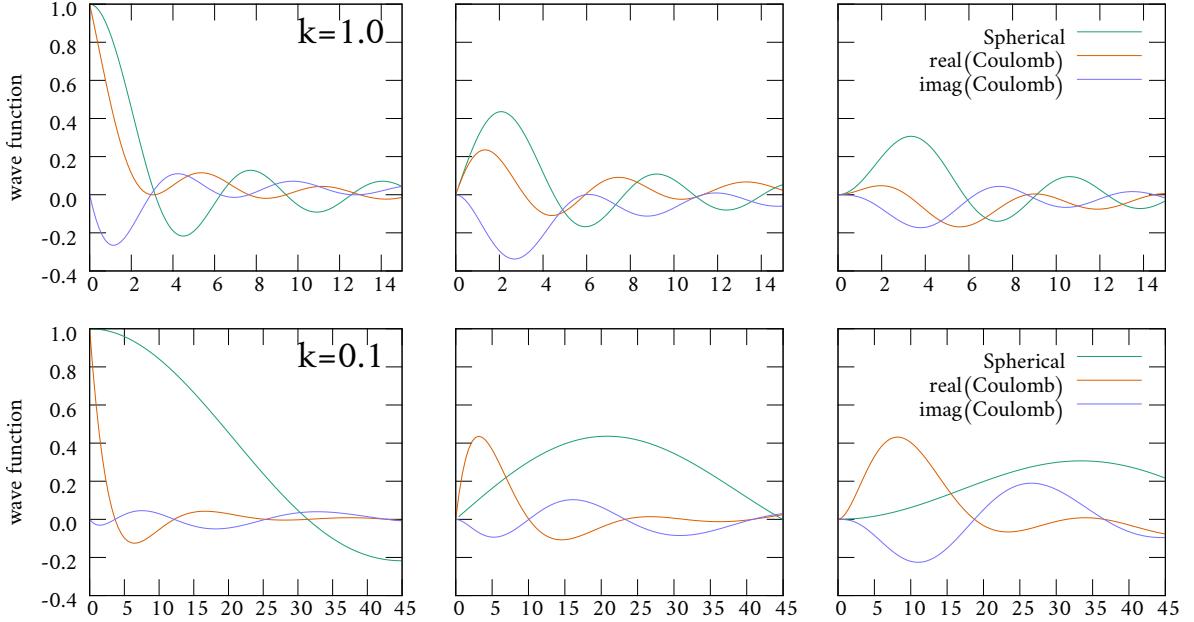


Figure 3.1: Radial part of spherical waves and Coulomb waves (confluent hypergeometric function approximated with 35 terms each) for $l = 0$ (left), $l = 1$ (centre) and $l = 2$ (right). The Coulomb waves are not normalised.

numerical solution corresponds to an approximation to $|\Psi_n\rangle \approx \frac{1}{k^+ - k^-} \int_{k^-}^{k^+} |\Psi_a(k)\rangle dk$ which would change its interpretation and normalisation.

In other works simulating PES in frequency domain only sparsely explicit calculations on the FEF are obtained [26, 102]. Instead, mainly two different representations of the photoelectron are found which are based on plane-wave expansions in spherically symmetric bases [34, 35, 104]. One of the expansions is that in spherical waves [33]

$$\Psi_{\mathbf{k}}^{\text{Sph}}(\mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(kr), Y_l^m(\theta, \phi) Y_l^{\dagger, m}(\theta_k, \phi_k) \quad (3.2)$$

where $k = |\mathbf{k}|$ and $r = |\mathbf{r}|$ are the lengths of the wave vector \mathbf{k} and spatial vector \mathbf{r} , respectively, $j_l(kr)$ are spherical Bessel functions that solve the radial SE (eq. (2.5) with $V(r) = 0$) and the arguments to the spherical Harmonics $Y_l^m(\theta, \phi)$ and (θ_k, ϕ_k) , are the angles of the spherical coordinate system in real-space and Fourier-space, respectively [34]. Another expansion of a plane wave often used is that in Coulomb waves

$$\begin{aligned} \Psi_{\mathbf{k}}^{\text{Coul}}(\mathbf{r}) = & \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l (2kr)^l e^{-\pi \frac{Z}{2k}} \frac{|\Gamma(l+1+i\frac{Z}{k})|}{\Gamma(2l+2)} \\ & e^{ikr} F_1(l+1-i\frac{Z}{k}, 2l+2, 2ikr) Y_l^m(\theta, \phi) Y_l^{\dagger, m}(\theta_k, \phi_k) \end{aligned} \quad (3.3)$$

where Z is the charge of the nucleus and F_1 is the confluent hypergeometric function of the first kind [104, 105]¹.

A third expansion that is available *e.g.* in the program ezDyson [34] is an asymptotic

¹ $F_1(\alpha, \gamma, z) = 1 + \frac{\alpha}{\gamma} z + \frac{\alpha(\alpha+1)}{\gamma(\gamma+1)} \frac{z^2}{2!} + \dots$

Coulomb wave expression for vanishing momentum in which the confluent hypergeometric function can be approximated by a Bessel function as

$$\lim_{k \rightarrow 0} F_1(l + 1 + \frac{i}{k}, 2l + 2, 2ikr) = (2l + 1)!(2r)^{-l-\frac{1}{2}} J_{2l+1}(\sqrt{8r}) \quad (3.4)$$

where $Z = -1$ is assumed and $J_{2l+2}(x)$ is the Bessel function that is connected to the spherical Bessel functions $j_l(x)$ via the relation $j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+\frac{1}{2}}(x)$ [33]. This case is separately available in `ezDyson` [34].

The spherical Harmonics [106] moreover have the form

$$Y_l^m(\theta, \phi) = (-1)^{(m+|m|)/2} i^l \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos(\theta)) e^{im\phi} \quad (3.5)$$

where $P_l^m(x)$ are associated Legendre polynomials [33]. The spherical harmonics are orthonormalised according to

$$\int Y_l^{\dagger m}(\phi, \theta) Y_{l'}^{m'}(\phi, \theta) d\mathbf{r} = \delta_{l,l'} \delta_{m,m'} \quad (3.6)$$

and have the property

$$\int Y_l^{\dagger m}(\phi, \theta) \mathbf{r} Y_{l'}^{m'}(\phi, \theta) d\mathbf{r} = \delta_{l,l' \pm 1} C_{l,l',m,m'} \quad (3.7)$$

if not both l and l' are 0 where $C_{l,l',m,m'}$ are Clebsch-Gordan coefficients. The relation (3.7) governs the dipole transition probabilities of molecular systems.

Both expansions (3.2) and (3.3) do not take the molecular potential into account but give an easy picture for the photoelectron. Since the spherical wave basis is obtained under the assumption of no potential $V(\mathbf{r})$, this is assumed to be a good approximation for photodetachement when the initial state is neutral whereas the Coulomb wave expansion takes into account the ESP of the remaining anion at larger distances to the molecule and thus is more reasonable for ionised remainder systems [104]. Due to these obvious deficiencies of the inflexible expansions, some modifications are used by several authors which involve the choice of an effective charge $Z^* < 1$ in the expansion (3.3) [104] and an orthogonalisation of the expansion with respect to the DO [104, 107–109]. The latter can be shown to be equivalent to a respective shift of the expansion centre such that the expectation value of the dipole moment of the DO vanishes [107].

In this work the spherical waves (3.2) are used as reference basis for the computed solutions for an easier interpretation and comparison of different results. To do so, the numerically obtained solution $|\Psi_n\rangle$ is projected onto spherical waves for different l and m which will be referred to as partial wave coefficient.

In addition to the previously discussed questions about the relation of analytic and numeric FEFs, the infinite degeneracy of the analytical solutions has no numerical counterpart and thus leads to problems which are discussed on the example of the ionisation of a hydrogen-like atom whose analytical FEF is of the form (3.3) but with arbitrary coefficients for each term whose only prerequisite is that their squares add up to one [33].

The Coulomb wave basis is, given its energy $E = \frac{1}{2}|\mathbf{k}|^2$, infinitely degenerate in the

direction of \mathbf{k} as well as in the quantum numbers l and m . However, the coefficients of the physically observable FEF are determined by the matrix elements of the dipole operator with the DO (2.16). Considering the ionisation of hydrogen in its ground state, the FEF is in one of the three p -waves because the probability to access any of the other vacuum-states with the correct energy vanishes due to dipole selection rules eq. (3.7) for spherically symmetric systems.

Unfortunately, as shown in section 6.1, the considerations made above are not true for the numerical solution anymore where a finite set of superpositions is obtained which, due to numerical treatment, differ in energy and thus can not be assigned to a common value of \mathbf{k} . Choosing the energetically best-fitting solution though might in principle result in a function with vanishing contribution of the p -type orbitals whereas, for a slightly changed computational scheme or target energy it could yield a solution with large p -contributions and high intensity, respectively.

3.1.1 Stieltjes Imaging

The Stieltjes imaging [103, 110–112] provides an elegant way to use the numerically obtained FEFs of a discrete character lying above the ionisation threshold for PES calculations. To correct on the different character of the spectrum and the smaller extend of the numerically obtained solution, the Stieltjes imaging approach uses spectral moments [113]

$$\mu_n = \int_0^\infty \epsilon^n df(\epsilon) \quad (3.8)$$

where $n < 0$ denotes the order of the moment, $\epsilon = E - E_0$ is the transition energy and

$$\frac{df}{d\epsilon} = \frac{2}{3}(E - E_0) \left| \langle \Psi_0 | \hat{\mathbf{d}} | \Psi_f \rangle \right|^2 \quad (3.9)$$

is the oscillator strength with the dipole operator $\hat{\mathbf{d}}$, the energies E_0 and E of the ground state $|\Psi_0\rangle$ and final state $|\Psi_f\rangle$, respectively. Since the final state can be of bound state character $|\Psi_\alpha\rangle$, where the energies are discrete, as well as of continuous character $|\Psi_\varepsilon\rangle$ with continuous spectrum, one can rewrite the spectral moment (3.8) as [110]

$$\mu_n = \sum_{\alpha} (E_{\alpha} - E_0)^n \left| \langle \Psi_0 | \hat{d} | \Psi_{\alpha} \rangle \right|^2 + \int_0^\infty \varepsilon^n \left| \langle \Psi_0 | \hat{d} | \Psi_{\varepsilon} \rangle \right|^2 d\varepsilon \quad (3.10)$$

where ε denotes the kinetic energy of the FEF. Since, in contrast to the analytic case (3.10), the numeric Hamiltonian has a discrete spectrum, the respective spectral moments here are of the form

$$\mu_n = \sum_{j=0}^N (E_j - E_0) \left| \langle \Psi_0 | \hat{d} | \Psi_j \rangle \right|^2 \quad (3.11)$$

where N denotes the number of eigenfunctions $|\Psi_j\rangle$ and the sum accounts for the bound as well as unbound states [103, 111]. Assuming that the first $2l - 1$ spectral moments can be restored by the numerical Hamiltonian in good approximation, they can be used to

obtain a histogram representation of the cross section of the form

$$\sigma(\varepsilon) = \frac{2}{3} \frac{df}{d\varepsilon} = \frac{2}{3} \begin{cases} 0 & 0 < \varepsilon < \varepsilon_1(l) \\ \frac{1}{2} \frac{(f_i + f_{i+1})}{\varepsilon_{i+1} - \varepsilon_i} & \varepsilon_j(n) < \varepsilon < \varepsilon_{j+1}(l) \\ 0 & \varepsilon_n(l) < \varepsilon \end{cases} \quad (3.12)$$

where $(\varepsilon_i, f_i)_{i=1,\dots,l}$ are a principal pseudo spectrum [111]. The values ε_i and f_i are obtained from an eigenvalue equation of a symmetric tridiagonal matrix whose diagonal elements α_i and off-diagonal elements β_i can be found as parameters a function

$$I(z) = \frac{\beta_0^2}{z - \alpha_1 - \frac{\beta_1^2}{z - \alpha_2 - \dots - \frac{\beta_{l-1}^2}{z - \alpha_l}}} \quad (3.13)$$

which contains the full information about the first $2l - 1$ spectral moments and has the alternative form [114]

$$I(z) = \frac{\mu_0}{z} + \frac{\mu_1}{z^2} + \dots + \frac{\mu_{2l-1}}{z^{2l}} \quad (3.14)$$

where μ_i are the spectral moments (3.11) [114]. The key task in Stieltjes imaging is the transformation from the form (3.14) to (3.13) [114].

In practice, the Stieltjes imaging is very demanding if energetically narrow transitions occur since many terms in expression (3.11) are needed for convergence, making this method efficient mainly for low energy range [26].

3.2 Finite Differences and Finite Volumes

The most common and straightforward approach to solve differential equations such as the SE numerically is via the so-called finite difference (FD) scheme. Starting from the one-particle SE in atomic units

$$\left(-\frac{1}{2} \nabla^2 + V(\mathbf{r}) \right) \Psi(\mathbf{r}) = E \Psi(\mathbf{r}) \quad (3.15)$$

where $V(\mathbf{r})$ is an arbitrary potential at this point. Considering a general problem where the low symmetry does not support a product ansatz as *e.g.* eq. (2.4) which reduces the dimensionality and thus the complexity of the problem, the kinetic energy operator has in a matrix representation at least 6 off-diagonal terms per line whose non-banded structure requires iterative solvers [115]. An important disadvantage of finite difference schemes is that they require the evaluation points to be on a regular grid whose stepsize is governed by the sharpest features in the system while local refinement is hardly available. If considering molecules and thus Coulomb-shaped potentials $V(\mathbf{r})$, the finest structures are expected to be close to the nuclei whereas at larger distances a respectively dense grid is not needed and thus computations of FEFs with a reasonable box size become very expensive [94]. Nonetheless, there are applications of this scheme to the SE [115, 116], some of them with massive parallelisation using MPI and multiple GPUs [117].

To overcome this bottleneck for systems with non-uniform parameters, often the finite volume method is used. The finite volume method is an integral method that is not

based on a regular grid. Instead, for the estimation of the kinetic energy Gauß's theorem $\int_V \nabla \mathbf{u}(\mathbf{r}) dV = \int_S \mathbf{u}(\mathbf{r}) \mathbf{n} dS$ is used where $\mathbf{u}(\mathbf{r})$ is a vector-valued function and \mathbf{n} is the normal vector on the surface S of the volume V under consideration. Chosing $\mathbf{u}(\mathbf{r}) = \nabla \Psi(\mathbf{r})$ yields the relation

$$\nabla^2 \Psi(\mathbf{r}) = \lim_{V \rightarrow 0} \frac{\int_{\partial V} \nabla \Psi(\mathbf{r}) \mathbf{n} dS}{V}. \quad (3.16)$$

This scheme becomes especially interesting when the finite volume elements are chosen to be Voronoi cells [118]. A Voronoi-tesselation is associated with a grid and is constructed such that the Voronoi cell T_i consists of all points in space that are closer to the point i than to any other points in the grid, see Figure 3.2 [119–121].

This description has the advantage that the quantities on the right-hand side of (3.16) can be associated with properties of the Voronoi-Cell, leading to the first-order approximation of the kinetic energy

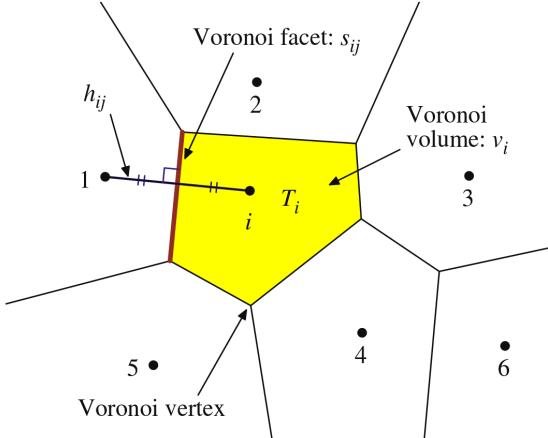


Figure 3.2: 2-dimensional Voronoi diagram on an arbitrary distribution of seven points [122].

$$\nabla^2 \Phi(\mathbf{r}_i) = \frac{1}{v_i} \sum_j^{\text{neighbours}} \frac{\Psi(\mathbf{r}_j) - \Psi(\mathbf{r}_i)}{h_{ij}} s_{ij} a \quad (3.17)$$

where v_i is the volume of the i -th Voronoi-cell (yellow area in Figure 3.2), $h_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centres of the i -th and j -th Voronoi-cells (bold black line) and s_{ij} is the area of the common facet of the i -th and j -th Voronoi cells (red line in Figure 3.2).

Such a scheme is applied, *e.g.*, by Son and Chu [118, 122] to the time-dependent SE, studying multi-photon ionisation of several molecular systems.

3.3 Pseudospectral Methods

Under the term (pse)udospectral methods a large group of methods is comprised which treat the differential equation of interest variationally using an orthogonal basis $\{\varphi_i(\mathbf{r})\}$, hence seeking for a solution of the form

$$\Psi(\mathbf{r}) = \sum_i^n c_i \varphi_i(\mathbf{r}) \quad (3.18)$$

where c_i are coefficients to be found [123]. In the pseudospectral methods the basis functions $\varphi_i(\mathbf{r})$ are smooth global functions, *e.g.* $\varphi_k(\mathbf{r}) = e^{ik\mathbf{r}}$, resulting in the Fourier space [124]. Alternatively Jacobi, Chebychef or Legendre polynomials are commonly used [125].

