



UNIVERSITY of
TASMANIA

KYA322

Atomic physics

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Identical particles

McIntyre Ch. 13 // Foot Ch. 3

Indistinguishable particles leads to strange behaviour: Bose-Einstein condensation of Erbium



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Learning outcomes

Week 3, lecture 1

**McIntyre §13.1 – 8.5 // Foot §3.2-3:
Identical particles**

- The symmetrisation principle
 - Bosons, fermions, and their wavefunctions
- Two-particle wavefunctions
 - The ground state wavefunction
 - What is the exchange interaction
 - What are the measurable consequences of indistinguishable particles?
- Beyond hydrogen
 - How can we understand the periodic table

Same same but different

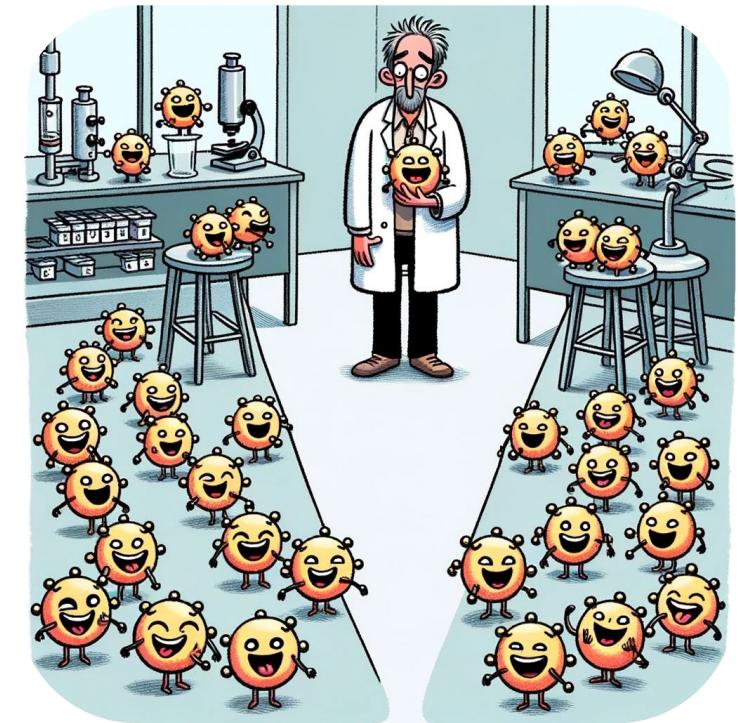
To study multielectron atoms, we need to reckon with fundamental particles being *identical*, that is, *indistinguishable*

Consider a two-electron system, and the states

$$|10\rangle = 1/\sqrt{2}[|+ -\rangle + |-\ +\rangle]$$

$$|00\rangle = 1/\sqrt{2}[|+ -\rangle - |-\ +\rangle]$$

Both states represent a state with one electron being spin up and another being spin down, but we have just seen that these states are distinct, with the states having total angular momentum of 1 and 0 respectively. What are the consequences of this?





Symmetrisation principle

To probe at the origin of particle spin and their associated exchange symmetry requires a study of quantum field theory, so we simply assert the *spin-statistics theorem*, which states:

Bosons (particles with integer spin) obey *Bose-Einstein statistics*, meaning their wavefunction is symmetric under particle exchange. This allows multiple bosons to occupy the same quantum state.

Fermions (particles with half-integer spin) obey *Fermi-Dirac statistics*, meaning their wavefunction is antisymmetric under particle exchange. This leads to the Pauli exclusion principle, which states that no two fermions can occupy the same quantum state simultaneously.

The symmetrisation principle states that the quantum state vector of a system of two (or more) identical particles must be either symmetric or antisymmetric with respect to exchange of the two (or any two) particles



Two particles in 1D

For a single particle, we have

$$H_{single} = \frac{p^2}{2m} + V(x)$$

and

$$H_{single}\varphi_n(x) = E_n\varphi_n(x)$$

For two particles, we have

$$H = \frac{p_1^2}{2m} + V(x_1) + \frac{p_2^2}{2m} + V(x_2)$$

and

$$H\psi(x_1, x_2) = E\psi(x_1, x_2)$$

$\psi(x_1, x_2)$ is the *two-particle* wavefunction, which has the normalisation condition

$$\iint |\psi(x_1, x_2)|^2 dx_1 dx_2 = 1$$

In the non-interacting case, the solution to the two-particle system is $\varphi_{n_a}(x_1)\varphi_{n_b}(x_2)$ with particles 1 and 2 in energy states n_a and n_b respectively, which gives the total energy $E_{n_a} + E_{n_b}$



Symmetrisation postulate

For the ground state

*Note that we are mixing wave functions and state vector notation, but hopefully it is clear



The complete state vector for two spin-zero bosons is comprised of the state $|\psi_{space}^S\rangle$ and only possible spin state $|SM\rangle = |00\rangle$:

$$|\psi_{11}^{SS}\rangle \equiv \psi_{11}^S(x_1, x_2)|00\rangle = \varphi_1(x_1)\varphi_1(x_2)|00\rangle$$

For two spin-1/2 fermions, we have the usual basis states $|11\rangle$, $|10\rangle$, $|1, -1\rangle$, and $|00\rangle$; however, only the $|00\rangle$ state can satisfy the symmetrisation postulate, so

$$|\psi_{11}^{SA}\rangle \equiv \psi_{11}^S(x_1, x_2)|00\rangle = \varphi_1(x_1)\varphi_1(x_2)|00\rangle$$

For the bosonic case, state $|00\rangle$ is the same as the uncoupled state $|s_1 s_2 m_1 m_2\rangle = |0000\rangle$ which is symmetric, whereas in the fermionic case, state $|00\rangle$ is the same as the uncoupled state $|s_1 s_2 SM\rangle = \left| \begin{smallmatrix} 1 & 1 \\ 2 & 2 \end{smallmatrix} 00 \right\rangle$ which is antisymmetric.



Symmetrisation excitation

For the first excited state

For the spin-0 boson case, symmetric spin state \Rightarrow symmetric spatial wave function

$$|\psi_{12}^{SS}\rangle \equiv \psi_{12}^S(x_1, x_2)|00\rangle = 1/\sqrt{2}(\varphi_1(x_1)\varphi_2(x_2) + \varphi_1(x_2)\varphi_2(x_1))|00\rangle$$

For the spin-1/2 fermion case:

- antisymmetric spin state $|00\rangle \Rightarrow$ symmetric spatial wave function

$$|\psi_{12}^{SA}\rangle \equiv \psi_{12}^S(x_1, x_2)|00\rangle = 1/\sqrt{2}(\varphi_1(x_1)\varphi_2(x_2) + \varphi_1(x_2)\varphi_2(x_1))|00\rangle$$

- Symmetric spin states $|11\rangle, |10\rangle, |1, -1\rangle$

$$|\psi_{12}^{AS}\rangle \equiv \psi_{12}^A(x_1, x_2)|1M\rangle = 1/\sqrt{2}(\varphi_1(x_1)\varphi_2(x_2) - \varphi_1(x_2)\varphi_2(x_1))|1M\rangle$$

where $M = 1, 0, -1$

This means the first excited state is degenerate for the fermionic case, but is non-degenerate for the bosonic case



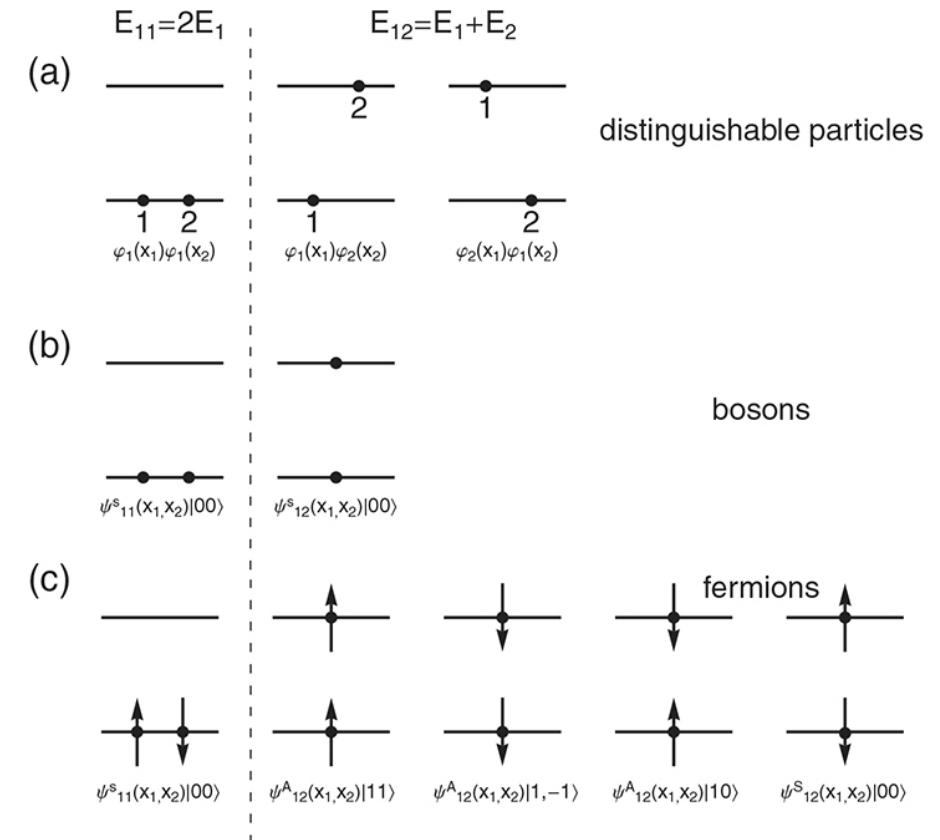
Mapping the states

The ground state is identical for the three cases of

- Distinguishable particles
- Identical bosons
- Identical fermions

The excited state is more complicated, with

- One state the same for the case of bosons and the singlet fermions
- Distinct states for the triplet state fermions