To find the corresponding coefficients, the problem is solved on a grid, leading to a linear system of equations. Depending on the technique used for determining the coefficients, it can be seen as a high-order FD or high-order FEM. One prominent advantage of this class of methods is that the error of the solution $\psi(\mathbf{r})$ usually decays exponentially with the number n of basis functions and the grid can be chosen coarsely, making the numerical scheme very efficient [125, 126]. In addition, many formulations allow for an implementation making use of the fast fourier transform [125].

A special representative subgroup of the pseudospectral methods are the so-called discrete variable representation (DVR) schemes which are frequently used to study electronic structure and vibrational problems in molecules [98, 127, 128]. Since this scheme is applicable in one dimension only, often symmetry-adapted coordinates such as spherical coordinates are used product functions such as (2.4) are applied.

The basis functions used in this scheme commonly are Lagrange polynomials [95, 127, 128] whose nodes are chosen by a general Gauß quadrature rule [127] or from a quadrature rule for the radial Coulomb function which is in particular popular whene electronic structure problems are considered [126, 128]. Even if the DVR provides a flexible and fast-convergent basis, an extension to higher dimensionality can only be achieved by a product ansatz and thus is applicable to problems with high symmetry.

Moreover, as for the other pseudospectral methods, the system matrices are dense and thus the solution is numerically expensive. This is at least partially solved by using a hybrid scheme of the finite element and DVR scheme where the DVR scheme is used on small segment only, connected by single bridge-functions each [95, 127].

3.4 Radial Basis Functions

The radial basis function (RBF) technique is based on an arbitrary point distribution with very general properties. The ansatz functions $\varphi_i(\mathbf{r})$ used in this technique need to be spherically symmetric, *i.e.* $\varphi_i(\mathbf{r}) = \varphi_i(|\mathbf{r}|)$ and are placed at the grid points on a given domain. The RBF-scheme is used not only for solving differential equations but is also a usefull tool for interpolation of scattered data in arbitrary dimensions [129] and surface reconstruction from scattered data [130].

Among the commonly used functions are, besides linear and cubic ones, multiquadratic ($\sqrt{r^2 + r_0^2}$), inverse multiquadratic ($(r^2 + r_0^2)^{-\frac{1}{2}}$) and Gaussian ($\exp(-\frac{r^2}{2r_0^2})$) functions are to be mentioned where r_0 is the radius, respectively [131, 132].

If the parameter r_0 is chosen reasonably, the scheme is numerically stable and fast convergeing [131], but the choise of r_0 can be non-trivial especially for highly non-regular grids where a good quality of the representation between two points with a large distance require a respectively large radius r_0 whereas too large radii can make the scheme numerically instable for close-lying points. Moreover the resulting system matrices are dense due to the global definition of the ansatz functions, making it computationally expensive when large domains are considered.

3.5 Finite Elements

In the FEM the differential equations to be solved are formulated in their weak form which is an integro-differential equation and can be understood as a generalisation of the differential equation [36]. Starting with the well-known (strong) form of the SE defined on a domain Γ in atomic units which are used here and in the following chapters

$$-\frac{1}{2}\nabla^2\Psi(\mathbf{r}) + V(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad \mathbf{r} \in \Gamma \quad (3.19)$$

with the condition

$$\Psi(\mathbf{r}) = 0 \quad \mathbf{r} \in \partial\Gamma \quad (3.20)$$

for the boundary domain $\partial\Gamma$ which is assumed to be Lipschitz continuous. The first term in equation (3.19) corresponds to the kinetic energy and $V(\mathbf{r})$ is a potential that is not further specified at this point. The unknowns of this equation are the wave function $\Psi(\mathbf{r})$ and respective energy E . To bring equation (3.19) into the weak form, it is first multiplied by the complex conjugate of a test function $\Phi(\mathbf{r})$ which fulfils the same boundary conditions and needs to be differentiable. In the second step, one integrates over the whole space of interest resulting in the equation

$$\int d\mathbf{r} \left(-\frac{1}{2} (\nabla^2\Phi^*(\mathbf{r})) \Psi(\mathbf{r}) + V(r)\Phi^*(\mathbf{r})\Psi(\mathbf{r}) \right) = E \int d\mathbf{r} \Phi^*(\mathbf{r})\Psi(\mathbf{r}). \quad (3.21)$$

The kinetic energy term can be symmetrised using Green's first identity $\int_{\Gamma}(\nabla^2\Psi)\Phi^*d\mathbf{r} = \int_{\partial\Gamma}(\nabla\Psi)\Phi^*ds - \int_{\Gamma}(\nabla\Psi)(\nabla\Phi^*)d\mathbf{r}$ to obtain the final expression

$$\int_{\Gamma} d\mathbf{r} \left(\frac{1}{2} (\nabla\Phi^*(\mathbf{r})) (\nabla\Psi(\mathbf{r})) + V(r)\Phi^*(\mathbf{r})\Psi(\mathbf{r}) \right) = E \int_{\Gamma} d\mathbf{r} \Phi^*(\mathbf{r})\Psi(\mathbf{r}) \quad (3.22)$$

$$\Phi(\mathbf{r}) = 0 \quad \Psi(\mathbf{r}) = 0 \quad \mathbf{r} \in \partial\Gamma \quad (3.23)$$

which is denoted as the weak form of the SE. A function $\Psi(\mathbf{r})$ is considered as a solution of (3.22) if the equation holds for any test function $\Phi(\mathbf{r})$. Since usually only real-valued bases functions are used, in the literature the complex conjugation is omitted. Moreover, from a mathematical point of view, since $\Phi(\mathbf{r})$ is an arbitrary function, complex conjugation does not change anything here but it will be shown later that it is more reasonable from a physical point of view if the weak formulation is defined as given in equation (3.22).

The weak formulation (3.22) has two main changes in its properties compared to the strong formulation (3.19). The first is that any solution of (3.19) solves (3.22) while the space of solutions of the weak form is larger since only first derivatives need to be defined, which lead to the terms weak and strong respectively. In addition, a weak solution is defined only up to a cardinal number of zero; hence changing the values of a given solution $\Psi(\mathbf{r})$ along a finite number of planes in three dimensions yields a function that still solves (3.22). These properties play an important role here since they allow *e.g.* the use of piecewise linear basis functions as they are commonly used in the FEM scheme which do not have a second derivative and whose first derivative is undefined on certain planes.

As usual for numerical methods, in the FEM scheme one restricts the search for solutions to a subspace spanned by a finite set of test functions for both $\Psi(\mathbf{r})$ and $\Phi(\mathbf{r})$,

leading to the Petrov-Galerkin scheme. To get best flexibility for the wave function, the domain Γ is subdivided into finite volume elements with a close packing. These volume elements, denoted as finite elements, give this method its name. Having this subdivision of space, the ansatz (basis) functions $\varphi(\mathbf{r})$ used to construct $\Psi(\mathbf{r})$ and $\Phi(\mathbf{r})$ are defined as piecewise polynomials being non-zero only on one or few elements.

Considering Γ to describe a 2D-plane, the elements can be, for example, triangles as shown in Figure 3.3. Enumerating the vertices of the triangles as $\mathbf{r}_i i = 1, \dots, N$, the piecewise linear (Lagrange-) basis functions are defined as

$$\varphi_i(\mathbf{r}_j) = \begin{cases} 1 & j = i \\ 0 & j \neq i \end{cases} \quad (3.24)$$

resulting in two-dimensional “hat” functions as depicted in Figure 3.3 for an index i . This definition of a

basis ensures continuity of the solution over Γ while the first derivatives are continuous only within each element. To assure continuity of the first derivatives as well, second order polynomials are needed. At the border of Γ , respectively truncated

“hat” functions are used whose coefficients are given by the boundary condition.

As usual in variational schemes, the wave function of interest is constructed as a linear combination of these basis functions $\Psi(\mathbf{r}) = \sum_i c_i \varphi_i(\mathbf{r})$ where c_i are weighting coefficients. The test functions are chosen from the same space of ansatz functions, testing each basis separately $\Phi(\mathbf{r}) = \varphi_j(\mathbf{r}), j \in 1, \dots, N$. Hence, the SE (3.22) with the finite basis reads

$$\sum_i \int d\mathbf{r} \left(\frac{1}{2} (\nabla \varphi_i(\mathbf{r})) (\nabla \varphi_j(\mathbf{r})) + V(r) \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \right) c_i = E \sum_i \int d\mathbf{r} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) c_i \quad \forall j \in \{1, \dots, N\} \quad (3.25)$$

which is the j -th component of the generalised matrix eigenvalue problem

$$\left(\frac{1}{2} \mathbb{A} + \mathbb{V} \right) \mathbf{c} = E \mathbb{M} \mathbf{c}. \quad (3.26)$$

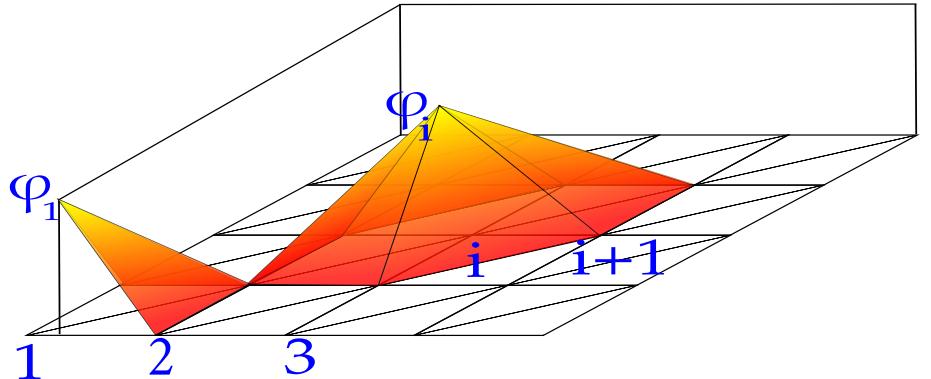


Figure 3.3: Example of finite elements in 2D of triangular shape and linear basis functions $\varphi_i(\mathbf{r})$ defined on them.

with

$$\mathbb{A}_{ij} = \int d\mathbf{r} (\nabla \varphi_i(\mathbf{r})) (\nabla \varphi_j(\mathbf{r})) \quad \mathbb{V}_{i,j} = \int d\mathbf{r} V(\mathbf{r}) \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \quad \mathbb{M}_{i,j} = \int d\mathbf{r} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \quad (3.27)$$

and the vector \mathbf{c} in equation (3.26) contains the coefficients c_i to be found.

The quality of this basis depends strongly on the size and shape of the finite elements: The stronger the solution varies, the smaller element sizes or higher order ansatz functions are required to be able to represent the wave function. Knowledge about ranges of sharp structures and areas with smooth variation of the wave function $\Psi(\mathbf{r})$ hence is crucial for the setup of a good mesh.

In chapter 4 more details about the finite element formulation are given with a special focus on how to setup a grid that is well suited for describing free particles in quantum mechanics.

3.6 Wavelets

The wavelet method was developed in the 1980s [133] as a generalisation of the Fourier transform that combines the advantages of the Fourier space and the FEM. Similar to the FEM, it is based on a local basis but the wavelets have some characteristic scales similar to the wavelength in the Fourier basis, so that they can be used to decompose objects into features of different scales as a generalisation of the Fourier transform [133–135]. Even though wavelets possess very advantageous properties, they are to date not very well-established. The most prominent and widely distributed application of Wavelets is compression of data as used, for example, in the jpeg2000 standard [136].

In general, a wavelet is a basis of the function space $L_p(\mathbb{R}^d)$ *i.e.*, the space of functions $\phi(\mathbf{r})$ for which $\int \phi(\mathbf{r})^p d\mathbf{r} < \infty$ where $\mathbf{r} \in \mathbb{R}^d$ and p is a positive integer. A particular wavelet is defined by a finite set of orthonormal mother wavelets $\varphi_i(\mathbf{r})$ for which a series of functions

$$\varphi_{i,j,\alpha}(\mathbf{r}) = m^{\frac{j}{2}} \varphi_i(\mathbb{M}^j \mathbf{r} - \boldsymbol{\alpha}) \quad (3.28)$$

with the matrix \mathbb{M} whose eigenvalues have modulus larger than one, $m = |\det(\mathbb{M})|$ and the running indices $j \in \mathbb{Z}$ and $\boldsymbol{\alpha} \in \mathbb{Z}^d$ can be defined which span $L_p(\mathbb{R}^d)$ [134]. In practice, this very general definition is often restricted by additional requirements such as orthogonality of $\varphi_{i,j,\alpha}(\mathbf{r})$ or utilisation of only one mother-wavelet $\varphi(\mathbf{r}) = \varphi_i(\mathbf{r})$. For brevity, in the following only the space $L_2(\mathbb{R})$ with $\mathbb{M} = 2$ is considered which corresponds to the original definition of wavelets [137]. The most prominent representatives are the Daubechies wavelets that are shown in Figure 3.4 which are a set of orthogonal wavelets with compact support and increasing smoothness. Especially the first-order Daubechies wavelet, more commonly known as the Haar-wavelet, is famous and by far the easiest existing orthogonal wavelet basis. In contrast to most other bases, in principle no smoothness properties are required but are desired since the functions to be represented are usually smooth [138].

Besides their broad use in data compression and analysis, wavelet bases also provide a handy tool to solve partial differential equations and are found to have similar numerical properties as the FEM [135, 139]. When applying a wavelet basis to solve a partial differ-

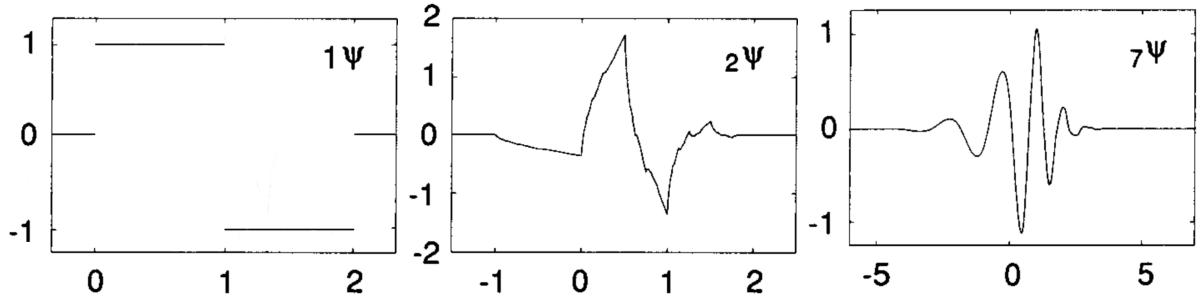


Figure 3.4: Daubechies wavelets of the orders 1, 2 and 7 (from left to right) [138].

ential equation, the weak form (3.22) is used [134]. However, not all wavelets form a valid basis for partial derivatives since, for example, the Haar-wavelet has a constant derivative of zero and the Daubechies-wavelet 2 (shown in Figure 3.4) is only semi-differentiable at some points [140]. However, the generality of the wavelet formulation allows to use problem-specific bases that are, *e.g.*, especially adapted to certain pseudo-differential operators, increasing the speed of convergence [134]. Finding such optimised bases in a systematic way is under current research and one can expect that they can be used for numerically stable, fast and accurate partial-derivative solvers [134, 141].

3.7 Hybrid Methods

In the previous sections a large variety of different methods are presented with different advantages and disadvantages which make them suitable for different applications. Moreover, there is a large number of approaches that combine the ideas of some of the above-mentioned methods to use the advantages of the respective methods together. In this section, several of these methods are presented which seem to be the most prominently used. One of the most prominent combinations of the above-mentioned methods is the FE-DVR scheme [95, 127] that was mentioned in chapter 2.2 already. In the FE-DVR scheme, a one-dimensional finite element scheme is used with comparatively large elements on which a DVR representation is used, but usually using the strong formulation of the respective partial-derivative equation. In this approach, more flexibility compared to the DVR scheme is obtained since in addition to the degree of polynomials in use, also the size of the elements can be varied which is especially advantageous for problems involving a Coulomb potential where the local kinetic energy varies strongly [98]. Moreover, the usually dense Hamiltonian and overlap matrix of DVR representation changes to a block-structure, with block being coupled to each other by single columns and rows [95]. A generalisation to multiple dimensions is the so-called spectral element used by several authors [142–144] for quantum mechanical problems. In contrast to the FE-DVR-scheme, it is based on the weak formulation and typically uses higher order Chebychev or Lagrange polynomials [142] and hence allows for larger elements than usual FEM. Thus, it can be also understood as a high order FEM scheme, combining the flexibility of FEM with the fast convergence of the pseudospectral basis. The spectral elements are found to be well suited for linear problems but require a complex implementation and lead to denser system matrices. The larger density in the resulting matrices in general leads to a reduced numerical stability and computationally more expensive solution strategies. Finally, com-

plex geometries usually benefit more from smaller elements than from higher order bases [145].

A successfull combination of spectral elements with the FEM is the so-called spectral difference method [146, 147]. In this scheme, a spatially uniform grid is used (as usual in the finite difference scheme) while employing a pseudospectral basis on the respective elements. The appealing properties of this method are an exponential convergence as known from finite difference methods by employing the sparseness of the equation system obtained in FEM [146]. More advanced methods based on the spectral difference schemes are available as well [147, 148] but are for brevity not discussed here in more detail.

4 | Finite Element Methods

As a conclusion of the previous chapter one can see that the number of methods that are currently available to describe a FEF in presence of an intricate electrostatic background potential is not that large. In this work, the method of choice to model the free electron function is the FEM which has been applied to quantum-mechanical problems by several authors [149–152]. However, to the best of my knowledge, only the bound state problems were addressed so far. A brief review of these works is given in section 4.1. Besides its large flexibility and computational efficiency pointed out in section 3.5, the large amount of available FEM libraries [56, 153–156] that are developed mainly for engineering problems is another advantage of practical importance due to the complexity of the generation of a suitable mesh, assembling of matrices and solution of matrix equations.

In the following chapter, the integration of the matrix elements (section 4.2) and set up of the mesh (section 4.3) will be described. Thereby the focus is put on the application to the one-particle SE that is to be solved with molecular electrostatic potential (ESP). Since the interest thereby is on free particle solutions, the spectrum is expected to be very dense and the wave function to be delocalised, requiring well-designed boundary conditions. A discussion of various boundary conditions and mimicing asymptotic behaviour available for FEM is described in section 4.4.

4.1 Finite Element Methods for Electronic Structure Calculations

The FEM is mainly known from engineering disciplines where it is used in a broad range of applications such as modelling of fluids [157, 158], heat transfer and flow [159–161] or material deformation under mechanical stress [162, 163]. However, also several different quantum-mechanical problems have been addressed with this method: electronic structure methods for small systems such as light atoms [149, 164–167] or diatomics [168], model oscillator systems [150] and solid state problems [169, 170]. Moreover, even Hartree-Fock [151] and DFT calculations on systems up to the size of benzene [152, 171, 172] have been performed, yielding results comparable to those obtained by the usual LCAO approach.

The above-mentioned applications have shown that the FEM is able to obtain reasonable results for molecular systems where the errors were comparable to those obtained with standard quantum-chemistry schemes even though their computational costs are higher. Here, usual quantum-chemical methods are more suited, since local basis functions localised on atoms are more convenient for bound problems. This suggests however that

the FEM should be a robust tool for the description of unbound states which represents a very non-trivial task for conventional techniques.

4.2 Setup of the Equation System

In section 3.5 the basics of the FEM were described and the generalised eigensystem shown in eq. (3.26) for the SE was derived. Here this is taken as starting point and a closer look at the computation of the matrix elements as well as solving strategies for the large sparse generalised eigenproblems are taken.

The generalised eigenproblem as given in eq. (3.26) consists of three matrices. Since the ansatz functions (shape functions) $\varphi_i(\mathbf{r})$ have only a small support, most of the matrix elements are zero. However, in two and three dimensions no distinct band structure is achievable and the matrices are irreducible. Thereby matrix elements are zero when the elements involved are not neighboured as can be followed from Figure 3.3 where a linear basis function of a 2D-mesh is shown. The computation of the non-zero matrix elements involve an integration as, *e.g.*, the overlap integral $\mathbb{M}_{i,j} = \int d\mathbf{r} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r})$ of ansatz functions. In practice these integrals are performed on a standard reference element and than scaled according to the Jacobian of the respective linear transformation that transforms the reference element to the physical one. Since these functions are the same for all elements, the evaluation of the integrals on the reference elements can be done via a lookup-table or an efficient numerical integration scheme whose order is given by the shape functions. The matrix elements $\mathbb{A}_{i,j} = \int d\mathbf{r} (\nabla \varphi_i(\mathbf{r})) (\nabla \varphi_j(\mathbf{r}))$ consist of overlap integrals of known functions similar to those of \mathbb{M} . The only matrix containing system-specific information is the potential $\mathbb{V}_{i,j} = \int d\mathbf{r} \varphi_i(\mathbf{r}) V(\mathbf{r}) \varphi_j(\mathbf{r})$ which requires numerical integration involving a reasonable approximation to $V(\mathbf{r})$ which can be obtained via interpolation of known points or using exact values computed at the given quadrature points.

After assembling the matrices the eigenpair (e_i, \mathbf{c}_i) of the system

$$\left(\frac{1}{2} \mathbb{A} + \mathbb{V} \right) \mathbf{c}_i = e_i \mathbb{M} \mathbf{c}_i \quad (4.1)$$

need to be found, where the energy e_i is the closest to the target kinetic energy of the photoelectron. Since matrices with dimensions of several thousands typically occur, numerous schemes have been developed to solve them efficiently [173–176], and are described in section 4.5.3. Despite the numerical complexity because of the high dimensionality of this problem (several thousands of basis functions) the second problem is due to the fact that the eigenenergies e_i are expected to be close to each other since the corresponding exact Hamiltonian has a continuous spectrum in this energy range. It is well known in numerics that this leads to instabilities especially for the eigenvectors, making a regularisation of the problem (described in section 4.5.2) indispensable.

4.3 Element Types and Mesh Types

Among the FEM formulations several flavours were designed for different purposes. Given a certain equation to be solved in FEM, there are in general two systematic ways to

increase the accuracy. The first way is to increase the number of elements which is referred to as the h -FEM approach [42]. The refinement of the mesh is in principle always possible but technically demanding since it is not known in which regions of a mesh are too coarse in general [42]. To overcome this, some FEM implementations such as that of **Libmesh** [56] which is used here, provide an iterative mesh refinement scheme, adapting the mesh using local error estimations and thus is fully automatic [56]. However, these schemes are numerically demanding and hence can be only applied to benchmark systems.

The second strategy is called p -FEM. In the p -FEM scheme, the order p of the test functions is increased, resulting in smoother and more flexible solutions at the price of incrementing dimensionality [177]. Standard FEM-libraries usually have only $p = 1, 2$ implemented, but high-order polynomials are also reported [155]. Combined schemes where the grid-size as well as the element order are adapted is referred to as hp -FEM [178]. These schemes are in principle promising but require detailed knowledge about the solution to setup the parameters reasonable in order to keep the computational demands in a feasible range.

Besides different refinement strategies, finite element types also vary in the way in which global smoothness is ensured and the numerical integration is obtained. While for Lagrange elements the shape functions are evaluated at certain inner or boarder points, *e.g.* in Argyris or Hsieh-Clough-Tocher elements also first or even second derivatives are evaluated [38, 179]. Moreover, one distinguishes conforming and the more general non-conforming meshes [180]. In case of the latter, more general structures are supported as *e.g.* hanging nodes which occur when a vertex of one element is on the edge of another as illustrated in Figure 4.1a [38]. The setup of the mesh is, as mentioned above already, critical to the quality of the solution and hence of special importance. Moreover, it is technically non trivial to set up a close packing of volume elements with the desired properties in a systematic way. Although in principle any element shape can be chosen, in three dimensions only tetrahedral (simplex), prism- and pyramid-shaped as well as hexahedral elements commonly are used. By choosing the element shape and the polynomial order, the element type of shape functions are fully defined.

When considering meshes to describe molecular properties it is clear that the element size should be smaller in the vicinity of the nuclei while it may be larger at longer distances. One way to create a hexahedral mesh with local refinement is to start with a coarse uniform lattice and subdivide the hexahedra where necessary as shown in Figure 4.1a for a benzene molecule. Another way is to setup small regular cubic grids around the nuclei and expand them radially in boxes of growing size as shown in Figure 4.1b. These brick-shaped elements however have the disadvantages that the regular cube-like structures therein might be not well-suited for atoms and molecules having higher symmetries.

Another approach used by Lehtovaara *et al.* [171] is to put layers of polyhedra around the atoms with increasing number of vertices and size. Thereby the overlapping regions of these polyhedra are removed by excluding the vertices that are closer to a different atom. The mesh obtained with this procedure for a benzene molecule [152] is shown in Figure 4.1c.

When restricting oneself to tetrahedral elements, other design principles are possible: Since they are simplexes in three dimensions, they can be designed from general grids using, *e.g.*, Voronoi [119] or Delaunay [181] tessellations from a set of points with the re-

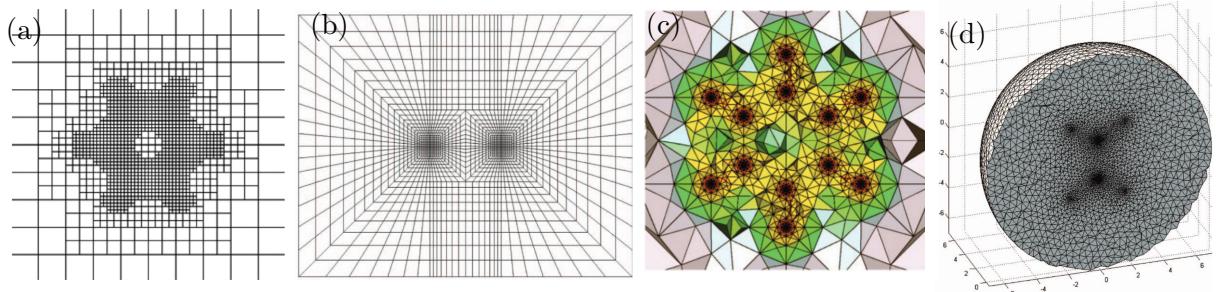


Figure 4.1: 2D cuts through 3D meshes for molecular systems obtained with different schemes for local refinement: (a) hexahedral elements adapted for the benzene molecules [152] (b) hexahedral mesh for a diatomic [151] (c) Polyhedral mesh for a benzene geometry [171] (d) Adaptive refined tetrahedral Mesh for ethylene. [151]

quired properties. Son and Chu [118, 122] constructed sets of points resembling molecular geometries by inserting N spherical grids with different radii r_i around the atoms and cutting off the overlapping regions. The respective radii are chosen as

$$r_i = \frac{il}{N - i + \frac{lN}{r_{\max}}} \quad i = 1, \dots, N \quad (4.2)$$

where r_{\max} is the radius of the largest sphere and l is a parameter smoothly changing between a linear $l \rightarrow \infty$ and a $1/r$ -mapping. For the angular distribution of grid points they suggested the use of Lebedev-grids [182] and a Womersley design [183, 184]. A more detailed discussion about the choices of grids is given in section 5.2.1.

A more entangled method is used by Alizadegan *et al.* [151]. They start with an initial guess for the wave function and create a grid whose distances are inverse proportional to the second gradient of the electron density

$$d \propto \left[\max \left\{ \left| \frac{\partial^2 \rho}{\partial x^2} \right|, \left| \frac{\partial^2 \rho}{\partial y^2} \right|, \left| \frac{\partial^2 \rho}{\partial z^2} \right| \right\} \right]^{-1}. \quad (4.3)$$

which gives an estimate for the error due to linear approximation within each element. After solving the eigenvalue equation on this grid, they recompute another mesh on the basis of the new function, iterating this procedure several times. A cut through a mesh obtained by this procedure is shown in Figure 4.1d.

4.4 Boundary Conditions

Boundary conditions have not been addressed in this thesis so far for any of the methods but play an important role for the properties of the solution. In many cases, the boundary condition (BC) leads to uniqueness of the solution or at least it determines the branch to be sought as, *e.g.* outgoing or incoming waves in case of the Helmholtz equation. The simplest case applicable to the SE are Dirichlet-boundaries, requiring the wave function to vanish at the boundaries of a finite region. In the FEM this condition can be applied especially simple by setting the coefficients of the outermost shape functions to zero. This truncation, however, strongly influences the wave function and discretises the spectrum since only integer numbers of radial nodes can occur. To ensure a reasonable low error in

energy, large domains are required. Considering a particle with 0.1 eV kinetic energy, its wavelength is 4.4 Å and the box would need to have a diameter of several tens of Ångstroms which is not feasible any more while kinetic energies in the meV-range lead to unfeasibly large domains.

Besides the numerical restriction to a finite box also mapping schemes can be used as *e.g.* $x = \tan(\frac{y}{2})$ that maps the range $[-\infty : \infty]$ to $[-\pi : \pi]$ [125]. However, using such a mapping directly leads to arbitrarily high oscillations in the mapped region and thus to arbitrarily sharp features in the mapped range. Since the solution of unbounded differential equation occurs in many fields, a large set of boundary conditions is available of which the most important ones are presented in the following sections.

4.4.1 Complex Absorbing Potential

The complex absorbing potential (CAP) is a method often found in the literature when describing quantum mechanical problems with infinite extent [63, 64, 185]. In this scheme, an artificial potential that is usually of quadratic form

$$W_{\text{CAP}}(\mathbf{r}) = \begin{cases} -i\eta(\mathbf{r} - \mathbf{r}_0)^2 & \mathbf{r} > \mathbf{r}_0 \\ 0 & \text{else} \end{cases} \quad (4.4)$$

is added where \mathbf{r}_0 is larger than the region where the solution is to be evaluated. Such a potential damps the reflection of the wave function at the boarders and thus enhances the quality of states obtained on a finite region [186, 187] and can be shown to be equivalent to the complex scaling schemes where a variable transformation [188] $r \rightarrow re^{i\theta}$ is applied [185, 187]. The imaginary potential (4.4) leads to a nonhermitian term in the Hamiltonian and thus complex eigenvalues whose real part is interpreted as the energy of the respective state and the imaginary part is considered as its lifetime [188].

However, studies with different shapes of these potentials show that it influences the wave function not only close to the boarders and a proper design of the parameters is non-trivial [189]. To minimise the error due to the CAP, the parameter η can be chosen such that its dependency on the energy vanishes in first order, *i.e.* $\eta \frac{dE}{d\eta} = 0$ [67, 189]. Moreover, due to non-hermiticity the usual scalar product is not suitable when calculating overlap integrals any more. Too strong η introduces reflections, too weak η lead to unstable resonances, making them strongly basis-set dependent [189]. Moreover, for Helmholtz problems, a dependence of the error on the frequency was observed [190].

4.4.2 Non-Reflecting Boundary Conditions

The term non-reflecting BC (or absorbing BC) describes a large class of BCs for problems on an infinite domain where the domain is subdivided into a finite computational domain and a residual infinite part [191]. Thus, also the previously described R-matrix approach as well as the infinite elements described in section 4.4.4 belong to this group of BCs. More modern approaches are perfectly matched layer schemes [192–194] that are, similar to the scheme described in ref. [95], based on variable transformations and are not discussed here in more detail.

Absorbing BCs can in principle be applied to any kind of system but is particularly

prominent for the Helmholtz problem [191, 195–197]. However, the setup of a reasonable BC that fulfills the requirement of not reflecting the solution back into the finite region of interest is not solved for general problems yet and is still under research [191, 197].

As an example for a non-reflecting BC, here the mode-matching scheme [198] is presented which yields a particularly simple formalism. In this scheme, the solution of the Helmholtz problem in the finite, inner, and infinite region is considered as two different variables, each described by the equations

$$\nabla^2 \Psi_1 + V(\mathbf{r}) \Psi_1 - E \Psi_1 = 0 \quad \nabla^2 \Psi_2 - E \Psi_2 = 0 \quad (4.5)$$

whereby the outer function needs to satisfy the Sommerfeld condition $r^\alpha \left(\frac{\partial \Psi_2}{\partial r} - ik\Psi_2 \right) \rightarrow 0$. The quantities Ψ_1 and Ψ_2 are moreover coupled by

$$\Psi_1 = \Psi_2 \quad \nabla \Psi_1 \mathbf{n} = \Psi_2 \mathbf{n} \quad (4.6)$$

that ensure continuity of the solution and the gradient normal to the boundary [198]. To ensure the Sommerfeld condition, one uses a respective basis in the outer region, *e.g.* Spherical waves. Using the mode-matching scheme with finite elements, the eq.s (4.5) result in matrices similar to eq. (3.26) that are coupled by (4.6) that enter the weak formulation since the application of Greens' first identity in eq. (3.22) leads to an extra term.

4.4.3 The Boundary Element Method

The boundary element method (BEM) can be used as a self-standing method for solving partial differential equations using the weak formulation [199, 200]. In its pure form, the BEM solves the problems using only conditions given at its boundaries that are connected to the volume properties via Greens' theorem, the Gauss-Ostrogradskii (divergence) theorem as well as Stokes theorem [201]. Even though the BEM procedure suffers strongly from the restriction of being applicable only to linear systems for which a fundamental solution is known as well as the disadvantage of leading to dense, unsymmetric matrix equations [200] it has some popularity until these days [202–204]. But its main advantages come into play when being used with the FEM [205] where the FEM can be used to obtain an accurate solution in the inner region and the boundaries are treated with the BEM. Considering an unbound domain as, *e.g.* the problem of the outgoing electron, the infinite domain Γ can be divided into a finite region Γ_i where the ionic ESP leads to a system-specific wave-function and the remaining domain Γ_o in which the time-independent SE reduces to the Helmholtz-problem whose fundamental solutions are well-known and thus the BEM is applicable [200, 206].

4.4.4 Infinite Elements

The infinite element approach was developed in the 1980-ths for acoustical calculations and is specifically designed for the Helmholtz equation and can be understood as a advancement of the BEM that is specialised for the Helmholtz equation. The general idea of the infinite elements is that the solution of the radial Helmholtz equation in spherical

symmetry is well-known to be of the form

$$\Psi(r) = \left(\frac{a}{r} + \frac{b}{r^2} + \dots \right) e^{ikr} \quad (4.7)$$

where $k = |\mathbf{k}|$ is the absolute value of the momentum of the particle and the prefactors thus correspond to different angular momenta of the outgoing electron. In the complete limit any function fulfilling the Sommerfeld radiation condition [43] can be represented.