A schematic of the lowest energy levels for a two-particle system

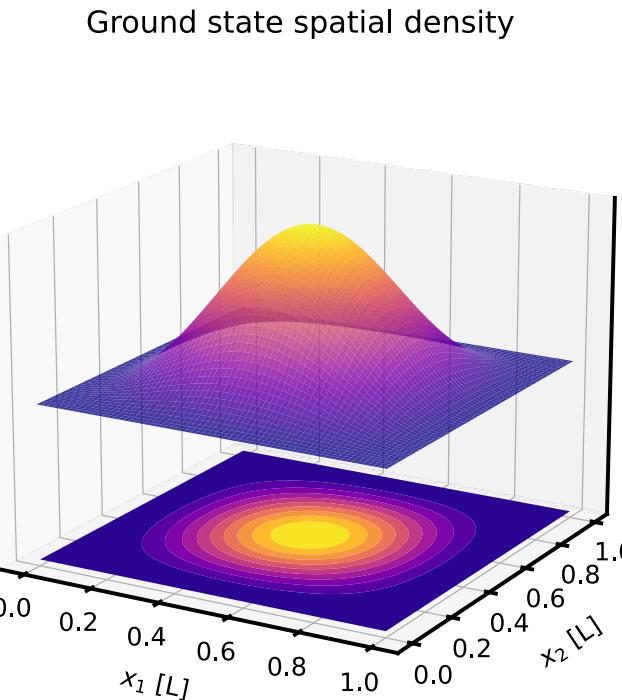


The spatial wave function

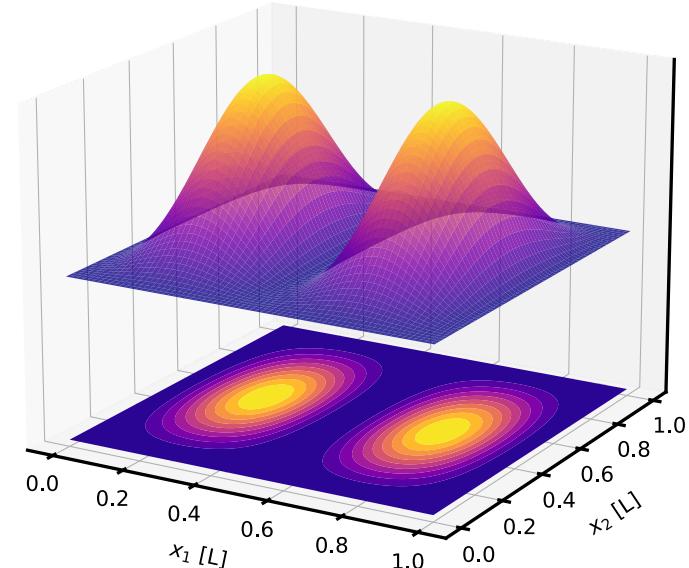
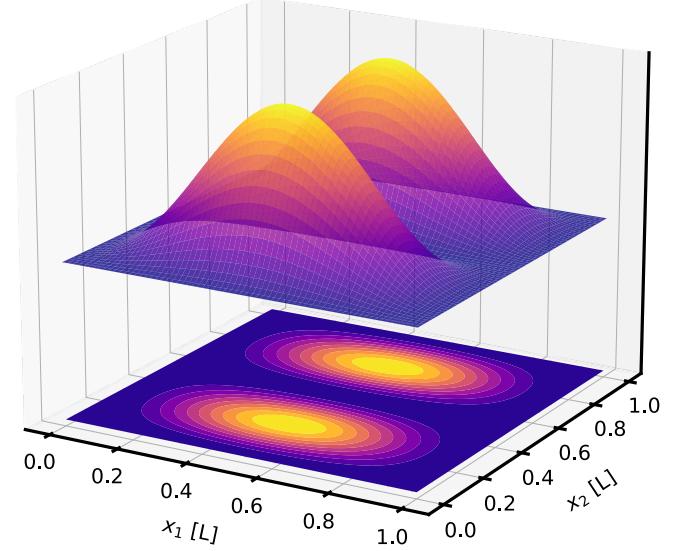
For visualisation purposes, let us consider the infinite square well. Then we know

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

meaning we can construct the ground and excited state spatial wavefunctions, subject to symmetrisation



The ground state is the same for distinct particles, identical bosons, and identical fermions



For distinguishable particles, the first excited state depends on the type of particle (spin $\frac{1}{2}$ shown)



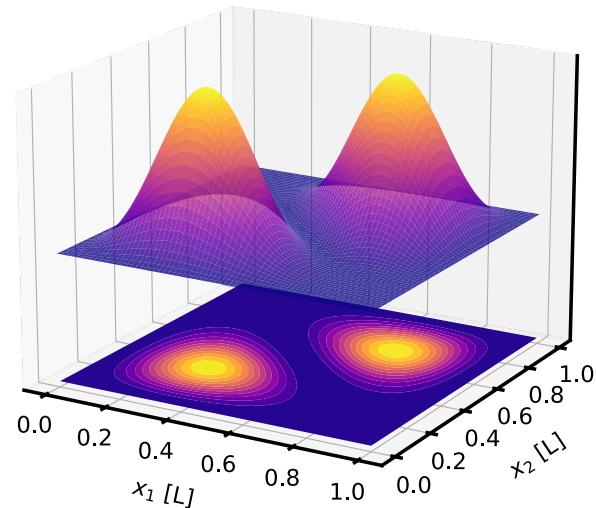
Excited states

In the case of identical bosons, there is only one state: the symmetric wave function $\psi_{12}^S(x_1, x_2)$

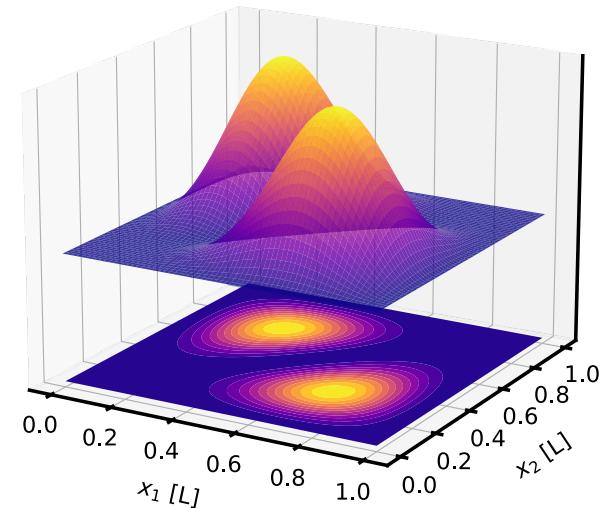
In the fermionic case, the excited state can either be symmetric or antisymmetric, depending on the spin state

Note the probability density of the asymmetric state $\psi_{12}^A(x_1, x_2)$ is zero along the line $x_1 = x_2$, that is two fermions cannot be in the same location \Rightarrow Pauli exclusion!

Symmetric spatial density

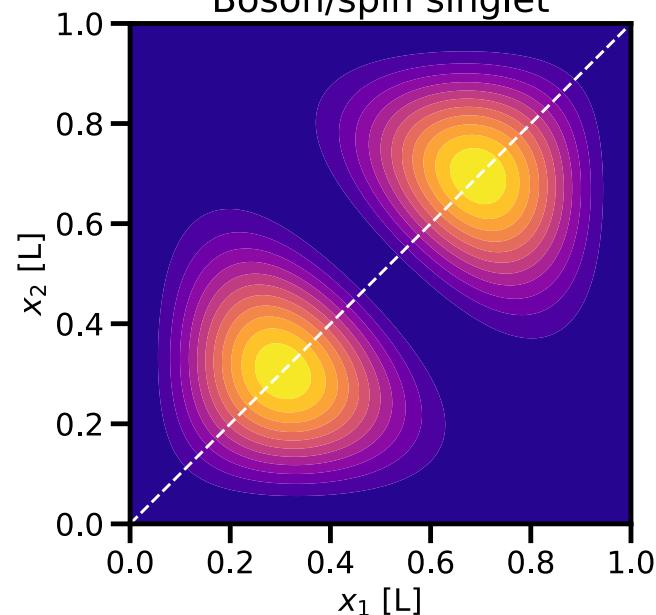


Antisymmetric spatial density

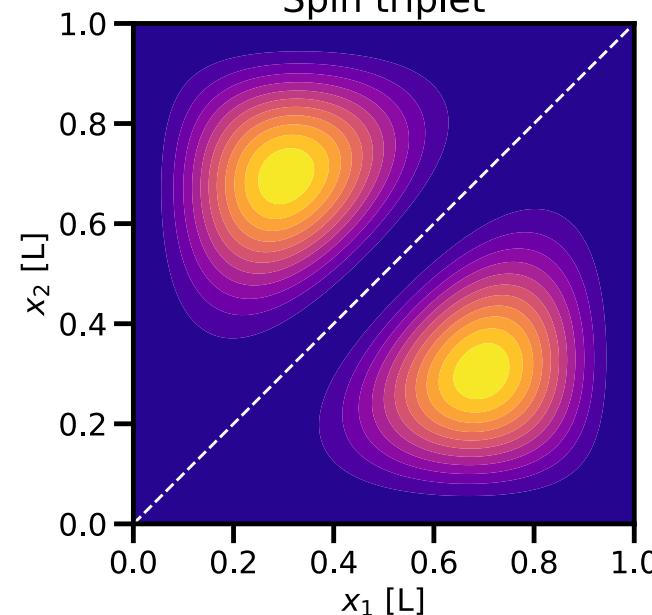


Two-particle probability densities

Boson/spin singlet



Spin triplet



These states show “attraction” and “repulsion”



The exchange interaction

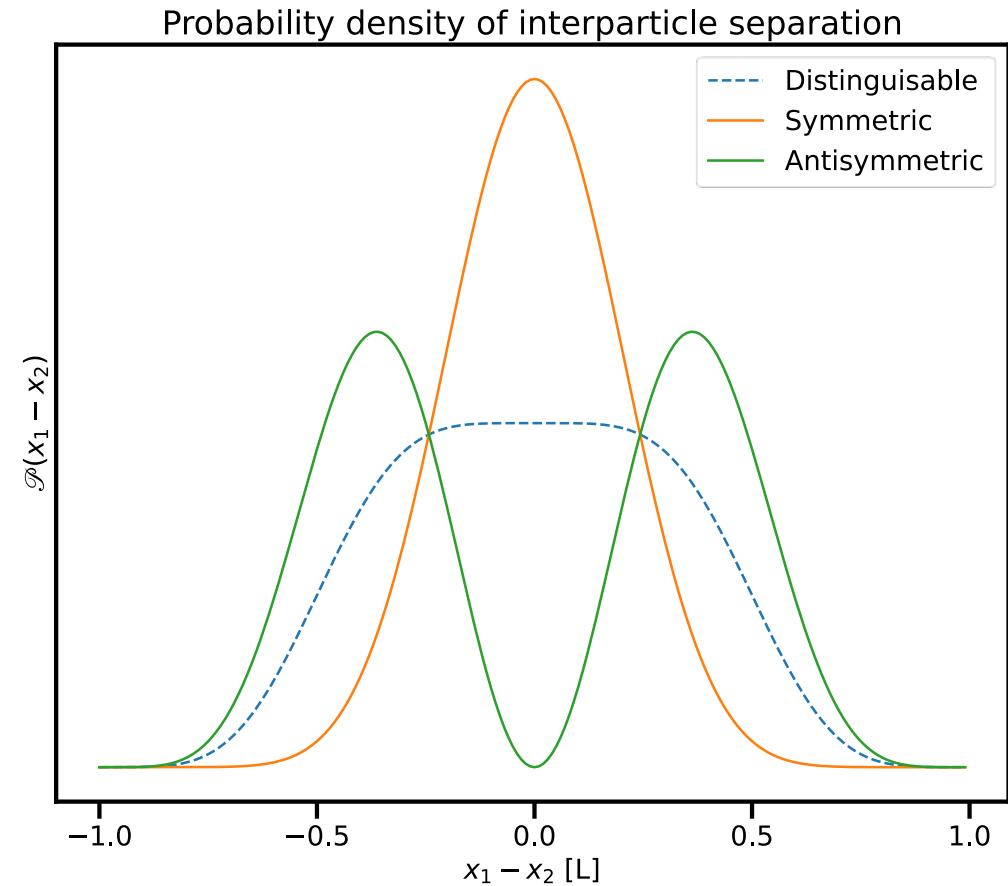
To this point, our particles are **non-interacting**, so what is this apparent attractive/repulsive interaction?

Symmetrisation imposes this behaviour!

Tutorial:

The exchange interaction can be quantified by examining the quantity $\langle (x_1 - x_2)^2 \rangle$

The consequences of symmetrisation become more pronounced with an increased number of particles...



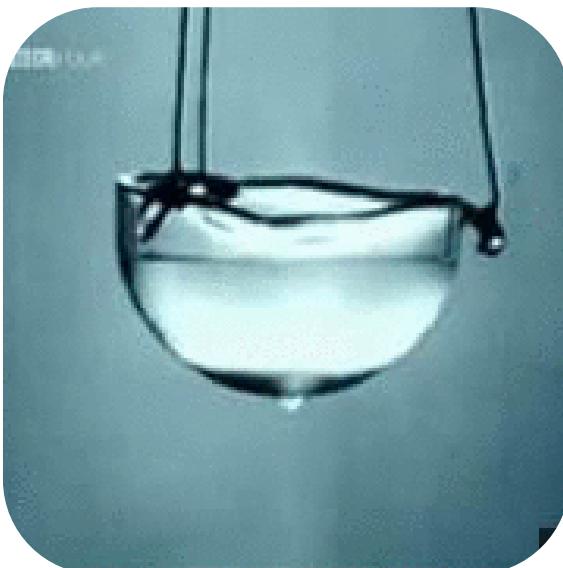
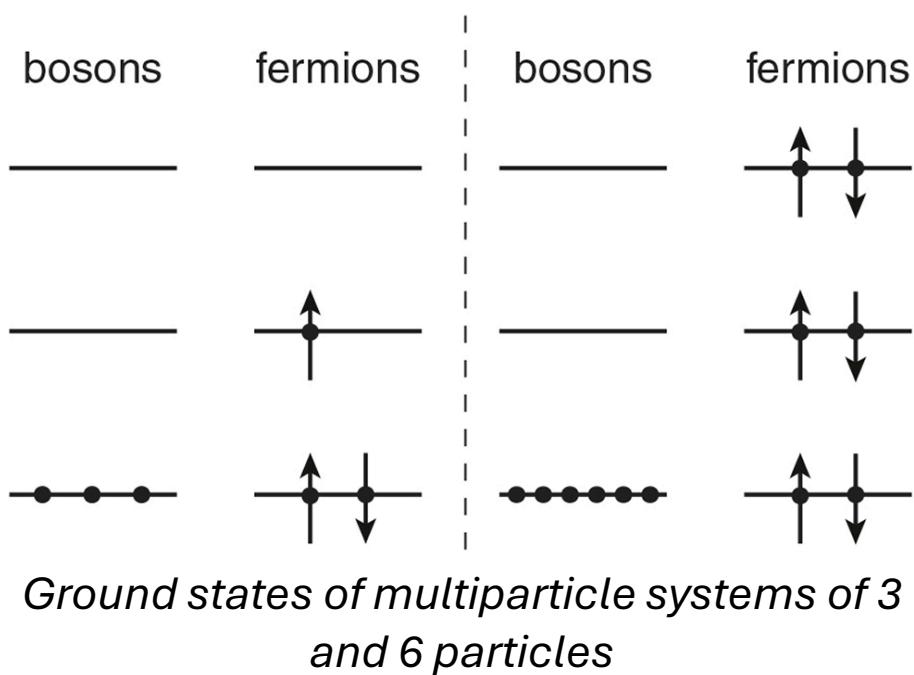
Probability density for the first excited state for a system of two particles in an infinite square well



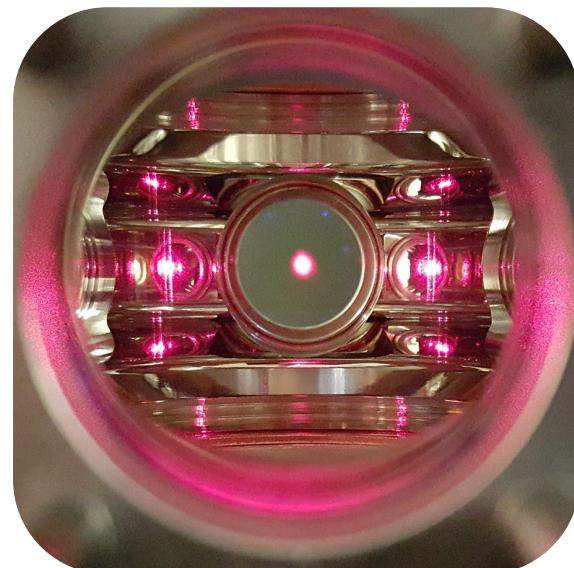
Cool consequences

With increasing particle number, fermions and bosons behave differently.

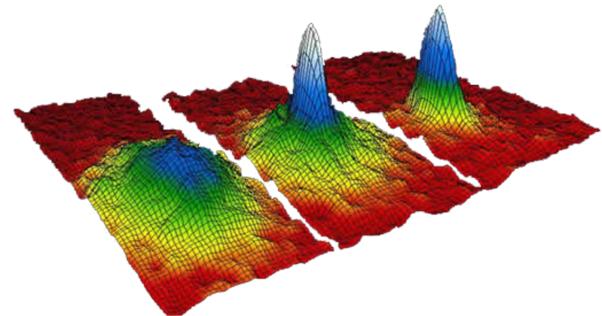
For example, attraction between bosons at high density leads to a macroscopic wavefunction, a Bose-Einstein Condensate (BEC)