To use this asymptotic information, in the infinite element region a layer of elements is set onto the outer surface of the finite element region in which the shape functions are of the form (4.7). To fulfill the continuity conditions, the front-face of these elements coincides with the outer face of the respective finite element, while their radial faces have ray-like edges with a common centre in the middle of the finite element region.

Over the decades several formulations of infinite elements were developed which each make an ansatz for the solution of the form

$$\Psi(\mathbf{r}) = \varphi(\mathbf{r}) e^{ik(r-r_0)}, \quad (4.8)$$

where $\varphi(\mathbf{r}) = f(r)\varphi_2(\mathbf{r})$ is a product of a transversal shape function $\varphi_2(\mathbf{r})$ which is orthogonal to the radial direction r . The function $f(r)$ is a multipole expansion *i.e.* a polynomial in $\frac{r_0}{r}$ where Jacobi-polynomials turned out to be most stable [207, 208]. The differences in the formulations are introduced by the test functions applied [41].

Burnett Elements

In the original Burnett formulation, the test functions are given in the form

$$\Phi(\mathbf{r}) = \varphi(\mathbf{r}) e^{-ik(r-r_0)}. \quad (4.9)$$

In the literature, usually the sign in the exponent is changed due to the use of another convention in the notation of the weak formulation 3.22. Important is, however, that in the equation later on the test and ansatz functions enter both with same oscillatory factor, introducing oscillations with $e^{2ik(r-r_0)}$ in the Hamiltonian. These oscillations make the Hamiltonian non-hermitian and introduce a strong dependence on the energy $E = \frac{k^2}{2}$. Moreover it was found that this formulation can lead to numerical instabilities [41] and a wrong asymptotic behaviour.

This reformulation though lead to a quadratic eigenvalue problem instead of the generalised eigenvalue problem from before. However, assuming that the difference between the eigenvalues of (4.12) and the target energy of the outgoing electron is small, the quadratic eigenvalue problem can be approximated by the generalised eigenvalue problem (3.26) by setting k to the respective target momentum in the Hamiltonian.

Conjugate Burnett Elements

To get rid of the oscillatory terms, a modification of the test functions applied was introduced such that, in the notation used within this thesis, the test functions coincide with

the space of ansatz functions, having the form

$$\Phi(\mathbf{r}) = \varphi(\mathbf{r})e^{ik(r-r_0)}. \quad (4.10)$$

An important disadvantage of this formulation is, however, that in this formulation integrals with infinite contribution arise which cannot be treated in as Cauchy principal values as done in the unconjugated scheme [208]

Asley-Leis Formulation

To regularise the matrix elements, an additional damping is needed. Since the ansatz function (4.8) should not be changed for physical reasons, Astley suggested to chose test functions of the shape

$$\Phi(\mathbf{r}) = D(r)\varphi(\mathbf{r})e^{-ik\mu(r)} \quad (4.11)$$

where in three dimensions $D(r) = \frac{1}{r^2}$ [40]. This choise of basis functions is done at the expense that the Hamiltonian (3.27) is not hermitian.

Even though the oscillating term e^{ikr} cancels out, the Hamiltonian is energy dependent and thus the generalised eigenvalue problem (3.26) formulated in chapter 3.5 changes to

$$\mathbb{A}\mathbf{c} + ik\mathbb{B}\mathbf{c} - k^2\mathbb{C}\mathbf{c} = 0 \quad (4.12)$$

with

$$\mathbb{A}_{i,j} = \int \left(V(\mathbf{r})D(r)\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) - \frac{1}{2}D'(r)\varphi_i(\mathbf{r})\varphi'_j(\mathbf{r}) + \frac{1}{2}D(r)\varphi'_i(\mathbf{r})\varphi'_j(\mathbf{r}) \right) d\mathbf{r} \quad (4.13)$$

$$\mathbb{B}_{i,j} = \frac{1}{2} \int (-\mu'(r)D'(r)\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) + D(r)(\varphi'_i(\mathbf{r})\varphi_j(\mathbf{r}) - \varphi_i(\mathbf{r})\varphi'_j(\mathbf{r}))) d\mathbf{r} \quad (4.14)$$

$$\mathbb{C}_{i,j} = \frac{1}{2} \int ((D(r)\mu'(r)\mu'(r) + 1)D(r)\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})) d\mathbf{r} \quad (4.15)$$

where the prime is used as short-form of the spacial derivative and the relation $E = \frac{1}{2}k^2$ is used [42].

This formulation has been shown to be computationally robust for exterior acoustics [209, 210]. The introduced imaginary part of the eigenvalue can be considered as a broadening of the line width and thus as a lifetime as well as an uncertainty of the energy. However, this is not very meaningfull since the ansatz is done in pratically in such a way that the wave function is not changed in an unphysical sense. To understand the respective results, here a symmetrised ansatz is suggested in the following.

Symmetrised Formulation

Besides those formulations mentioned above, further infinite element formulations are used [42]. For example, a formulation to the Burnett-elements using a quadratic decay was applied to the harmonic oscillator [52] and DFT calculations [51] successfully. However, the application of infinite elements to FEFs is to my knowledge a novelty in this work.

Since the Astley-Leis elements suffer from their non-symmetric space of ansatz- and test-functions whereas the conjugate Burnett formulation has problems due to infinitely

large matrix elements, here a symmetric but damped ansatz of the form

$$\Psi(\mathbf{r}) = D(r)^p \varphi(\mathbf{r}) e^{ik\mu(r)} \quad (4.16)$$

$$\Phi(\mathbf{r}) = D(r)^p \varphi(\mathbf{r}) e^{ik\mu(r)} \quad (4.17)$$

is suggested where $\varphi(\mathbf{r})$ is of the form as before but $D(r) = \frac{1}{r^2}$ with $p > 0$ ensures that the matrix elements are finite-valued. The basis formulation (4.16) changes the mass and potential energy matrices only in a trivial way whereas the kinetic energy matrix, which is in the original Astley-Leis formulation non-hermitian, becomes now

$$\begin{aligned} \int (\nabla \Phi_i^*(\mathbf{r})) (\nabla \Psi_j(\mathbf{r})) d\mathbf{r} &= \int D^{2p} \left(p^2 \frac{D'(r)D'(r)}{D^2(r)} + p \frac{D'(r)}{D(r)} (\varphi_i(\mathbf{r})\varphi'_j(\mathbf{r}) + \varphi'_i(\mathbf{r})\varphi_j(\mathbf{r})) \right. \\ &\quad \left. + (\varphi'_i(\mathbf{r})\varphi'_j(\mathbf{r}) + ik\mu'(r)) (\varphi_i(\mathbf{r})\varphi'_j(\mathbf{r}) - \varphi'_i(\mathbf{r})\varphi_j(\mathbf{r})) - (ik\mu'(r))^2 \varphi_i(\mathbf{r})\varphi_i(\mathbf{r}) \right) d\mathbf{r} \end{aligned} \quad (4.18)$$

4.5 Solving Large Eigenvalue Problems

In finite element applications such as those being proposed in this work, matrix equations with hundreds up to hundredthousands of dimensions need to be solved. This requires elaborate strategies, using the sparsity of these matrices.

The focus here is on solving the generalised eigenvalue problem (3.26) and the quadratic problem (4.12) respectively. However, efficient strategies are only known for regular eigenvalue problems of the form

$$\mathbb{A}\mathbf{x} = \lambda\mathbf{x}. \quad (4.19)$$

Hence, the more general forms will be rewritten to become (4.19) as discussed in sections 4.5.1 respectively. Moreover, since the state of interest is a free state, one needs to expect a high density of states for an appropriate mesh. This, however, is a well-known problem in numerical methematics since almost degenerate eigenvalues are very sensitive to small perturbations and their respective eigenvectors even more. Though section 4.5.2 addresses these problems and a way for numerical stabilisation is sketched.

Finally in section 4.5.3 a few methos are presented showing how a small number of approximate eigenpairs can be obtained in a numerically efficient way from the usual eigenproblem (4.19).

4.5.1 Generalised Eigenproblem

The most straight-forward way to reformulate the generalised eigenvalue problem

$$\mathbb{A}\mathbf{x} = \lambda\mathbb{B}\mathbf{x}, \quad (4.20)$$

is to invert the matrix \mathbb{B} , obtaining the regular Eigenproblem $\mathbb{B}^{-1}\mathbb{A}\mathbf{x} = \lambda\mathbf{x}$. This way is possible as long as \mathbb{B} is invertable and not too large since inversion is a demanding task and the resulting matrix is not sparse anymore [211].

To prevent the use of dense matrices, libraries often do not operate with the matrices themselves but rather with a set of vector on which these matrices act [211]. The most popular scheme of this kind is the Rayleigh-Ritz projection where the initial problem is

approximated on a small subspace $\mathcal{V}_j = \text{span}\{\mathbf{v}_1, \dots, \mathbf{v}_j\}$, spanned by appropriate vectors \mathbf{v}_i .

Projecting the original problem (4.20) onto this subspace yields the new system $\Sigma_j \mathbf{s} = \theta \Theta_j \mathbf{s}$ where $\Sigma_j = \mathbb{V}_j^T \mathbb{A} \mathbb{V}_j$ and $\Theta_j = \mathbb{V}_j^T \mathbb{B} \mathbb{V}_j$ respectively which is only of dimensionality j . The matrix \mathbb{V}_j is unitary with the rows $(\mathbb{V}_j)_i = \mathbf{v}_i$. After solving this dense but small problem, the original eigenvectors can be approximated as $\mathbf{x}_j = \mathbb{V}_j \mathbf{s}_j$ and $\lambda = \theta_j$. The obtained eigenpair is a good approximation to the actual one as long as the subspace \mathcal{V}_j contains the respective solution or contains a vector which is at least close to it. A commonly used approach is the Krylov subspace.

4.5.2 Stabilisation of Eigenproblems

Independent of the efficiency and robustness of the eigensolver in use, seeking solutions of the SE for free particles means that eigenpairs are to be found whose energies are, if the numerical parameters are chosen well, very dense or even degenerate. Unfortunately, dense-lying eigenvalues lead to numerical difficulties and especially the eigenvectors are known to be unreliable in this case. In practice this means that the iterative schemes do not converge anymore, requiring a reformulation of the mathematical problem.

One way to circumvent the instabilities in the original problem (4.20) is to reformulate it as a minimisation problem [26]. Therefore eq. (4.1) is rewritten as $(\frac{1}{2}\mathbb{A} + \mathbb{V} - E\mathbb{M}) \mathbf{c}_i = 0$ where E is the target energy. Since this will have most likely no unambiguous solution, one minimises the residuum

$$\min_{\|\mathbf{x}\|=1} \left\{ \left\| \left(\frac{1}{2}\mathbb{A} + \mathbb{V} - E\mathbb{M} \right) \mathbf{x} \right\| \right\}. \quad (4.21)$$

Using the L_2 -norm, this is equivalent to finding the smallest eigenvalue of

$$\left(\frac{1}{2}\mathbb{A} + \mathbb{V} - E\mathbb{M} \right)^\dagger \left(\frac{1}{2}\mathbb{A} + \mathbb{V} - E\mathbb{M} \right) \mathbf{x}_i = \theta \mathbf{x}_i \quad (4.22)$$

where θ is a measure for the error in energy.

Whereas eq (4.22) is only an approximation to the original problem, it has the advantage that it is a quadratic expression. Similar schemes which are, in contrast to that mentioned above, only reformulations of the original problem are often referred to as spectral transformations [211]. One example is the harmonic extraction, where the eigenvalues of original expression (4.20) are first shifted such that the target value is 0, leading to the equation

$$(\mathbb{A} - \tilde{\lambda}\mathbb{M}) \mathbf{x} = (\lambda - \tilde{\lambda}) \mathbf{x} \quad (4.23)$$

where $\tilde{\lambda}$ is the target value of the original problem. Then, the equation is multiplied by \mathbb{A} , resulting in the problem

$$(\mathbb{A} - \tilde{\lambda}\mathbb{M}) (\mathbb{A} - \tilde{\lambda}\mathbb{M}) \mathbf{x} = (\lambda - \tilde{\lambda}) (\mathbb{A} - \tilde{\lambda}\mathbb{M}) \mathbb{M} \mathbf{x} \quad (4.24)$$

which is observed to lead to faster convergence for Krylov-subspace methods [211].

Further spectral transformations are the spectral folding [211] where the left and right

side of equation (4.23) are squared respectively which often leads to higher stability but the squaring of eigenvalues leads to ambiguities with respect to the eigenvalues λ of the original problem. The scheme that turned out to be most beneficial for the matrices used in this work is the shift and invert scheme where the inverted problem of eq. (4.23), *i.e.*

$$(\mathbb{A} - \tilde{\lambda} \mathbb{M})^{-1} \mathbb{M} \mathbf{x} = \frac{1}{\lambda - \tilde{\lambda}} \mathbf{x}, \quad (4.25)$$

is solved. The formulation (4.25) has the advantage that the transformed eigenvalues $\frac{1}{\lambda - \tilde{\lambda}}$ are well-separated and on the extrema of the new spectrum, making the convergence faster and more stable [212]. A more generalised transformation is the Cayley-transform which has two parameters $\tilde{\lambda}$ and $\tilde{\tilde{\lambda}}$ and yields the usual eigenvalue problem

$$(\mathbb{A} - \tilde{\lambda} \mathbb{M})^{-1} (\mathbb{A} + \tilde{\tilde{\lambda}} \mathbb{M}) \mathbf{x} = \frac{\lambda + \tilde{\tilde{\lambda}}}{\lambda - \tilde{\lambda}} \mathbf{x}. \quad (4.26)$$

Finally, a regularisation of eigenvalue problems can be performed using matrix preconditioners. Many different types of preconditioners are developed [213] but most of them are effective only on a small class of problems as *e.g.* especially well-suited for matrices originating from FEM-problems [214, 215] and can be even specialised to a FEM structure [216, 217] or for a particular physical problem [196]. Often their performance moreover depends on the solver to be used later [218]. This makes their effective use more intricate and can easily lead to higher costs than their benefit is. In this thesis, the shift-and-invert scheme (4.25) is used.

4.5.3 Solving Large Eigenproblems

For the computation of eigenpairs, many classes of solvers have been developed with various numerical properties. Besides direct solvers such as the Gauß-elimination, many iterative solvers have been developed that are especially well-suited for large but spares problems. Besides the famous Jacobi- and Gauß-Seidel algorithms which converge only in certain cases, also the Davidson method and several Krylov subspace methods are commonly used. For finite element problems, the Krylov subspace solvers turned out to be the most efficient class.

As discussed in the sections 4.5.1 and 4.5.2 already, the solution of a generalised eigenvalue problem involves matrix operations which need to be avoided to keep their sparse structure.

As a popular choise for such classes of problems, the Krylov subspace is used. An r -dimensional Krylov subspace is generated by a vector \mathbf{x} and a matrix \mathbb{A} and has the form

$$\mathcal{K}_r(\mathbb{A}, \mathbf{x}) = \text{span} \{ \mathbf{x}, \mathbb{A}\mathbf{x}, \mathbb{A}^2\mathbf{x}, \dots, \mathbb{A}^{r-1}\mathbf{x} \}. \quad (4.27)$$

If \mathbb{A} is sparse, the evaluation of these expressions is only of order $\mathcal{O}(d)$ where d is the dimensionality of \mathbf{x} . The vectors obtained with large powers of \mathbb{A} however usually become more and more linearly dependent. To prevent this, the vectors usually are orthonormalised subsequently.

An important issue in this scheme is a good choise for \mathbf{x} which crucially determines

the speed of convergence. If a reasonable start-vector is not given, the space \mathcal{K}_r needs to be extended by increasing r iteratively. The orthogonalisation method being used distinguishes different Krylov subspace methods such as the Arnoldi [219] or Lanczos [220]. In the particular implementation, the Krylov-Schur algorithm is used [212, 221]. To keep the dimensionality low, in this algorithm the subspace iteration is restarted after r reached a certain value, starting with a better guess \mathbf{x} .

5 | Applied Protocol

After describing different approaches to compute PESs in chapter 2 and pointing out why the DO formalism combined with a finite element method for the computation of the photoelectron function is well-suited for our needs, in this chapter the protocol as being used to obtain the PESs is presented.

In the first section the computation of the wave functions of initial (unionised) and final (ionised) states as well as the general procedure used to compute the DOs is described. Thereafter, in section 5.2.1 the setup of the finite element system that is used to compute the free electron function as well as the dipole matrix element are explained which is implemented in the program **FreeWilly** [55] in the framework of this thesis.

5.1 Bound State Functions

The DO formalism as it is described in 2.3 can be used with any self-consistent field method which can predict excited state energies and wave functions. In this work, density functional theory (DFT) is used for ground state calculations and its time dependent counterpart TDDFT to compute excited state energies. The DFT formalism which is introduced in the sections 5.1.1 and 5.1.2 has shown to be accurate and numerically cheap.

5.1.1 Ground State Density

The DFT is formally based on the Hohenberg-Kohn theorems [44] which state that the ground-state electron density determines the potential in the SE and with this also the wave-function. Moreover, the second Hohenberg-Kohn theorem states that the energy of the ground state can be found variationally from the density. Thus, the electron density contains all information needed and the computation of the N -electron wave function can be omitted. Since the Hohenberg-Kohn theorems do not point out a way how to determine the electron density without knowing the wave-function, usually the Kohn-Sham scheme [45] is used where the electrons are described as non-interacting particles in a respective pseudo-potential that is constructed such that the electron density of these Kohn-Sham orbitals corresponds to the real electron density. Since the particles do not interact with each other, the Kohn-Sham orbitals $\Psi_j(\mathbf{r})$ can be obtained from the one-particle SE

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \Psi_j(\mathbf{r}) = \epsilon_j \Psi_j(\mathbf{r}) \quad (5.1)$$

where ϵ_j is the binding energy of the respective Kohn-Sham orbital and the effective potential

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}) \quad (5.2)$$

can be separated into the external potential $V_{\text{ext}}(\mathbf{r})$, which consists of the attractive nuclear ESP and external fields, the electrostatic interaction of the particles where $\rho(\mathbf{r}) = \sum_{i \neq j} |\Psi_i|^2$ and the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ which contains the complexity of the electronic interaction [222]. The exchange correlation potential $V_{\text{xc}}(\mathbf{r})$ contains, besides contributions from exchange and correlation, also the error of kinetic energy in the Kohn-Sham scheme to account for the fact that the Kohn-Sham wave-functions differ from the real orbitals and thus have another kinetic energy as well [223].

Assuming that the Kohn-Sham orbitals coincide with the physical orbitals, the exchange potential acts on an orbital $\Psi_i(\mathbf{r})$ as

$$V_{x;j}(\mathbf{r})\Psi_i(\mathbf{r}) = \int \frac{\Psi_j^\dagger(\mathbf{r}')\Psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \Psi_j(\mathbf{r}) \quad (5.3)$$

and thus is non-local [223]. In DFT usually the exchange energy is approximated as a local functional of the density and its derivative, leading to the so-called local density approximation and gradient corrected functionals [222]. The Becke [224] exchange-functional used in this work has the form

$$E_x = \frac{3}{2} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \sum_{\sigma} \int \rho_{\sigma}(\mathbf{r})^{\frac{4}{3}} d^3\mathbf{r} - \beta \sum_{\sigma} \int \rho(\mathbf{r})^{\frac{4}{3}} \frac{x_{\sigma}(\mathbf{r})^2}{1 + 6\beta x_{\sigma} \sinh^{-1}(x_{\sigma}(\mathbf{r}))} d^3\mathbf{r} \quad (5.4)$$

where the first summand corresponds to the local density approximation and the second is a semi-empirical gradient correction, σ denotes the spin polarisations and $x_{\sigma}(\mathbf{r}) = \frac{|\nabla \rho_{\sigma}(\mathbf{r})|}{\rho_{\sigma}^{\frac{4}{3}}}$. The gradient correction in this functional is constructed such that the asymptotic behaviour of the exchange energy and electron density follow

$$\lim_{r \rightarrow \infty} E_x^{\sigma}(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} \quad (5.5)$$

$$\lim_{r \rightarrow \infty} \rho(\mathbf{r}) = e^{-a_{\sigma}|\mathbf{r}|} \quad (5.6)$$

with a_{σ} is a constant related to the ionisation potential of the system under study [224]. The prefactor of the gradient correction, β , was determined by fitting to several atomic noble-gas systems and is set to be $\beta = 0.0042$ in atomic units [224].

The correlation potential finally is defined as the functional derivative of the correlation energy with respect to the electron density $V_c(\mathbf{r}) = \frac{\partial E_c[\rho]}{\partial \rho(\mathbf{r})}$. In the case of the LYP-correlation energy functional is based on the Colle-Salvetti formula which estimates the correlation energy in the Hartree-Fock approach and introduces two parameters that are set by fitting to experimental data [225].

5.1.2 Properties of Excited States

The DFT is not only a well-established method to obtain ground-state properties of many different kinds of systems, but it has also a time-dependent counterpart, formally based on the Runge-Groß theorem [226]. Commonly, when referring to TDDFT, respective the linear-response scheme is meant [227]. It is a first order perturbation expansion and can be used to obtain the energies and occupation numbers of excited states using the so-called Casida-equation [228]

$$\begin{bmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^\dagger & \mathbb{A}^\dagger \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \quad (5.7)$$

where the matrix elements are

$$\mathbb{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + \int \int d\mathbf{r} d\mathbf{r}' \frac{\Psi_i(\mathbf{r})\Psi_a(\mathbf{r})\Psi_j(\mathbf{r}')\Psi_b(\mathbf{r}') - \Psi_i(\mathbf{r})\Psi_j(\mathbf{r})\Psi_a(\mathbf{r}')\Psi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (5.8)$$

$$\mathbb{B}_{ia,jb} = \int \int d\mathbf{r} d\mathbf{r}' \frac{\Psi_i(\mathbf{r})\Psi_a(\mathbf{r})\Psi_b(\mathbf{r}')\Psi_j(\mathbf{r}') - \Psi_i(\mathbf{r})\Psi_b(\mathbf{r})\Psi_a(\mathbf{r}')\Psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (5.9)$$

where i, j denote occupied and a, b virtual states and $\mathbb{1}$ is the unity matrix, ε_α are (Kohn-Sham) orbital binding energies of the Kohn-Sham orbitals $\Psi_\alpha(\mathbf{r})$. The indices i, j and a, b denote occupied and virtual orbitals with binding energy $\varepsilon_i, \varepsilon_a$ respectively [227]. The Casida equation (5.7) is a non-hermitian eigenvalue problem whose eigenvalues ω correspond to the transition energies and the eigenvectors denote the transition coefficients. The different blocks in equation (5.7) have different physical interpretation. As the negative sign of the transition energy in the lower block indicates, lower half of the eigenvector, denoted as \mathbf{Y} , corresponds to negative excitation energies ε_i and can be assigned to de-excitations from virtual orbitals which makes no physical sense if the reference state is a ground state [227]. Since the matrix \mathbb{B} contains usually only small elements, it is often set to zero which is referred to as Tamm-Dancoff approximation and reduces the original equation to a hermitian equation of half dimensionality [228].

5.1.3 OTRSH-scheme

One main issue concerned with the DFT-formalism is that the approximate exchange functional lead to wrong asymptotic behaviour of the electron density. The local density approximation leads to an exponential decay instead of $\frac{1}{r}$ and $\frac{1}{r^4}$ for the exchange and correlation terms respectively [46] which is improved significantly with gradient-corrected functionals but usually still yields spurious behaviour [222]. This wrong behaviour affects the obtained wave functions and thus the orbital energies [18].

To reduce this error, so-called range-separated hybrid (RSH) functionals are used, in which the DFT-exchange term as *e.g.* the Becke functional (5.4) is used for small interelectronic distances only, while at larger distances, where correlation effects are not that important, the Hartree-Fock exact-exchange (5.3) is used [229]. The interchange

between the schemes is done by the scheme

$$\frac{1}{r} = \underbrace{\frac{\alpha + \beta \operatorname{erf}(wr)}{r}}_{\text{exact exchange}} + \underbrace{\frac{1 - \alpha - \beta \operatorname{erf}(wr)}{r}}_{\text{DFT exchange}} \quad (5.10)$$

where $\alpha + \beta = 1$ and ω are parameters to be chosen. Besides taking the standard parameters that are fitted to a set of testing-systems, ab-initio schemes for choosing α and ω are available which are referred to as optimally-tuned RSH (OTRSH) schemes. Using such a scheme, the degrees of freedom obtained are used to optimise a particular system-property such as Koopmans' theorem by minimising the functional [46]

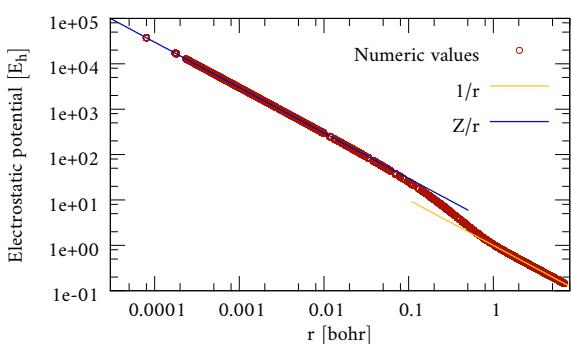
$$J(\alpha_{\text{opt}}, \omega_{\text{opt}}) = \min_{\alpha, \omega} \{|E_N(\alpha, \omega) - E_{N-1}(\alpha, \omega) - \varepsilon_{\text{HOMO}}|\} \quad (5.11)$$

or a similar one which can also account for lower-lying orbitals or the electron affinities which should resemble the binding energies of the lowest unoccupied molecular orbital (LUMO).

Another quantity to optimise is the derivative discontinuity [230–232] that is based on the fact that the exchange-correlation energy should be a straight line when varying the number of electrons from N to $N + 1$. The slope of that line corresponds to the binding energy of the respective electron and thus is discontinuous at integer numbers of electrons. The approximate exchange correlation functionals, however, usually do not fulfill this condition but the parameters α and β can be tuned such that only small deviations can be observed [46].

For this optimization procedure the Gaussian package G09 [54] is used with the 6-31G(d) [233, 234] basis set and the functional LC-BLYP [235]. The ground state DFT calculation, determination of geometries and the linear-response TDDFT calculations have been conducted with a locally modified version of NWChem [53], employing the basis set def2-tzvp [236] without symmetry restrictions. The Kohn-Sham orbitals (obtained by ground state DFT) and CI-coefficients (obtained by linear-response TDDFT which yields the configuration interaction singles expansion for a number of excited states) as well as the atomic overlap matrix are interfaced to the in-house software DYSON [32] that computes the DOs. The integration of the transition dipole matrix elements in eq. (2.16) finally is performed using ezDyson [34].

5.1.4 Obtaining the Electrostatic Potential and Dyson orbitals



The ESP used in this work is obtained with a modified version of NWChem [53] where the points, at which this potential should be computed can be set by the user. Setting these points to the quadrature points of the integration scheme requires some extra effort but has the great advantage that no interpolation is required. However, NWChem can compute the values only up to a minimum distance to the nuclei. The missing

Figure 5.1: Double-logarithmic plot of the radial projection of the ESP of atomic Lithium

points are chosen as Z/r where Z is the charge and r is the distance of the quadrature point to the closest nucleus which is a good approximation as Figure 5.1 shows. An interpolation of the data on the complete domain in **FreeWilly** [55] would require an interpolation-scheme for scattered data such as RBF interpolation [129–131], inverse distance interpolation [237, 238] or similar methods [239–241], but these methods give, if the parameters are not chosen accurately, spurious oscillations between the quadrature points and thus do not result in a smooth ESP.

The other external quantity needed to compute the intensities is the DO that is computed in the framework of this thesis with the in-house code **DYSON** [32]. The wave functions of the initial and final states are computed with the **NWChem**-code which is modified to produce more verbose output. The respective data are extracted and reformatted with a self-written script [242], creating the input for **DYSON**.

5.2 Free electron function

The FEF is computed with a finite element scheme using the program **FreeWilly** [55] developed in the framework of this thesis. It is based on the library **Libmesh** [56] which itself uses several libraries for the required linear algebra and the mesh-setup. As discussed in section 4, the most crucial step in a FEM simulation is the setup of the grid. The **FreeWilly**-code supports several closely related setup-schemes of which the most important are described in the following.

5.2.1 Setup of the Grid

In the program **FreeWilly** the finite elements is obtained from a set of points via Delaunay triangulation (see ?? for details) using the library **tetgen** [243]. The distribution of these points is responsible for the quality of the obtained solution via many parameters in a non-trivial way. It is expected that the most important of these parameters are

The molecular geometry Close to the cores it should be denser, at larger distances a coarser grid is possible.

The kinetic energy of the photo electron which gives the maximum distance between two points

The largest angular momentum of the Dyson orbital determines the angular momentum of the photoelectron to be resembled.

To account for these properties in the best way, here a similar scheme to that suggested by Son and Chu [122] is utilised. In this scheme, the molecular region is composed of spheres with different radii, centred at the nuclei each and whose overlapping regions are cut off. To yield a reasonable mesh, the radii of these spheres need to be larger than the bond lengths to avoid holes or interatomic gaps in the molecule, *e.g.* between different ligands. Using such a scheme, the global grid is determined by the size of the largest sphere r_{\max} , the number N of spheres being used for each atom as well as the radial distribution of the size of spheres and angular distributions of points on each sphere, respectively.

For the radial distribution of N spheres, Son and Chu [118] suggested the radial distribution

$$r_i = \frac{iq}{N - i + \frac{qN}{r_{\max}}} \quad i = 1, \dots, N \quad (5.12)$$

where q is a parameter that determines the distance between the most inner spheres. Using this function, the smallest spheres ($i \ll N$) are scaled linearly with distances r_{\max}/N whereas the distance of the largest spheres depends non-trivially on the parameters but can become very large if q is small whereas large q lead to almost uniform distribution of spheres.

To obtain better control of the distance between the inner spheres and the maximum distance which needs to be considerably smaller than the wave length, in this work the formula

$$r_i = \frac{iq}{\left(\frac{N}{i}\right)^p \left(\frac{Nq}{r_{\max}} - 1\right) + 1} \quad i = 1, \dots, N \quad (5.13)$$

is suggested which has two degrees of freedom q and $p \geq 1$ where the condition $N > \frac{r_{\max}}{q}$ needs to be fulfilled to ensure positive radii. Here q is the asymptotic distance between two spheres whereas the distance of inner spheres can be tuned by the power $p+1$ so that the inner spheres can be tuned to become very dense.

While the distribution of spheres follows, at least on a qualitative level, a clear scheme since it should always resemble the local kinetic energy, the distribution of points on the surface of each sphere more complicated. Here, a regular distribution is a good choice, but on the non-linear topology of the sphere, regularity is in general more challenging. While so-called geodesic grids are popular in earth sciences [244–246], their construction allows only for exponentially growing mesh-sizes. Another common approach is to use quadrature points of integration rules of a given order which lead to Lebedev-grids [182, 247] and spherical t-designs [248, 249] that are found more often in quantum chemical contexts [250–253] and will be used in this thesis. Further methods involve the search of extrem such as minimisation of the Riesz s-energy, and other geometric properties [254–257] or a set of qualitatively lower but computationally much easier schemes such as the spherical fibonacci mapping [258, 259].

Since in finite element theory the sphere neither needs to be really round nor is there any global functional defined on it, the complicated distributions described above may be not even needed. An other approach therefore is to use an algorithm that gives just a more or less uniform distribution.

The above mentioned techniques show the large variety of different approaches and it is not very clear which one will meet our needs best. Moreover, here the problem is not only two dimensional but the whole sphere (not only its surface) needs to be subdivided. Hence, besides the question of a radial density of different spherical surfaces, also the number of points per sphere as function of the radial distance needs to be considered.

Besides the tricky question about this mapping, also the number of points per sphere depending on the radial distance needs to be considered. In [118] this is chosen to be constant without further discussion but of course there are several possible design criteria as well. Besides a constant number, also a constant spherical density (hence $N \propto r^2$) are possible; However, it might be sensible to follow a similar idea than in the radial mapping: Being fine close to the nuclei and get coarser with increasing distance. In particular, I

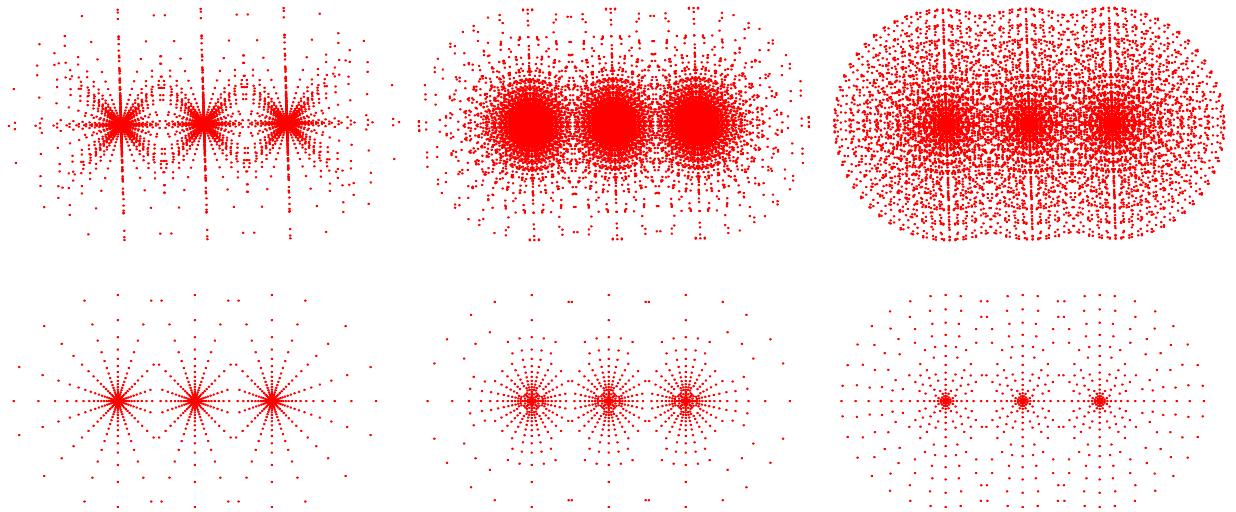


Figure 5.2: Examples of point-distributions for a CO₂-molecules with $r_{\max} = 3$ a.u. and 18 spheres, in the upper row the full mesh, below cuts through the molecular plane. left: constant number of points, radial scheme (5.12) with $q = 0.7$; centre: radial scheme (5.12) with number of points according to (5.15) with $q = 0.7$; right: radial distribution (5.13) with $q = 0.7$, $p = 2$ and number of points per sphere (5.14)

followed the design rule of keeping the space between points in radial direction similar to space between points in angular distribution. Hence, $d_{\text{spheric}} = \sqrt{\frac{4\pi r_i^2}{N_i}} \approx r_i - r_{i-1}$. For the above described radial schemes, this results in

$$N_i = \frac{4\pi}{\left(1 - \frac{i-1}{i} \frac{\frac{N-i+\frac{lN}{r_{\max}}}{N-i+1+\frac{lN}{r_{\max}}}}{\right)^2} \quad (5.14)$$

for the first scheme and

$$N_i = \frac{4\pi}{\left(1 - \frac{i-1}{i} \frac{\left(\frac{N}{i}\right)^p \left(\frac{lN}{r_{\max}} - 1\right) + 1}{\left(\frac{N}{i-1}\right)^p \left(\frac{lN}{r_{\max}} - 1\right) + 1}\right)^2} \quad (5.15)$$

for the latter.