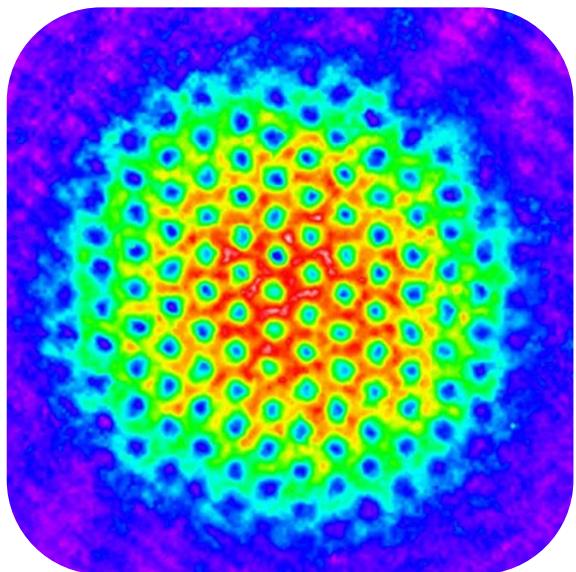
Helium becomes a superfluid at 2.18 K



Ultracold lithium atoms in a magneto-optical trap



The first BEC in a dilute atomic gas



A BEC of rubidium atoms acts as a superfluid

Interacting particles

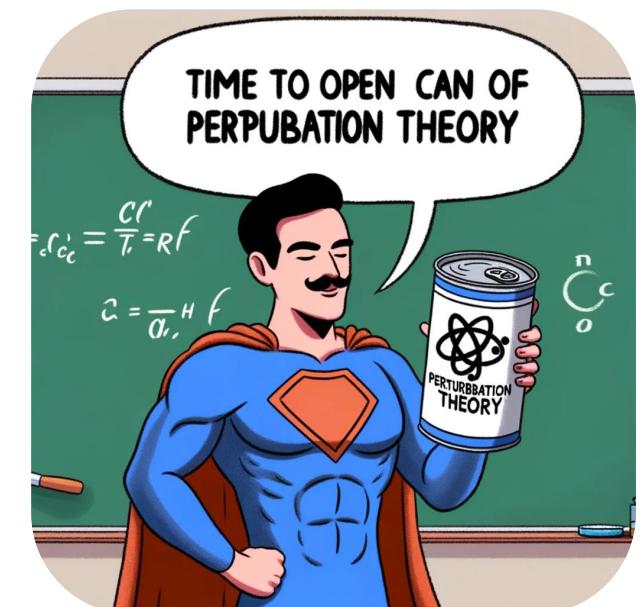
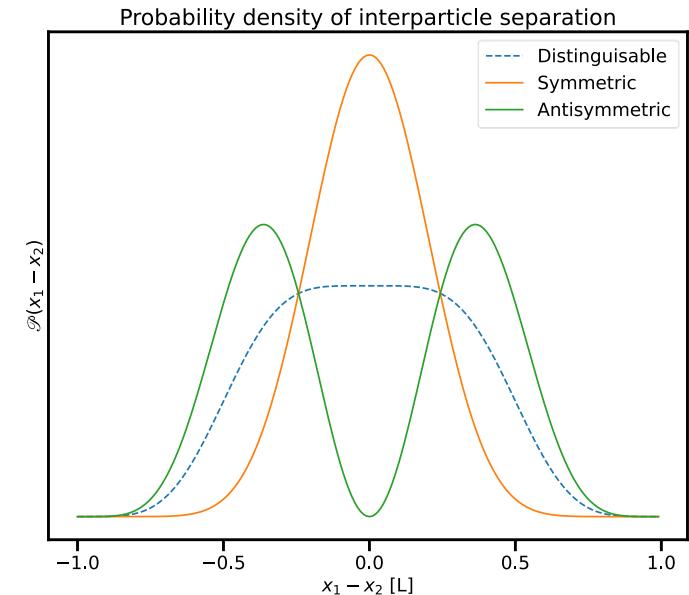
Symmetrisation leads to an attraction/repulsion of identical particles *without* interactions. With interactions, this leads to energy shifts which depend on the symmetry of the states.

Once again, we shall look at identical particles in an infinite square well to build our understanding of the physics

Assume an interaction potential between the particles V_{int} which depends only on the separation, i.e.

$$H' = V_{int}(x_1 - x_2)$$

and that the associated energy is small.



The direct integral

The first-order energy correction is

$$E^{(1)} = \langle \psi^{(0)} | H' | \psi^{(0)} \rangle$$

We assume that the interaction is spin independent:

$$\begin{aligned} \langle \psi^{(0)} | H' | \psi^{(0)} \rangle &= \langle \psi_{\text{spatial}} | \langle \psi_{\text{spin}} | H' | \psi_{\text{spin}} \rangle | \psi_{\text{spatial}} \rangle \\ &= \langle \psi_{\text{spatial}} | H' | \psi_{\text{spatial}} \rangle \end{aligned}$$

For identical spin-0 bosons, the ground state is

$$|\psi_{11}^{ss}\rangle = \psi_{11}^S(x_1, x_2)|00\rangle = \varphi_1(x_1)\varphi_1(x_2)|00\rangle$$

which gives

$$\begin{aligned} E_{11}^{(1)} &= \langle \psi_{11}^S | H' | \psi_{11}^S \rangle \langle 00 | 00 \rangle \\ &= \langle \psi_{11}^S | V_{int}(x_1 - x_2) | \psi_{11}^S \rangle \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varphi_1^*(x_1)\varphi_1^*(x_2) V_{int}(x_1 - x_2) \varphi_1(x_1)\varphi_1(x_2) dx_1 dx_2 \equiv J_{11} \end{aligned}$$

where J_{nm} is the *direct integral*

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\varphi_n(x_1)|^2 V_{int}(x_1 - x_2) |\varphi_n(x_2)|^2 dx_1 dx_2$$

The *direct integral* quantifies the interaction energy between the probability densities $\mathcal{P}_n(x_1) = |\varphi_n(x_1)|^2$ and $\mathcal{P}_m(x_2) = |\varphi_m(x_2)|^2$



The exchange integral

The perturbed ground-state energy is then

$$E_{11} = 2E_1^{(0)} + J_{11}$$

The result is the same for spin-1/2 fermions.

The first excited state for identical bosons is

$$|\psi_{12}^{SS}\rangle \equiv \psi_{12}^S(x_1, x_2)|00\rangle = 1/\sqrt{2}(\varphi_1(x_1)\varphi_2(x_2) + \varphi_1(x_2)\varphi_2(x_1))|00\rangle$$

and so the first-order perturbation is

$$\begin{aligned} E_{12}^{(1)} &= \langle\psi_{12}^{SS}|H'|\psi_{12}^{SS}\rangle\langle00|00\rangle \\ &= J_{12} + K_{12} \end{aligned}$$

where K_{nm} is the *exchange integral*

$$K_{nm} \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varphi_n^*(x_1)\varphi_m^*(x_2) V_{int}(x_1 - x_2) \varphi_n(x_2)\varphi_m(x_1) dx_1 dx_2$$

The energy of first excited state of the system is then

$$E_{12} = E_1^{(0)} + E_2^{(0)} + J_{12} + K_{12}$$

The *exchange integral* quantifies the interaction between the particles' wavefunction when they “exchange” positions, arising from the symmetrisation requirements. It provides a measure of how one particle influences the other due to their indistinguishability



Fermionic excited state energies

For identical spin-1/2 fermions, the excited state spatial wavefunction can either be symmetric or antisymmetric, depending on the spin state.

As spin does not alter the perturbation calculation \Rightarrow

$E_{12}^{(1)} = J_{12} + K_{12}$ for the singlet spin state (i.e. the same as the bosonic case)

For the triplet spin state, the spatial wavefunction is antisymmetric:

$$\begin{aligned} E_{12}^{(1)} &= \langle \psi_{12}^A | H' | \psi_{12}^A \rangle \langle 1M | 1M \rangle \\ &= J_{12} - K_{12} \end{aligned}$$

which when combined with the singlet spin state gives the energy of first excited state

$$E_{12} = E_1^{(0)} + E_2^{(0)} + J_{12} \pm K_{12}$$

Recall that

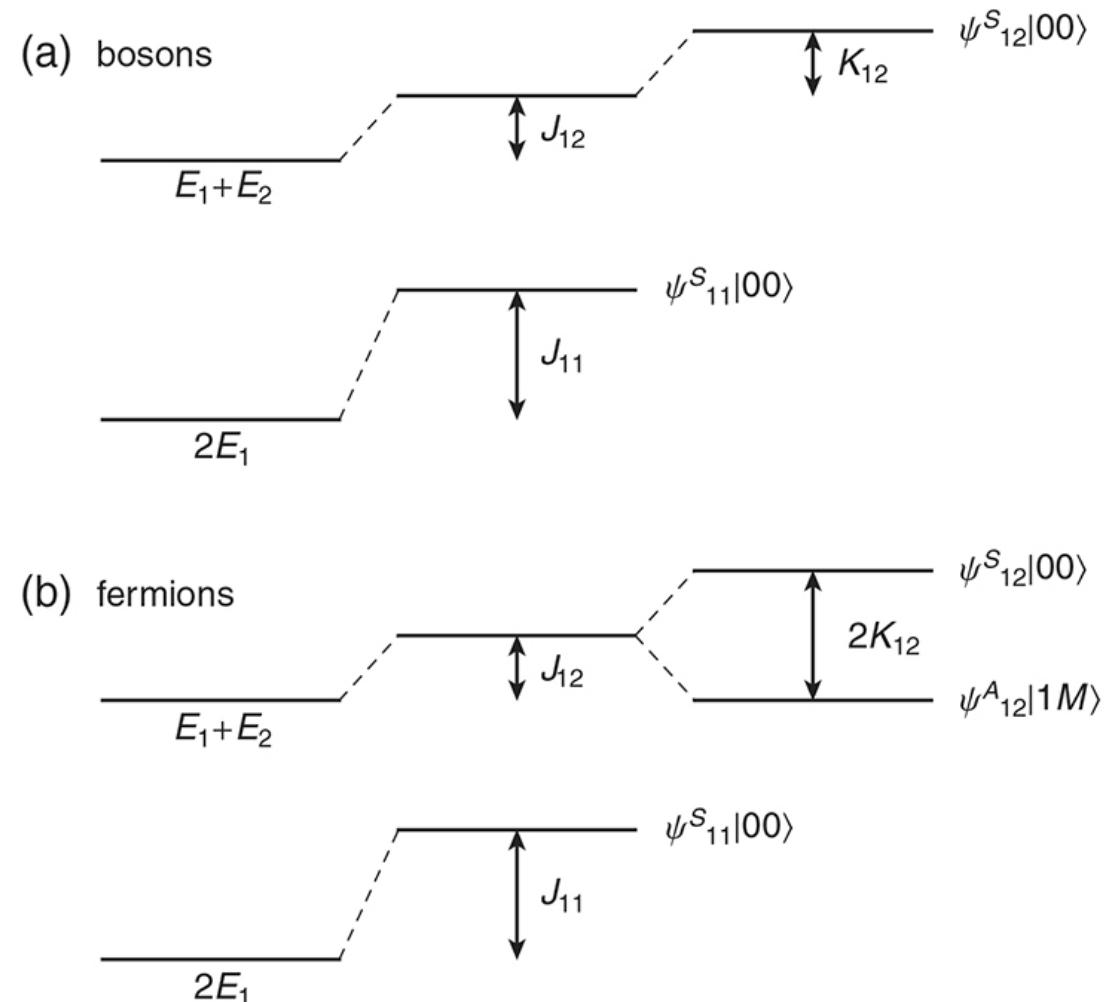
$$\begin{aligned} |\psi_{12}^{AS}\rangle &\equiv \psi_{12}^A(x_1, x_2) |1M\rangle \\ &= \frac{1}{\sqrt{2}} (\varphi_1(x_1)\varphi_2(x_2) - \varphi_1(x_2)\varphi_2(x_1)) |1M\rangle \end{aligned}$$

where $M = 1, 0, -1$

Indistinguishable energy shifts

Things of note:

- Direct integral raises all energy states, a result of the Coulomb interaction (repulsion between particles)
- Exchange integral is more complex:
 - “Attraction” from symmetrisation increases Coulomb repulsion
 - “Repulsion” decreases the repulsion
- Energy depends on spin
 - No spin in the Hamiltonian!



Energies and state vectors for the ground and first excited states of identical particles in a square well

He(lium)re we come

Symmetrisation and the Pauli exclusion principle are fundamental to understanding atomic structure

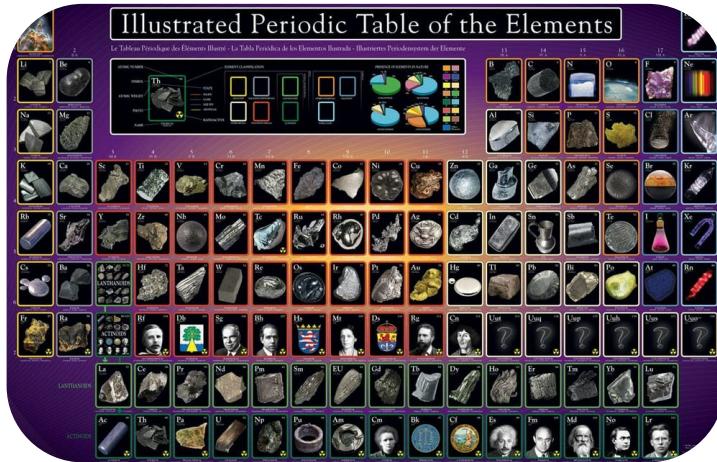
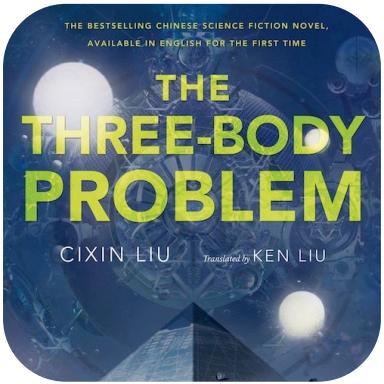
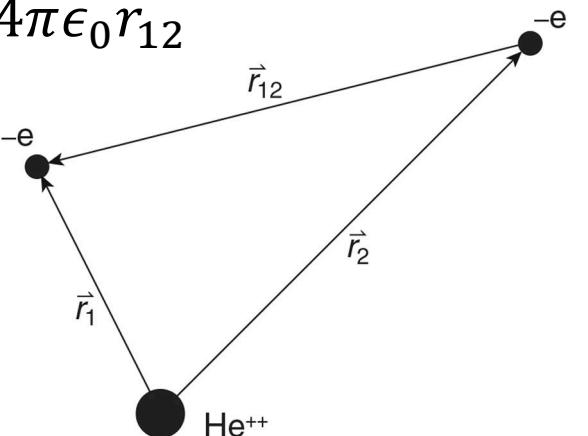
The simplest system beyond hydrogen is helium, which provides a tractable example of a three-body problem

The Hamiltonian is similar to that of hydrogen, but includes a correction for the doubly charged nucleus, and the interaction between electrons:

$$H = \left(\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} \right) + \left(\frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where r_{12} is the separation of the electrons as shown. We write $H = H_0 + H'$, where

$$H' = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$



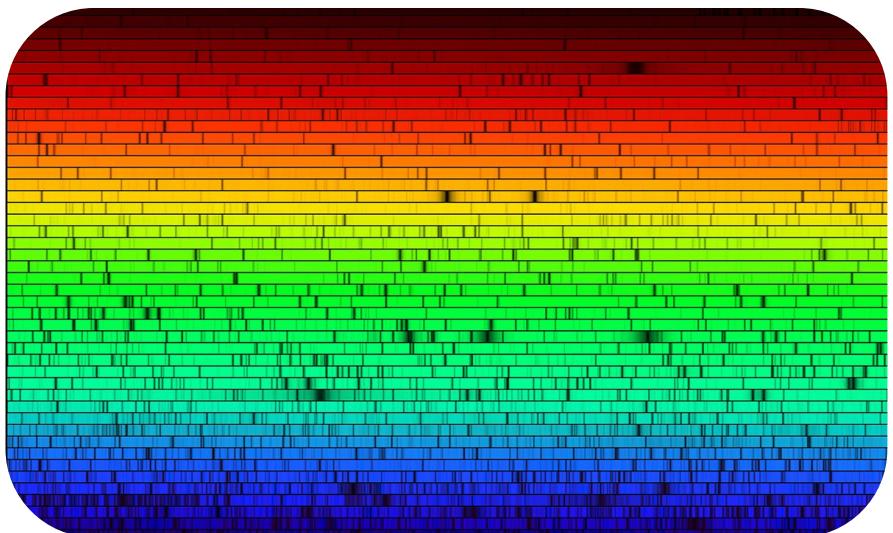
The Pauli exclusion principle is fundamental to understanding the periodic table



A helium discharge lamp. We'd love to predict that spectrum!

Discussion:

Provide an estimate of the (double) ionisation energy of Helium



The solar spectrum

The spectra of helium

The helium wavefunction

Given the groundwork we have put in, we know what will be our helium wavefunction. The eigenstates will have the form

$$|\psi\rangle = |\psi_{\text{spatial}}\rangle |\psi_{\text{spin}}\rangle$$

and overall must be antisymmetric under electron exchange. Individual spatial electronic wavefunctions will be hydrogenic

$$\psi_{\text{spatial}}(\mathbf{r}) = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

and the symmetrised wavefunctions for the two-electron system are

$$\begin{aligned}\psi_{n_a l_a m_a, n_b l_b m_b}^S(\mathbf{r}_1, \mathbf{r}_2) &= 1/\sqrt{2}[\psi_{n_a l_a m_a}(\mathbf{r}_1)\psi_{n_b l_b m_b}(\mathbf{r}_2) + \psi_{n_a l_a m_a}(\mathbf{r}_2)\psi_{n_b l_b m_b}(\mathbf{r}_1)] \\ \psi_{n_a l_a m_a, n_b l_b m_b}^A(\mathbf{r}_1, \mathbf{r}_2) &= 1/\sqrt{2}[\psi_{n_a l_a m_a}(\mathbf{r}_1)\psi_{n_b l_b m_b}(\mathbf{r}_2) - \psi_{n_a l_a m_a}(\mathbf{r}_2)\psi_{n_b l_b m_b}(\mathbf{r}_1)]\end{aligned}$$

The spin component is constructed from two identical spin-1/2 particles, yielding eigenstates $|SM\rangle$ for spin $S = 0, 1$, that is, the triplet and singlet states

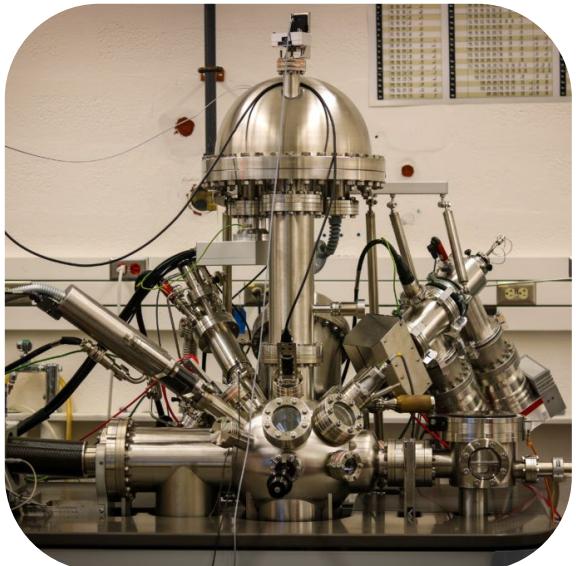
$$\begin{aligned}|11\rangle &= |++\rangle \\ |10\rangle &= 1/\sqrt{2}[|+-\rangle + |-+\rangle] \\ |1, -1\rangle &= |--\rangle \\ |00\rangle &= 1/\sqrt{2}[|+-\rangle - |-+\rangle]\end{aligned}$$