The respective radii and number of points per sphere are shown in Figure 5.3. Special mapping schemes are the constant radial mapping $r_i = ai$ which corresponds to a constant spherical grid density $N_i = 4\pi a^2 i^2$ and an exponential map $r_i = q^i r_0$ which would require a constant number of spherical grid points $N_i = \frac{4\pi q^2}{(1-q)^2}$ according to the rule derived above.

Since some of the spherical schemes described above allow only for certain numbers of points each, here, the best approximation is used respectively.

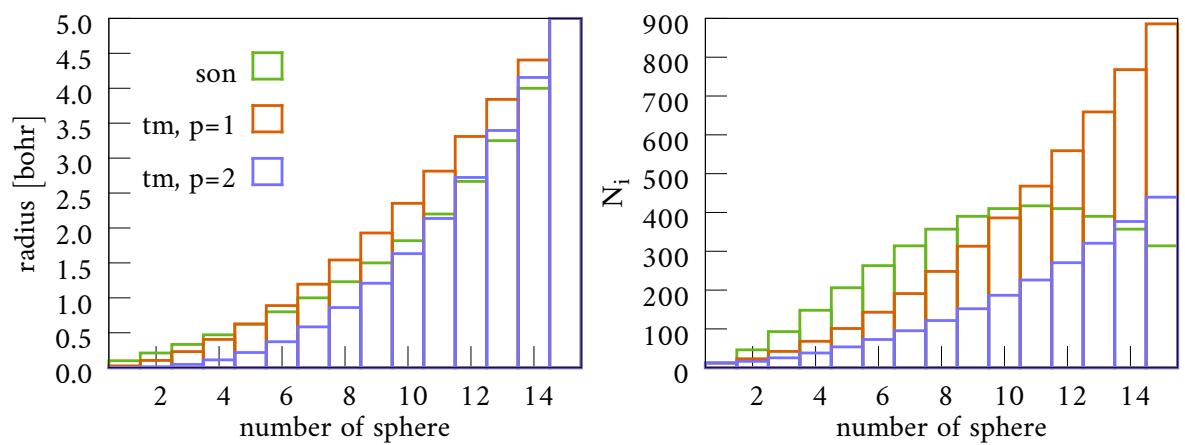


Figure 5.3: Comparison of the radius (left) and number of points (right) of the different spheres ($N = 15$, $r_{\max} = 5$ and $q = 2$) for the different radial schemes (5.12) and (5.13).

6 | Results

In the previous chapters, many different methods that can be used to compute PESs numerically are described and in chapter 5 the method used within this work is described in more detail. In this chapter some results are shown and explained.

Since the method developed in this work combines several techniques that have not been used together so far and several conceptual questions need to be clarified before computing actual PESs, in section 6.1 two BCs are compared in their influence on the wave-function. In section 6.2.1 further benchmarking calculations on some numerical parameters are shown. For simplicity, these calculations were performed using a Lithium atom as test system.

In section 6.3 further results for atomic Lithium are presented, showing several conceptual

6.1 Comparison of Boundary Conditions

In section 4.4, many BCs which give rise to diverse properties for the solution are briefly described. Detailed comparisons of some of these BCs are studied in various works [190, 191, 260–262] for several systems. For simplicity, here only two BCs are studied in more detail. First, in section 6.1.1 several properties of the grids introduced in section 5.2.1 are studied with Dirichlet boundaries which are particularly easy to set up and understand in their physical consequences. In section 6.1.2, several properties of the mesh with infinite elements are investigated. Since it turns out that the solutions obtained with infinite elements are very sensitive to the parameters, this study is performed more extensively. For simplicity, the tests shown here are on atomic systems using, unless specified otherwise, an analytic Coulomb potential with charge 1, corresponding to the ionised hydrogen atom.

6.1.1 Dirichlet Boundary Condition

Dirichlet boundaries are conceptually the easiest BCs but are known to have a large influence on the solution, especially for continuous functions since they reflect outgoing waves fully. Moreover, its requirement for the solutions to vanish at the boundaries results in an artificial discretisation of the radial solution similar to that of bound states which leads to a banded spectrum with a size-dependent energy gap between two states with same angular momentum. Moreover, these boundaries enforce the real and imaginary part of the solution to be identical up to symmetry operations (such as rotations and reflections for spherical systems) which does not hold for continuum waves such as Coulomb waves as can be seen in Figure 3.1 and plane waves that have a constant phase shift.

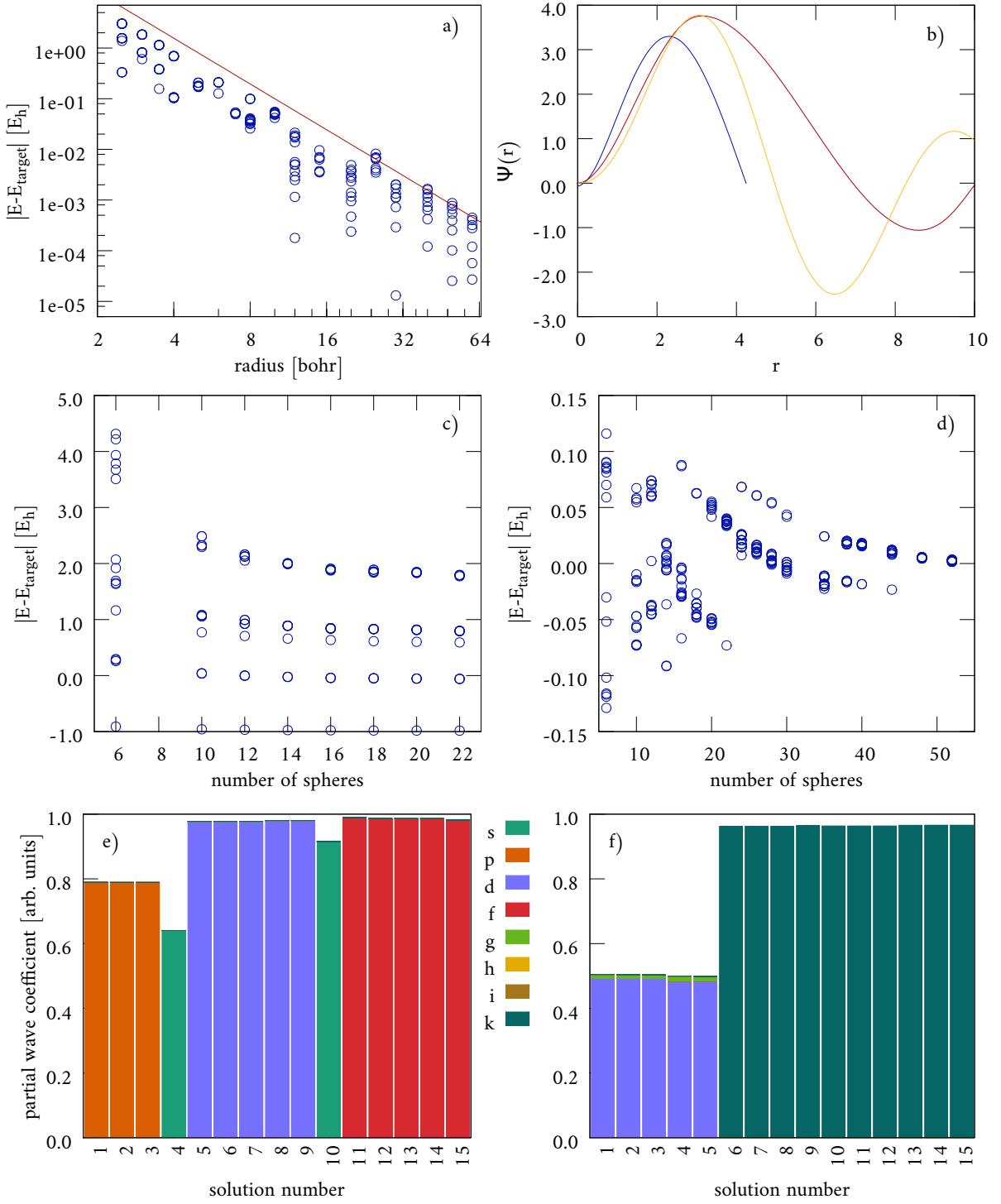


Figure 6.1: Several properties of the solutions obtained with Dirichlet BCs using different box sizes:

a) double-logarithmic plot of the error in energy of the energetically closest solutions in dependence on the radius b) radial part of d -wave functions obtained with different box-sizes($r = 4$, blue line and $r = 10$, red line); Coulomb wave (yellow line) for comparison. c) and d) plot of the error in energy for radii of 4 bohr, and 10 bohr, varying the number of spheres in the box e) and f) show the partial wave coefficient (6.1) of different angular momenta of the respective solutions with $r = 4$ and $N = 16$ (left) as well as $r = 10$ and $N = 38$, respectively.

These properties are found in various tests conducted to find reasonable parameters for application to more complex systems. In Figure 6.1 a), the error in the energy of 20 solutions is shown for different radii. The comparison with the red line, which shows a cubic decay, shows that the error is inverse proportional to the volume of the box. The number of spheres is kept constant at $N = 20$. The influence of the number of spheres on the energies is shown in the panels c) and d) of Figure 6.1. In these figures several branches of solutions can be seen that correspond to different angular momenta. For smaller radii ($r = 4$, panel c)), these branches are well-separated but become closer and finally interfere with each other at larger radii ($r = 10$, panel d)) where also strong coupling of angular momenta can occur. Following the expectations, the energies of the respective branches decay when the number of degrees of freedom is increased. The lowest panels in Figure 6.1 show the contributions from plane wave functions with respective kinetic energy and different angular momentum where the partial wave coefficient is defined as

$$|\langle \Psi_{\text{num}} | \Psi_k^{\text{Sph}} \rangle|^2 \quad (6.1)$$

where $|\Psi_{\text{veck}}^{\text{Sph}}\rangle$ is the spherical wave (3.2) and $|\Psi_{\text{num}}\rangle$ denotes the respective numerically obtained solution. For numerical reasons, here the comparison is done against the spherical waves and not against Coulomb waves. In Figure 6.1 b), two solutions with $l = 2$ along one axis are shown (the fifth one for $r = 4$ and the first one for $r = 10$) for two different box-sizes and compared to the Coulomb wave.

However, the density of solutions is not the only important quantity: To obtain reasonable intensities, the respective angular momentum is more important to obtain reasonable results. Respective tests show that for a given energy of the photoelectron of $E = 0.566$ Hartree the obtained solutions have a well-defined angular momentum only for small boxes where the critical radius is in the order of $r_{\text{max}} = 10$ bohr. For larger meshes, the states have large contributions from different angular momenta and are very sensitive to different parameters such as the number of spheres N_i and the parameters p and q of the distributions of the spheres (5.13) and (5.12) respectively. Moreover, for example the comparison of the Figures 6.1 e) and f) shows that solutions on larger meshes tend to have higher angular momenta which is an important argument in favour of smaller boxes since for most atomic systems angular momenta larger than 4 are not of interest.

6.1.2 Infinite Elements

Several questions and conceptual problems have been posed in the previous chapters which require some investigation to get an understanding of the properties of the numerical setup described so far. Among these questions is the formulation of infinite elements, discussed in section 4.4.4 of which the most important ones are studied in section 6.1.2.

Comparison of Formulations

Before having a closer look at the convergence of different parameters, first the formulation of infinite elements to be used later is investigated. Since the unconjugated Burnett-formulation was not very successful [42], the conjugated formulations of Burnett and Astley-Leis both have interesting features to use for quantum mechanical problems.

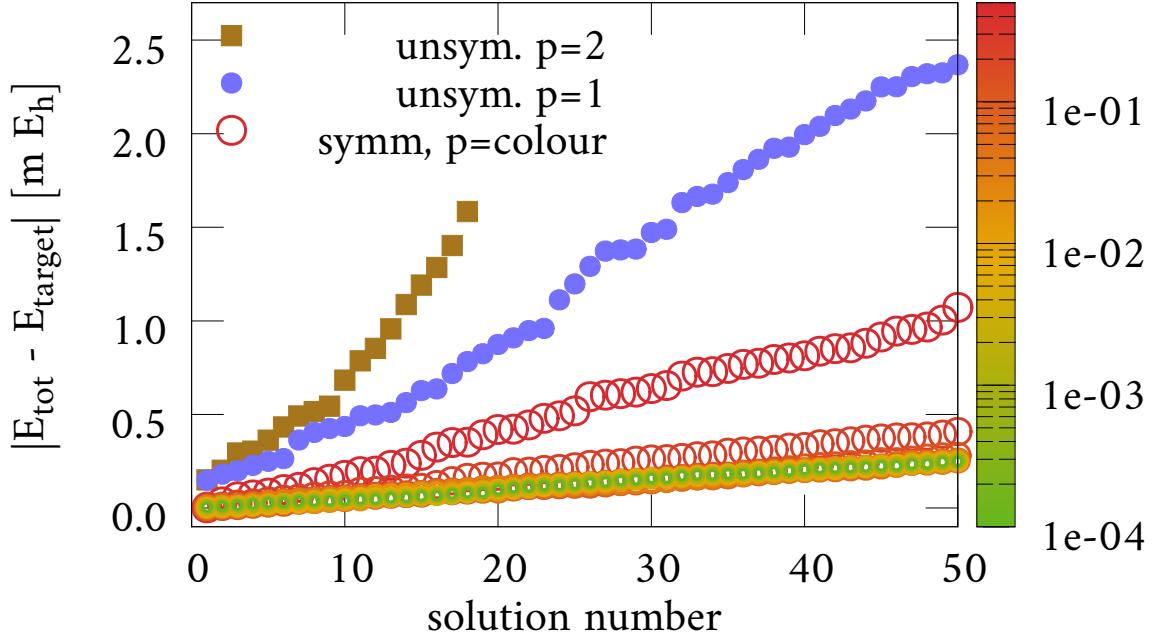


Figure 6.2: The first 50 eigenvalues obtained with the original Astley-Leis formulation (imaginary part not shown) and with the symmetrised form (4.16).

Since the conjugated Burnett elements lead to infinitely large matrix elements, here the Astley-Leis elements (4.11) are compared with the symmetrised form (4.16) using different powers p . Moreover, to study the influence of the damping function in the Astley-Leis formulation (4.11) in more detail, also a test function space similar to eq. (4.11) but using the squared damping function $D(r)^2$ instead of $D(r)$.

The 50 real solutions whose energy is closest to the target value of 15.44 eV ($0.5675 E_h$) obtained with the original Astley-Leis formulations with the damping function taken to the powers $p = 1, 2$ as well as the symmetrised formulation (4.16) suggested in this thesis with powers $p < 0.5$ are shown in Figure 6.2. For the unsymmetric formulations only the real part is shown which is assigned to the physical energy of the respective state. The results shown in Figure 6.2 show clearly that the obtained density of states decreases with the power p and converges for $p \approx \frac{1}{8}$ for the given parameters (the radial mapping scheme (5.13) is used with $N = 25$, $l = 0.5$, $p = 2.5$ and $r_{\max} = 7$ bohr.).

The dependence of the obtained spectrum of the Hamiltonian on the power of the damping function shows that, at least for FEFs, the asymptotic behaviour is crucial for the properties of the wave function. The dependence converges for $p = 1/8$, see also Figure A.2 in supplement. Moreover, even for small powers $p \approx 10^{-4}$, no numerical instabilities are observable so that there is some freedom in this parameter and it does not need to be optimised for different systems individually. The observations made on the convergence-properties using the spectrum in Figure 6.2 are supported by the projections of the solutions on spherical waves of which some are shown in Figure 6.3.