Combining these, the only antisymmetric states are

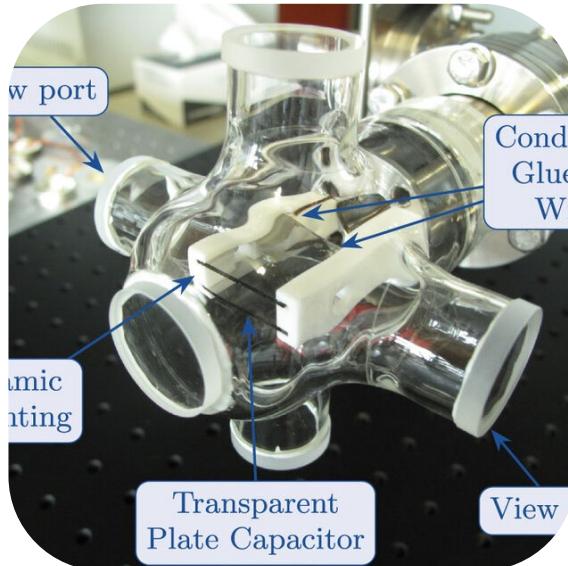
$$\begin{aligned}|\psi_{n_a l_a m_a, n_b l_b m_b}^{SA}\rangle &= |\psi_{n_a l_a m_a, n_b l_b m_b}^S\rangle |00\rangle \\ |\psi_{n_a l_a m_a, n_b l_b m_b}^{AS}\rangle &= |\psi_{n_a l_a m_a, n_b l_b m_b}^S\rangle |1M\rangle\end{aligned}$$

Electrons interact too!

$$H = \left(\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} \right) + \left(\frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$



*X-ray photoionisation
spectroscopy*



Absorption spectroscopy



A channel electron multiplier

Crank the handle

The ground state is nondegenerate, so we calculate the first-order correction to the energy via

$$\begin{aligned} E_{1s,1s}^{(1)} &= \langle \psi_{1s,1s}^{SA} | H' | \psi_{1s,1s}^{SA} \rangle \\ &= \langle \psi_{1s,1s}^S | \frac{e^2}{4\pi\epsilon_0 r_{12}} | \psi_{1s,1s}^S \rangle \langle 00 | 00 \rangle \\ &= \int \int \psi_{100}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned}$$

which is of the form of the previously defined *direct integral*

$$J_{nl,n'l'} = \int \int |\psi_{nlm}(\mathbf{r}_1)|^2 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{nlm}(\mathbf{r}_2)|^2$$

The direct integral is often a bit rough to compute, but this is just an exercise in cranking the handle...

Assignment:

Compute the direct integral for the ground state of helium and show the first-order correction to the energy is

$$E_{1s,1s}^{(1)} = \frac{5}{2} \text{ Ry} = 34 \text{ eV}$$

The ionisation energy is then

$$E_{1s,1s}^{(1)} = -108.8 + 34 = -74.8 \text{ eV}$$

which compares well to the measured value of -79.005154539(25) eV

Discussion:

Why is this energy positive?
What are we still missing?

Excited states of helium

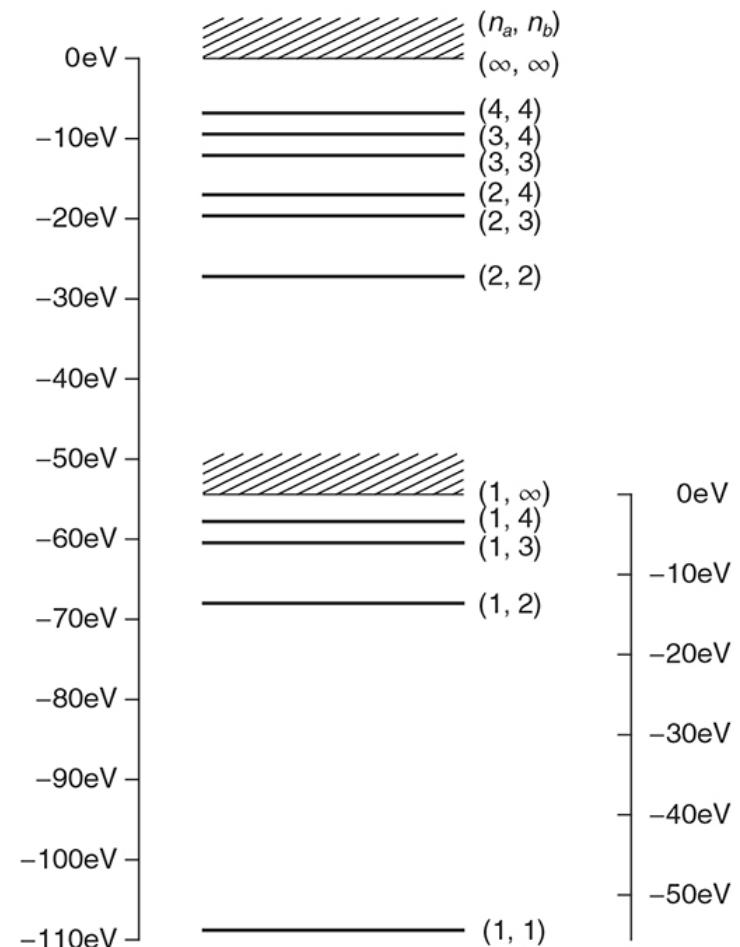
All doubly-excited states lie above the single ionisation threshold. These states are *autoionizing*, being very short-lived and are not of interest to us

The zeroth-order energy of a state with principal quantum numbers n_a and n_b is

$$E_{n_a, n_b}^{(0)} = -\text{Ry} Z^2 \left(\frac{1}{n_a^2} + \frac{1}{n_b^2} \right)$$

We only consider states with $n_a = 1$ and $n_b \neq 1$; however, these are more complicated as:

- The excited electron is in a different spatial state \Rightarrow both symmetric and antisymmetric states allowed
- Hydrogenic states are degenerate in ℓ and m



Zeroth-order energy-level diagram for helium

The first excited state

For $n_a = 1$ and $n_b = 2$:

$$|\psi_{1s,2\ell}^{SA}\rangle = |\psi_{1s,2\ell}^S\rangle |00\rangle = 1/\sqrt{2}[\psi_{100}(\mathbf{r}_1)\psi_{2\ell m}(\mathbf{r}_2) + \psi_{100}(\mathbf{r}_2)\psi_{2\ell m}(\mathbf{r}_1)] |00\rangle$$

$$|\psi_{1s,2\ell}^{AS}\rangle = |\psi_{1s,2\ell}^A\rangle |1M\rangle = 1/\sqrt{2}[\psi_{100}(\mathbf{r}_1)\psi_{2\ell m}(\mathbf{r}_2) - \psi_{100}(\mathbf{r}_2)\psi_{2\ell m}(\mathbf{r}_1)] |1M\rangle$$

For both the symmetric and antisymmetric spatial case, there are four possible states: $2s$ ($\ell = 0, m = 0$) and the three $2p$ states ($\ell = 1, m = 0, \pm 1$). Combined with the spin singlet and triplet states, there are sixteen possible states, all of which are degenerate in the unperturbed system.

To find the first-order correction to the energy, we must apply degenerate perturbation theory to these states.

Fortunately, the perturbation Hamiltonian is diagonal, so we need only compute the elements

$$E_{1s,2\ell}^{(1)} = \langle \psi_{1s,2\ell}^{SA} | H' | \psi_{1s,2\ell}^{SA} \rangle$$

$$E_{1s,2\ell}^{(1)} = \langle \psi_{1s,2\ell}^{AS} | H' | \psi_{1s,2\ell}^{AS} \rangle$$

for the symmetric and antisymmetric spatial states respectively.

Energy splitting of the first excited states

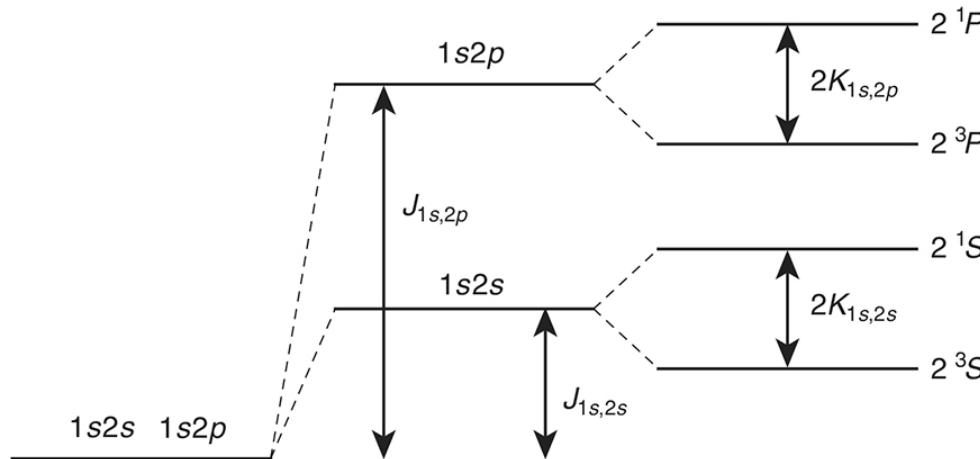
In the same way as we have seen previously, we can express the energy perturbation in terms of *direct* and *exchange* integrals

$$E_{1s,2\ell}^{(1)} = J_{1s,2\ell} \pm K_{1s,2\ell}$$

where the + (−) sign refers to the (anti)symmetric spatial state and corresponding singlet (triplet) spin state, and the generalised exchange integral is

$$K_{n\ell,n'\ell'} = \int \int \psi_{nlm}^*(\mathbf{r}_1) \psi_{n'\ell'm'}^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \psi_{nlm}^*(\mathbf{r}_2) \psi_{n'\ell'm'}^*(\mathbf{r}_1) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

which can be evaluated directly.