As shown in the Figure 6.3, the nature of the states obtained is in all cases strongly mixed in the quantum number l with significant contributions even for $l > 7$. However, the relative contributions of the angular momenta critically depends on the power p ,

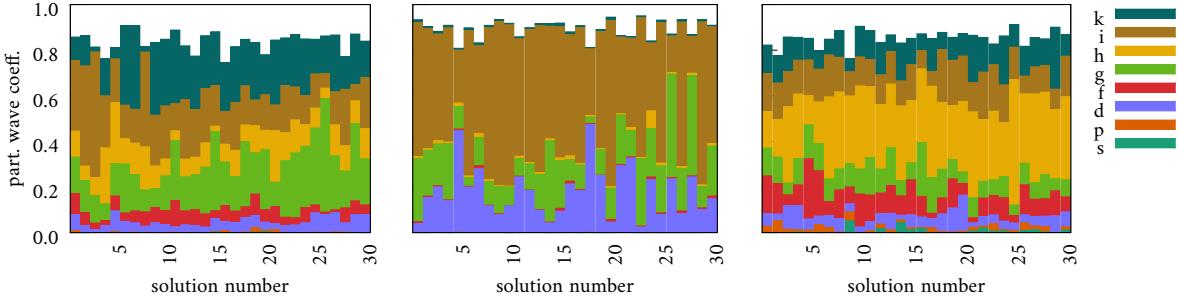


Figure 6.3: Decomposition of the first 30 solutions into spherical waves with angular momenta up to $l = 7$. Left: Astley-Leis-formulation ($p = 1$), middle: symmetrised form ($p = 0.5$) right: symmetrised form ($p = 10^{-4}$).

making a reasonable choice of this parameter important. Further it is expected that the convergence of p depends on further parameters such as the box-size and kinetic energy of the photoelectron which is, however, not studied here in more detail. Instead, in the following the power of the damping function D is chosen to be $p = 0.0001$ if not specified differently. This value is far in the convergence region of Figure 6.3 and thus is hoped to be reasonable also for other systems.

Radius of the Finite Element Region

Similarly to the Dirichlet BCs discussed in section 6.1.1, also for infinite element the size of the finite element region has a strong influence on the solution, even if the dependency is weaker as can be seen in Figure 6.4 where the energy of the energies closest to the target value is plotted for different box sizes. However, the energy-dependence on the box-size is much weaker than in the case of Dirichlet BCs as the comparison with the $\frac{1}{r^3}$ -curve in Figure ?? and 6.1 shows.

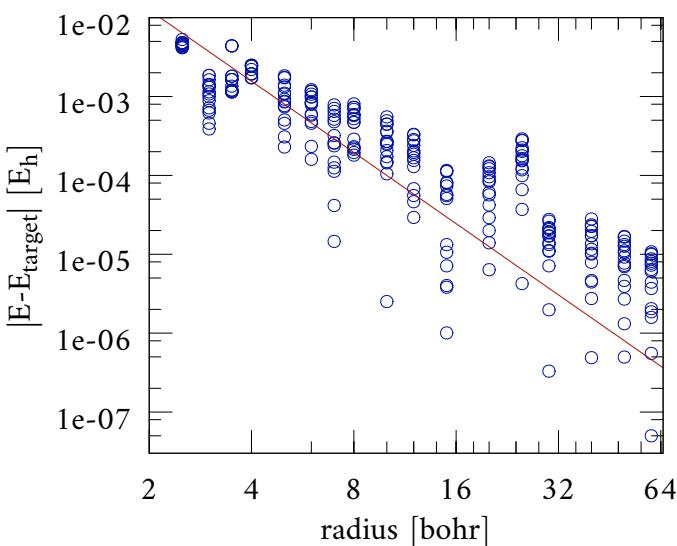


Figure 6.4: Double-logarithmic plot of the error in energy for different radii of the finite element region.

Moreover, the error in energy is in general much lower with infinite elements which is a further indicate for the higher accuracy of infinite elements compared to the Dirichlet boundaries. On the other side, also the angular momenta of the solutions are larger than those occurring with Dirichlet BC at the same box-size. This behaviour is observed to depend also on the formulation of infinite elements. Respective tests show, *e.g.*, that the mixing of angular momenta is stronger for smaller damping powers p . This coupling of different angular momenta can be explained by the very density of the spectrum which increases with

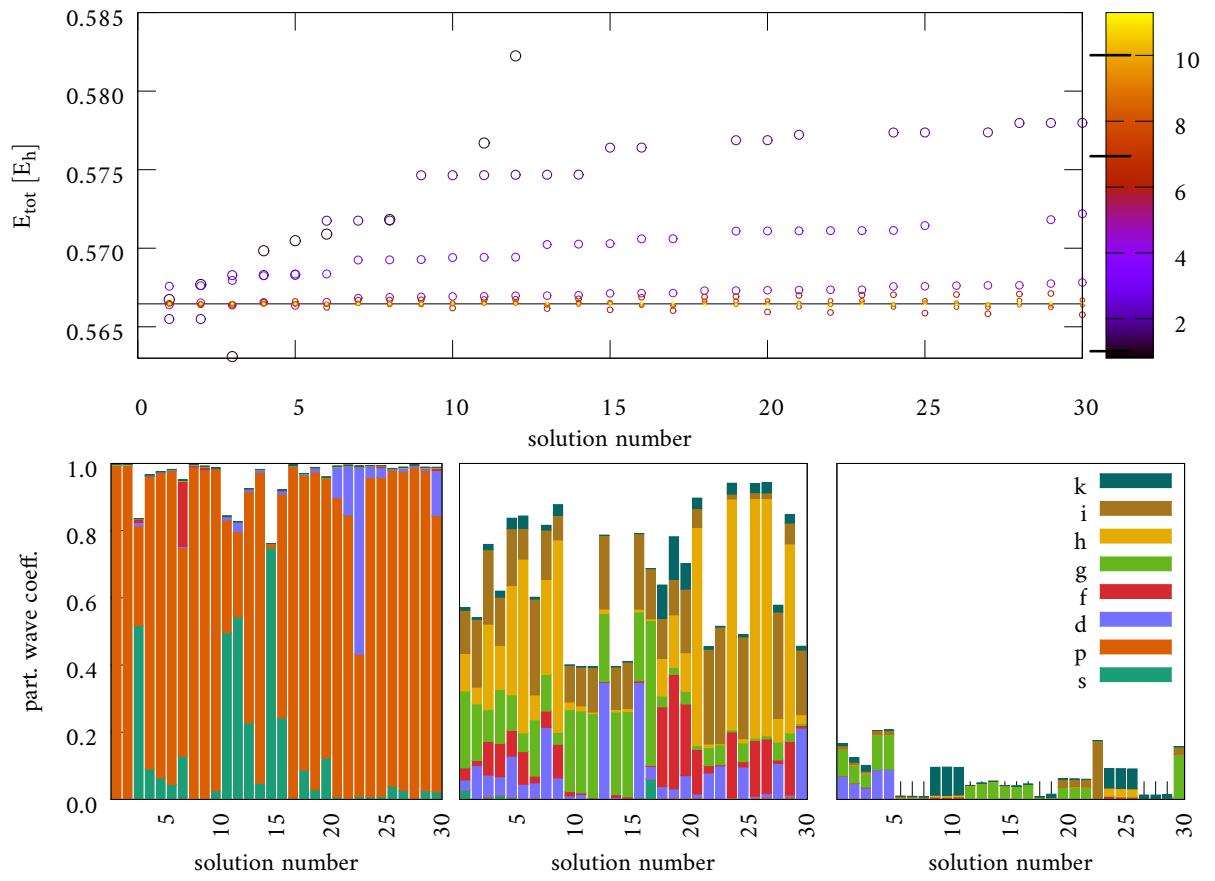


Figure 6.5: The eigenenergies for different box sizes (coloured dots in the upper panel) where the box size is denoted by the colour in atomic units. The lower panel shows the decomposition of the solutions into spherical waves for three box sizes, marked by a star in the colour bar respectively.

the radius as shown *e.g.* in Figure 6.5 but increases also with descending damping as illustrated in Figure 6.3.

This behaviour can be understood when recapitulating the influence of small perturbations (*e.g.* due to numerical cut-off) in form of a matrix \mathbb{E} of an hermitian matrix to its eigenvectors \mathbf{u}_i which has the form [263, 264]

$$\mathbf{u}'_i = \sum_{j \neq i} \frac{\mathbf{u}_j^\dagger \mathbb{E} \mathbf{u}_i}{\lambda_i - \lambda_j} \mathbf{u}_j \quad (6.2)$$

where λ_i is the eigenvector corresponding to \mathbf{u}_i . From eq. (6.2) now the coupling of angular momenta and strong dependence on the parameters for a dense spectrum, *i.e.* small $\lambda_i - \lambda_j$ becomes obvious.

Density of Spheres

Increasing the number of spheres has, as expected, some influence on the energies but also changes the angular momenta of the solutions. Similar to the behaviour found for Dirichlet BCs, also when using infinite element BCs a larger number of spheres leads to larger angular momenta as the comparison of the partial wave coefficients in Figure 6.6 for different numbers of spheres shows. Moreover, the error of the energy shown on the left side of Figure 6.6 indicates that the shown configurations are far from saturation. However, since high angular momenta are not desireable, a smaller number of spheres is better suited even though it is not converged. Moreover, the behaviour of the properties of the solutions when changing the number of spheres is not very systematic in the range shown. As an example, for $N = 10$ the energies are much more separated than is reflected also in the angular momenta which show a much weaker mixing than for the other configurations shown. Not only the unsystematic behaviour, the strong dependence of the angular momentum on the number of spheres as such is surprising since, in principle, the radial and angular nodes should be represented with a similar quality.

Radial Order

Using the infinite element scheme, an additional parameter is the order of the radial polynomial $f(r)$ in eq. 4.8. The increasing angular momentum with the radial order is, in contrast to the behaviour studied in section 6.1.2, not surprising. As mentioned in section 4.4.4, the first order infinite element term corresponds to the radial behaviour of an s -wave whereas higher radial orders describe the faster decaying waves with respectively larger angular momentum. Thus, choosing a low radial order ($o = 1$) leads to a better representation of low angular momenta and thus is favoured in this context.

Conclusion on Boundary Conditions

- Dirichlet BC: very slowly converging with box-size, radial function very poorly estimated for small boxes. But good convergence properties, eigenstates of angular momentum.
- CAP: algorithmic scheme to find single best energy, but not straight-forward to find some clear scheme if many solutions (have) to be taken into account.

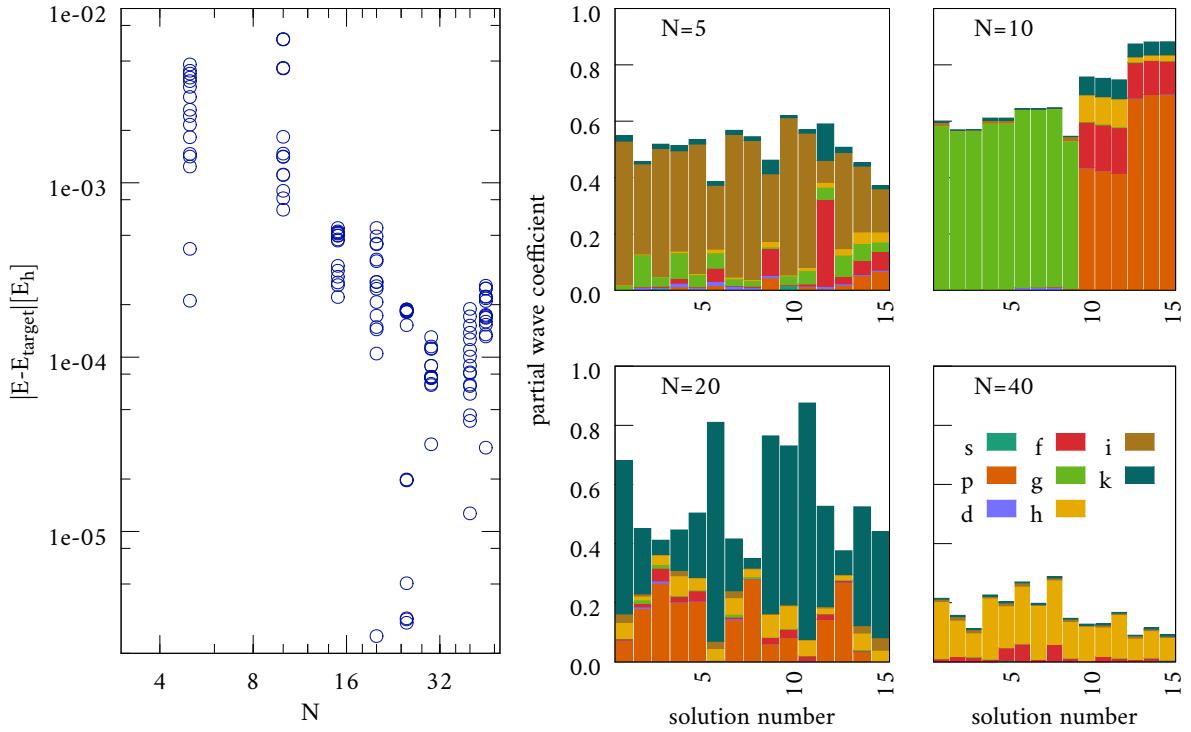


Figure 6.6: The energy (left panel) and partial wave coefficient (6.1) for different number of spheres N using infinite elements. The radius is $r = 10$ bohr.

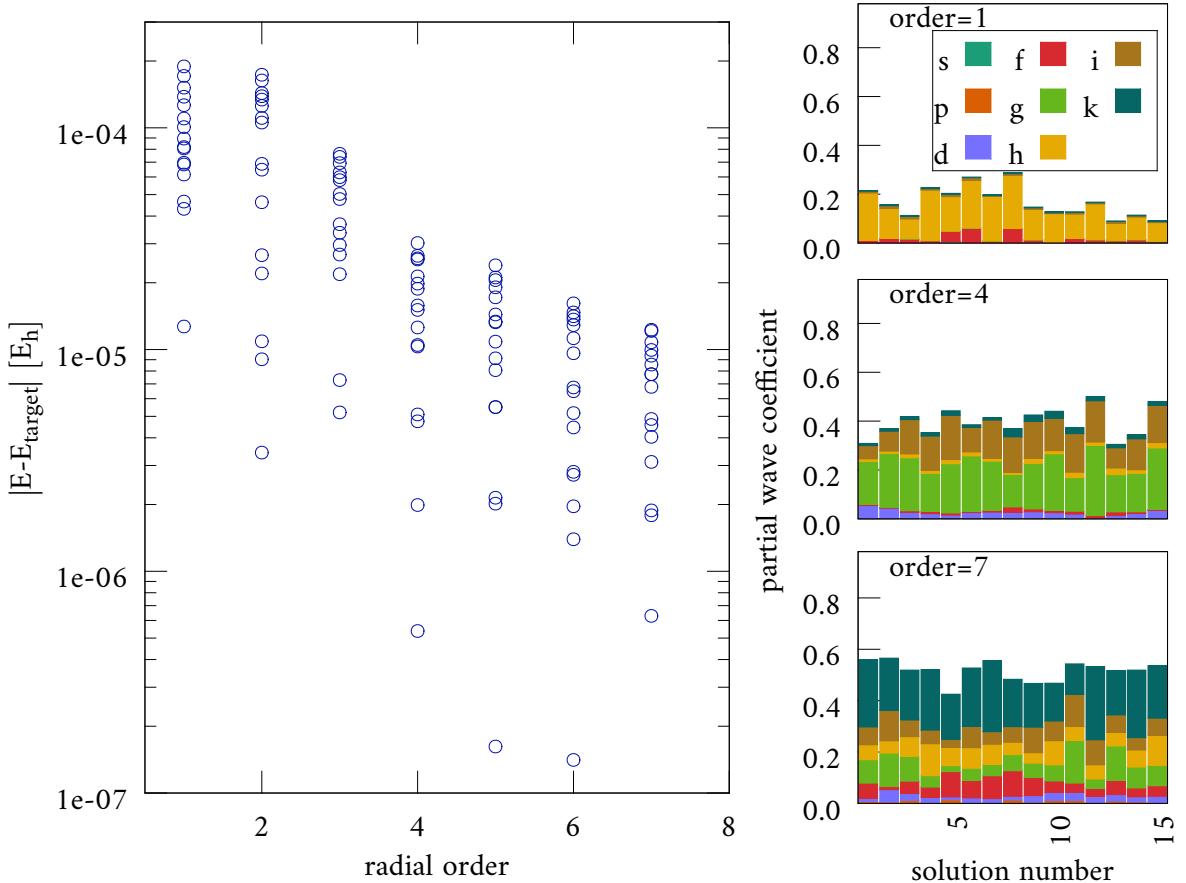


Figure 6.7: The error in energy for 15 solutions obtained with a box with radius $r = 10$ and $N = 40$ spheres using different orders of the multipole expansion $f(r)$, see eq. (4.8).

scheme	runtime [s]	DOS ^{a)} [$(mE_h)^{-1}$]	number of nodes
const	438	7	3255
tm	825	13	5132
son	891	4	6368

Table 6.1: The runtime, density of states and number of nodes used for the different radial mapping schemes that are described in the text.

^{a)}: density of states, averaged over 23 states

- infinite elements: from theory point best conditions but show chaotic behaviour due to almost-degeneracy in analytical subspace No algorithmic procedure known to find best parameters.

Results in the non-intuitive conclusion that less accuracy leads to better results.

6.2 Numerical Benchmarks and Stability Tests

6.2.1 Mesh-Construction and Quality

In section 5.2.1 several parameters for the setup of the grid were discussed whose numerical properties are compared and evaluated in this section. Here, three different schemes for distributing the concentric spheres are presented for the Lithium atom, each with a maximum radius $r_{\max} = 7$ bohr and $N = 20$ spheres. In the scheme denoted in Table 6.1 and Figure 6.8 (left) as “const”, the spheres are placed according to eq. (5.13) with $N_i = 74$ points on each sphere. The scheme denoted as tm also uses eq. (5.13) for the size of respective spheres but adapts the number of points per sphere according to (5.14). The last scheme tested here uses the radial mapping suggested by Son and Chu [118] (5.12) and the number of points per sphere (5.15). The parameters for the radial mapping are chosen as $l = 1.8$ and $p = 2.6$ and for the distribution of points on the spheres the Lebedev-scheme [182] is used, respectively. Some characteristic properties of the respective results are shown in Table 6.1. The runtime given in this table is only a rough estimation but seem to scale directly proportional to the number of nodes. Seemingly the radial mapping scheme (5.13) in combination with the angular density (5.14) seems to be advantageous compared to the others even though it should be noted that this may be different for other parameters and that the density of states in these calculations is not uniform so that an average over more or fewer states can influence the results qualitatively. However, the results may be very sensitive with respect to the change of parameters such as box-size and the parameter l , respectively. Moreover, during the creation of tetrahedra from the given point-sets a quality-check is done by the respective library [243] which adds or removes points to ensure well-shaped tetrahedra which may, however, alter the distributions considerably. These corrections of the point-set may be also responsible for the very similar distribution of the properties of the different tetrahedra. In Figure 6.8 (left), the distribution of the ratio of the longest edge to the height of the smallest side is shown. Here no significant differences between the schemes under investigation can be seen.

The angular distribution of points seems to be only of minor importance. As shown in the Figures 6.8 and A.1 in supplement, the statistics are very similar and also the obtained

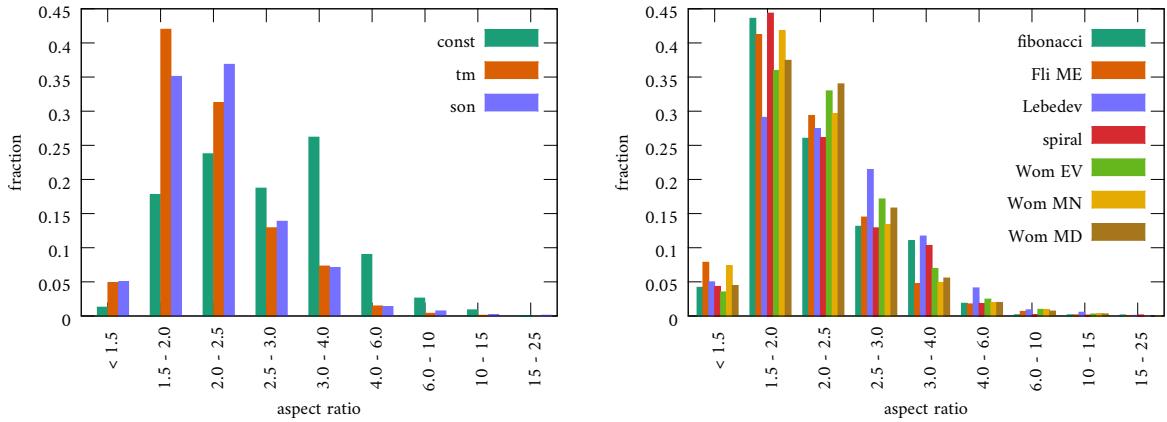


Figure 6.8: Distribution of aspect ratio (longest edge length divided by the smallest side height). Be aware that the ranges of the different bins differ.

density of states is very comparable. However, the angular distribution can play a larger role when considering non-spherical systems. In this work unless otherwise noted, the Lebedev scheme is used which provided the highest density of states (DOS) in this test. The impression of very similar properties of the meshes generated by different schemes is also supported by the statistics of further parameters of the tetrahedra, see Figure A.1. Concluding one can say that the procedures studied here yield meshes with similar quality.

6.2.2 Numerical Convergence

In the FEM scheme used to compute the FEF, several parameters governing numerical and physical characteristics are used such as box-size, target energy and subspace used for solving the eigensystem.

The size of the Krylov-subspace does not play a role for the quality of the solution as shown in Figure 6.9 for the symmetric formulation with a power $p = \frac{1}{2}$ of the damping function D .

Such a good behaviour can, however, only be observed for the symmetric case because in case of the non-hermitian formulation the ordering of the eigenvalues can not be done unambiguously.

6.3 atomic Lithium

As the smallest system that has multiple electrons in its anionic state as well, Lithium is a good test object that has theoretical as well as experimental reference data available, [68, 69, 265] even though its appearance in a work on ‘complex molecules’ might surprise. However, its photoelectron spectrum consists, except

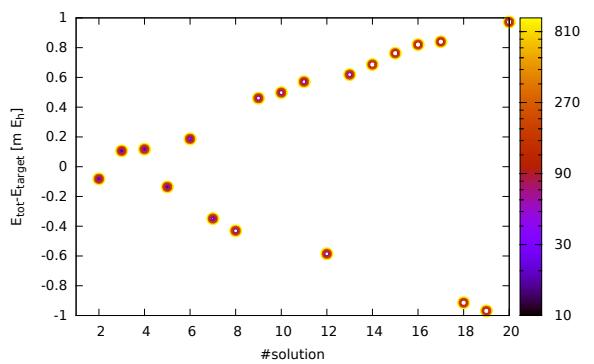


Figure 6.9: The energies of the 20 states that fit the target energy best, depending on the size of the Krylov-suspace, indicated by the colour.

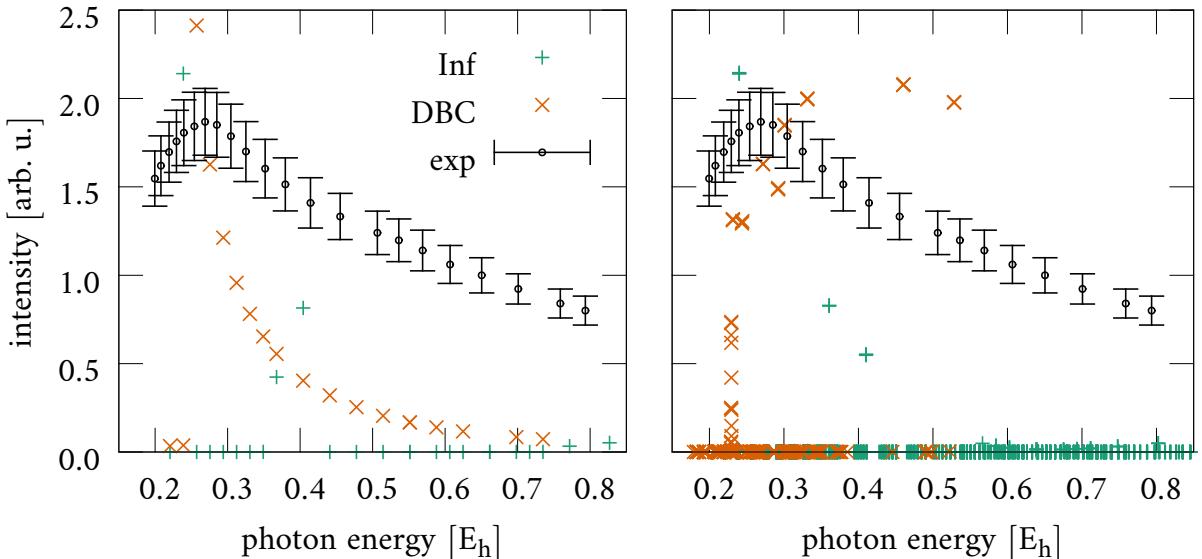


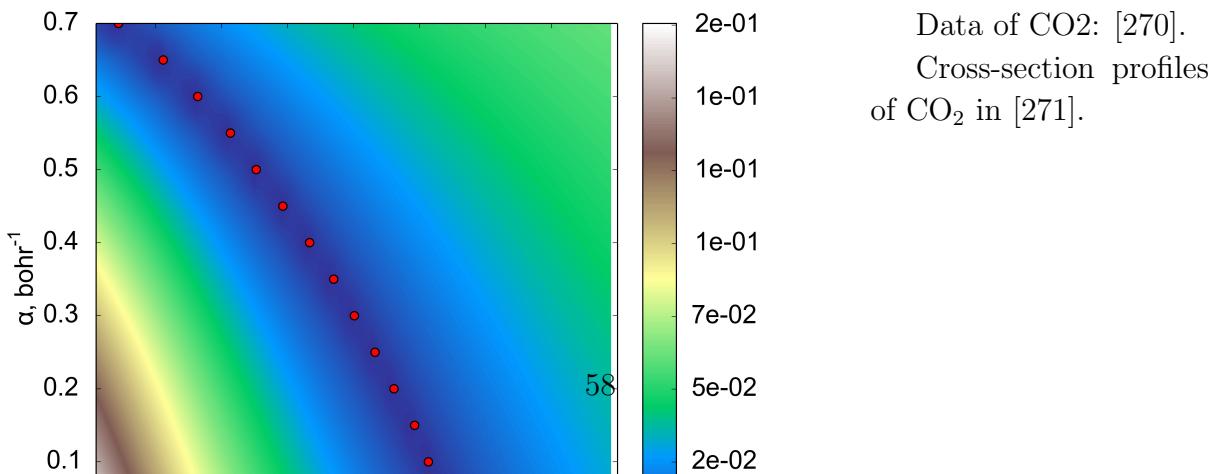
Figure 6.10: The photoelectron cross section of the Lithium atom as a function of the photon energy obtained with Dirichlet BCs (DBC) and with infinite elements (inf), compared to experiment [266]. In the left panel, the intensity is the sum over intensities for 80 FEFs respectively, in the right panel the intensities of single functions are shown.

for a single valence peak, only of the core electron spectrum. In this region the estimated binding energies are often not that good as those obtained for valence orbitals and, moreover, two out of four main peaks of the spectrum arise due to dipole-transitions in the bound part and thus are not accounted for due to the neglect of the conjugated Dyson orbital in eq. (2.14) [65].

However, the well-separated single valence peak allows a more detailed study of the photon energy dependence of the intensity of a single peak as shown in Figure 6.10 where experimental values are compared with several theoretical models. Since the protocol developed in this work does not provide absolute cross sections, the results obtained here are scaled to fit the reference data best. Moreover, it was shown in chapter 6.1.2 that the size of the FEM-region plays an important role for the nature of the obtained solutions but no conclusive scheme for a reasonable choice for the radius has been given so far.

6.4 Triatomic Linear Molecules

There are several studies on CO₂ [267–270], CS₂ [269, 270], COS [269, 270] and N₂O [270] CS₂ is known to have strong correlation effects [74]



6.5 water

The PES and threshold PES, where the kinetic energy of the photoelectron is kept constant instead of the energy of the photon, of water is experimentally well studied for different photon energies. As example, in Ref. [272] the PES of water and several TPES of water and heavy water are investigated with high resolution.

Similar high accuracy is achieved in Ref. [273]

where the PES of H_2O^+ and D_2O^+ are studied with a HeI source, radiating at 537 Angs. Further PES are available at higher photon energies: In [274], photons at energies of 1200 eV are used. A further study of Winter *et. al.* measured spectra at 60, 75 80, 100 and 120 eV in gas and liquid phase [1].

These studies are of interest here since they yield a variety of different test-cases on a single system that can be used to prove the method being used to be valid.

7 | Resumee

- is it worth the effort? - What energy-range is achievable? - Which effects are still missing?

- How to proceed with it?

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A | Appendix

A.1 Additional Data

To illustrate the very similar statistics obtained by the different mapping schemes described and discussed in section 6.2.1, in Figure A.1 further properties are shown, each normalised for better comparability. In the figures, the radius-edge ratio denotes the ratio of the radius of circumsphere divided by the sortest edge length.

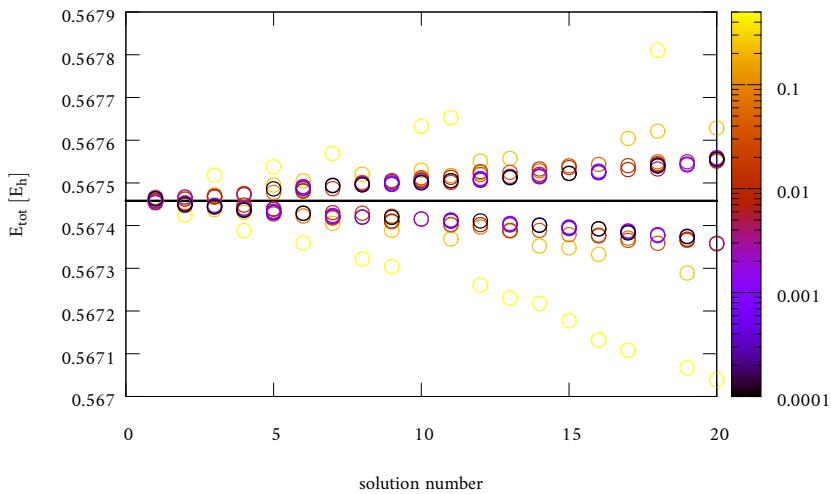


Figure A.2: The eigen energies of the first 20 solutions (circles) for different powers p of the damping function $D(r)$ which determines the colours. The spectra do not change significantly for $p < \frac{1}{8}$.

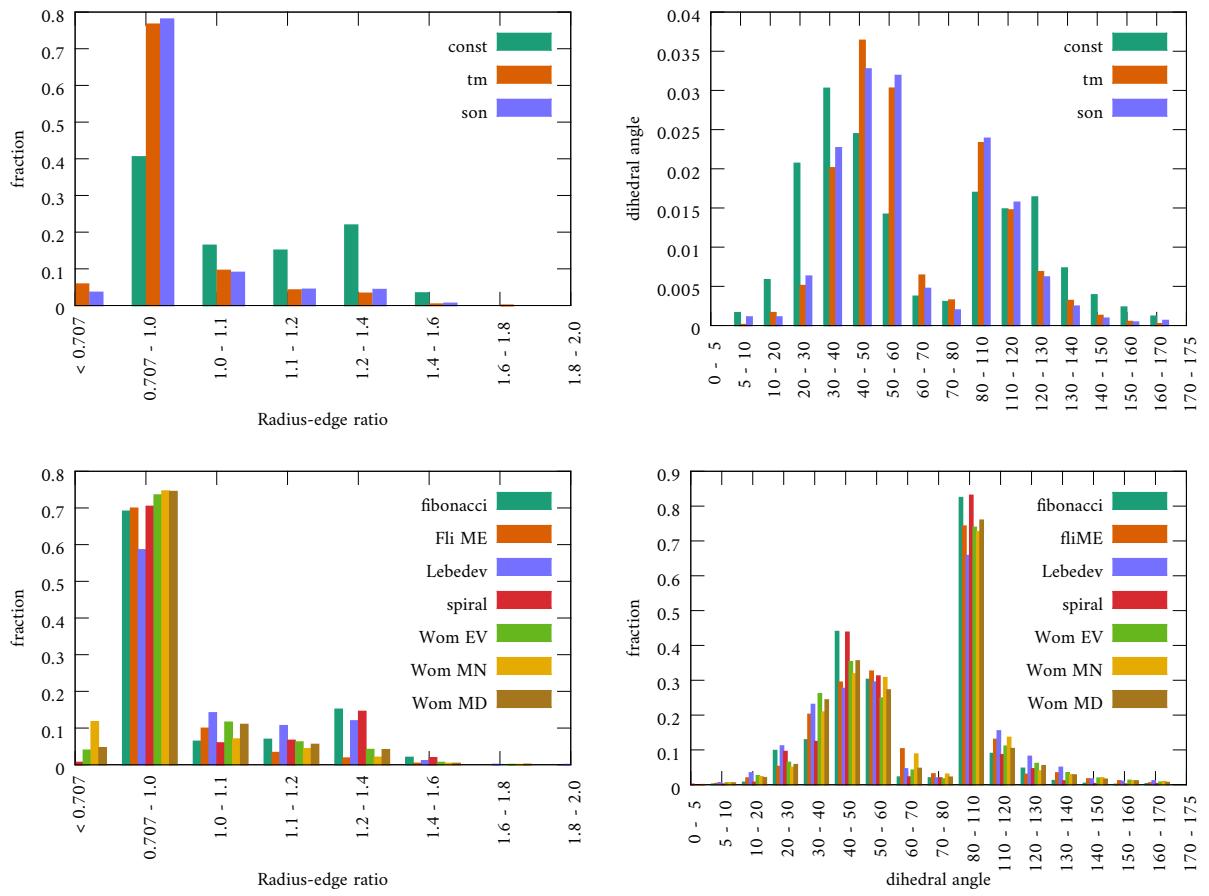


Figure A.1: Distribution of the ratio of radius and edge (left) and the dihedral angles (right) for the different radial schemes (top) and angular distributions (bottom) described in section 6.2.1.