Helium ground- and excited-state splitting,
labelled using $n^{2S+1}L$

Singlet ($S = 0$) state is above the triplet ($S = 1$) state, which is common to all excited states of helium

Metastable helium

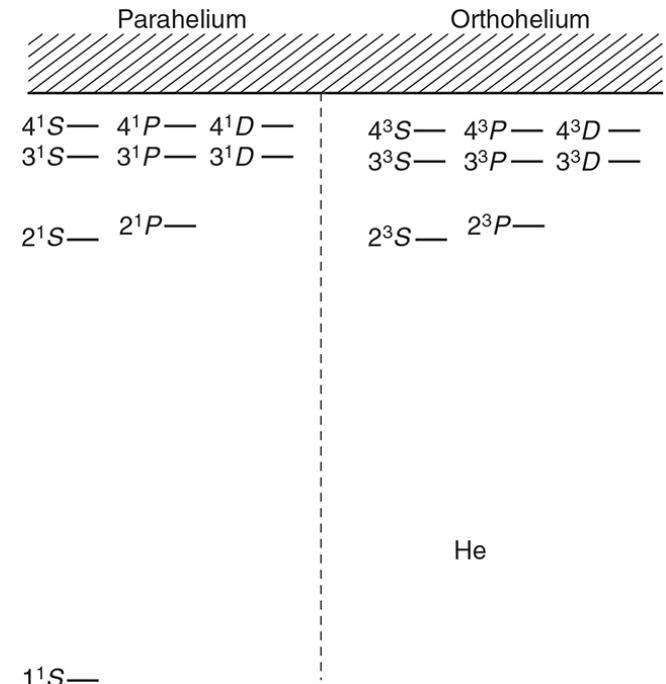
Singlet/triplet ordering can be understood via singlet state (converse for triplet)

- ⇒ Antisymmetric spin state
- ⇒ Symmetric spatial state
- ⇒ “Attraction” between electrons
- ⇒ Increase in Coulomb potential

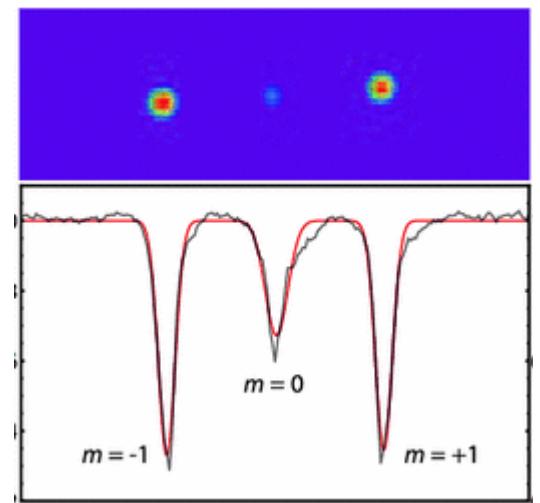
As we shall see, optical transitions between singlet and triplet states are forbidden, which led to the postulate that there were two types of helium: $S = 0$ and $S = 1$

In the case of $S = 1$: the “ground” state is 2^3S , that is, a state with $n_b \neq 0$!

This state allows for the production of *metastable* helium (lifetime ≈ 8000 s)

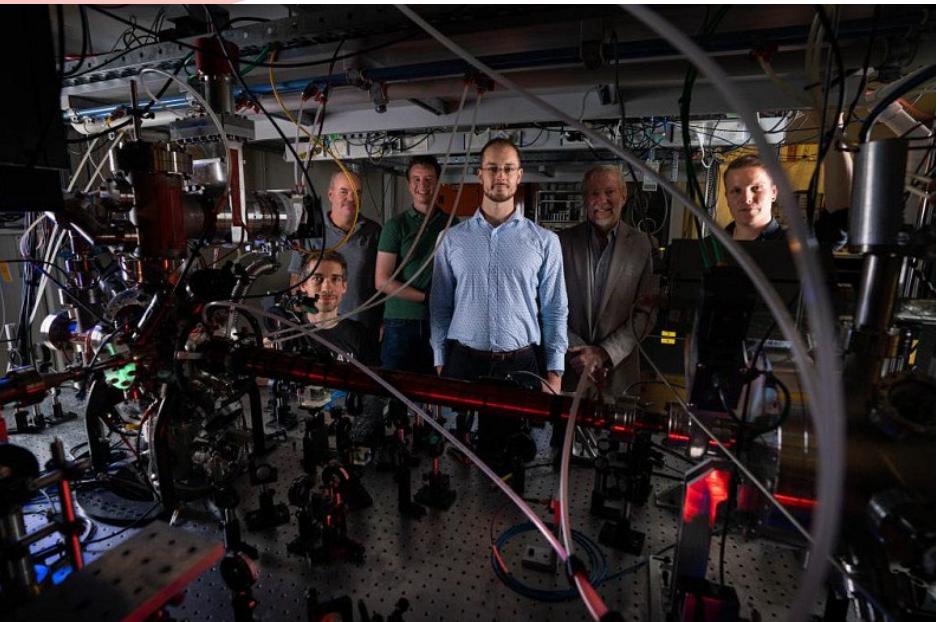


Heidelberg energy spectrum



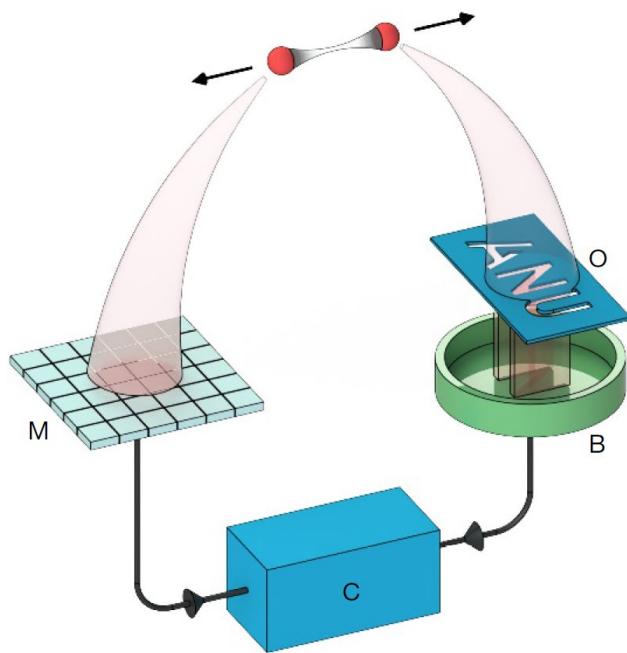
Bose-Einstein condensation of He^*

Metastable helium research in Australia

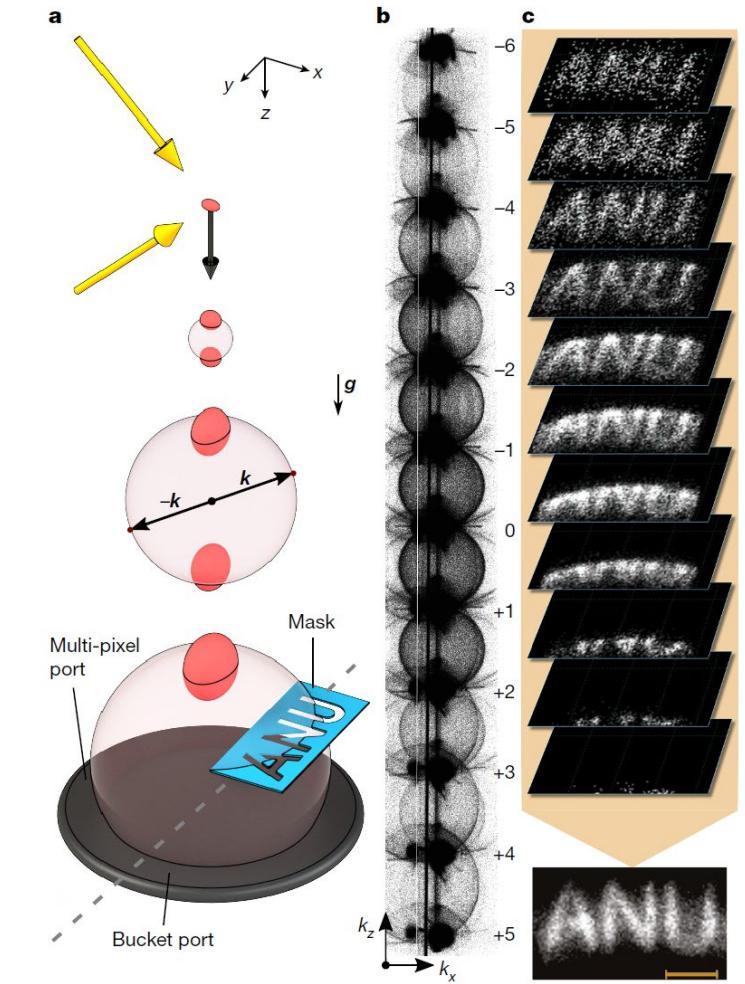


The He^* group and apparatus at the Australian National University

Ghost imaging with atoms



Ghost imaging requires correlation

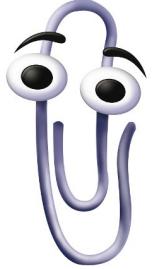


The construction of a ghost image

Ghost imaging with atoms (2016)

To lithium and beyond

Technically, states should be labelled with n , ℓ , m_ℓ , s and m_s , but $s = 1/2$ for all states



To zeroth approximation, multielectron atoms are hydrogenic states labelled with n , ℓ , m_ℓ , and m_s .

The energy depends only on n with ℓ and m_ℓ introducing a n^2 -fold degeneracy, and m_s introducing a 2-fold degeneracy

Each energy level n is referred to as a *shell*, and each nl orbital is referred to as a *subshell*. Each subshell has $2(2\ell + 1)$ possible states.

If electrons were bosons, increasing the number would further populate the ground state. But electrons are fermions, so we expect each additional electron to fill the lowest available hydrogenic energy state, filling each subshell with $2(2\ell + 1)$ electrons and each shell with $2n^2$ electrons



Shell (n)	Subshell Configuration	Degeneracy ($2n^2$)
1	$1s^2$	2
2	$2s^2 \ 2p^6$	8
3	$3s^2 \ 3p^6 \ 3d^{10}$	18
4	$4s^2 \ 4p^6 \ 4d^{10} \ 4f^{14}$	32
5	$5s^2 \ 5p^6 \ 5d^{10} \ 5f^{14} \ 5g^{18}$	50
6	$6s^2 \ 6p^6 \ 6d^{10} \ 6f^{14} \ 6g^{18} \ 6h^{22}$	72
7	$7s^2 \ 7p^6 \ 7d^{10} \ 7f^{14} \ 7g^{18} \ 7h^{22} \ 7i^{26}$	98

The filling of hydrogenic states based on asymmetry (Pauli exclusion principle)

Discussion:

This suggests that the periodic table should be pyramidal, and the 7 rows should yield 280 atoms. What are we missing?

...table table table... (the periodic table)

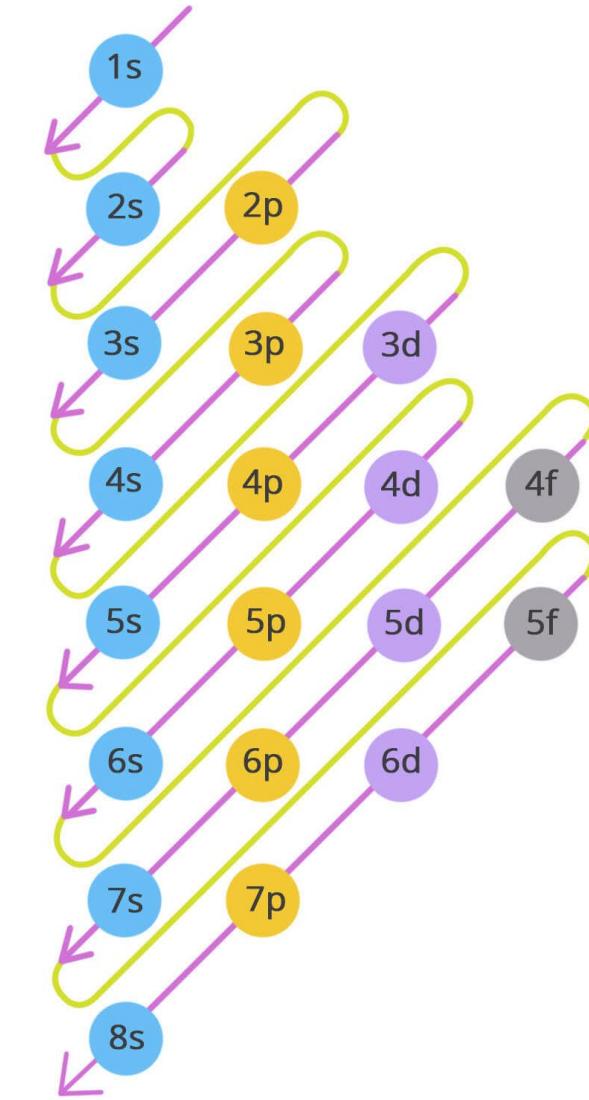
Periodic Table of the Elements

The periodic table displays the elements in a grid of 18 columns and 8 rows. Each element is represented by a colored box containing its symbol, name, atomic number, and atomic mass. The elements are color-coded into groups:

- Nonmetals:** Green (top left), yellow (bottom left), and orange (top right).
- Lanthanide:** Pink (center-left).
- Actinide:** Purple (center-right).
- Alkali Metal:** Dark green.
- Alkaline Earth Metal:** Blue.
- Transition Metal:** Purple (bottom row).
- Post-Transition Metal:** Yellow (bottom row).
- Metalloid:** Cyan.
- Noble Gas:** Red (top right).
- Halogen:** Orange (top right).
- Iron Metal:** Purple (middle row).
- Cobalt:** Purple (middle row).
- Nickel:** Purple (middle row).
- Copper:** Yellow (middle row).
- Zinc:** Purple (middle row).
- Gallium:** Yellow (middle row).
- Germanium:** Cyan.
- Arsenic:** Cyan.
- Selenium:** Green.
- Bromine:** Orange.
- Krypton:** Red.
- Rubidium:** Yellow.
- Strontium:** Yellow.
- Yttrium:** Yellow.
- Zirconium:** Yellow.
- Niobium:** Purple.
- Molybdenum:** Purple.
- Techneium:** Purple.
- Ruthenium:** Purple.
- Palladium:** Yellow.
- Silver:** Yellow.
- Cadmium:** Yellow.
- Indium:** Cyan.
- Tin:** Cyan.
- Antimony:** Cyan.
- Tellurium:** Cyan.
- Iodine:** Orange.
- Xenon:** Red.
- Cesium:** Yellow.
- Barium:** Yellow.
- Hafnium:** Purple.
- Tantalum:** Purple.
- Tungsten:** Purple.
- Rhenium:** Purple.
- Osmium:** Purple.
- Iridium:** Purple.
- Platinum:** Yellow.
- Mercury:** Yellow.
- Thallium:** Cyan.
- Lead:** Yellow.
- Bismuth:** Yellow.
- Po**
- At**
- Rn**
- Francium:** Yellow.
- Radium:** Yellow.
- Actinides:** Purple (bottom row).
- Rutherfordium:** Purple.
- Dubnium:** Purple.
- Seaborgium:** Purple.
- Bohrium:** Purple.
- Hassium:** Purple.
- Meltberium:** Purple.
- Darmstadtium:** Purple.
- Roentgenium:** Purple.
- Copernicum:** Yellow.
- Nihonium:** Yellow.
- Flerovium:** Yellow.
- Moscovium:** Yellow.
- Livermorium:** Yellow.
- Tennessee:** Yellow.
- Oganesson:** Yellow.
- La**
- Ce**
- Pr**
- Nd**
- Pm**
- Sm**
- Eu**
- Gd**
- Tb**
- Dy**
- Ho**
- Er**
- Tm**
- Yb**
- Lu**
- Ac**
- Th**
- Pa**
- U**
- Np**
- Pu**
- Am**
- Cm**
- Bk**
- Es**
- Fm**
- Md**
- No**
- Lr**

Arrows indicate the sequence of orbital filling from left to right across a period and down a group.

The periodic table: distinctly non-pyramidal



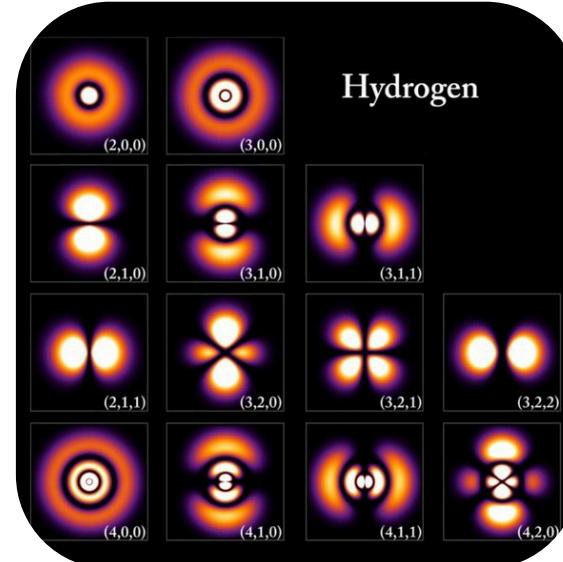
The Aufbau principle: how shells fill

Shielded from reality

The missing piece of the puzzle:
shielding of the nuclear charge by
inner shell electrons

- For a given n , higher values of ℓ correspond to orbits far from the nucleus
- Lifts degeneracy in ℓ
- Screening can be so large that it exceeds the hydrogenic $n \rightarrow n + 1$ energy

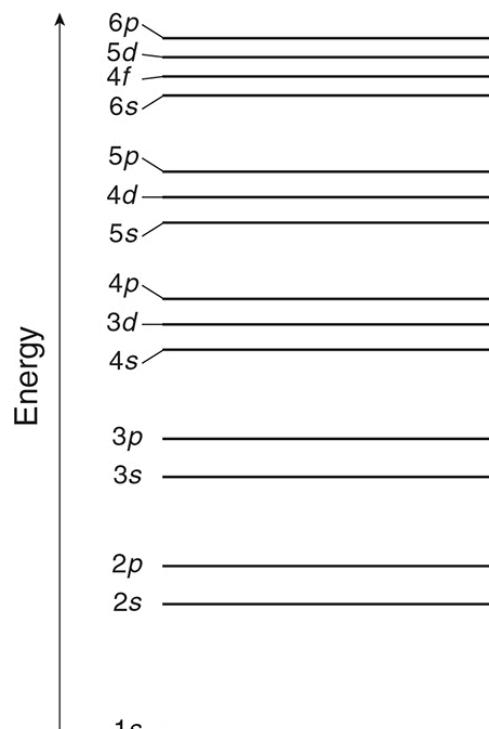
Anomalies exist, e.g.



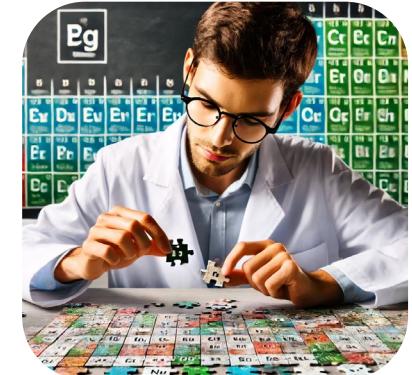
*The electronic distribution
is (unsurprisingly)
important to the energy*

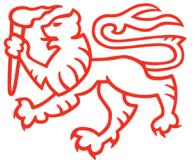
Row	Subshell Configuration	Number of Atoms			
1	$1s^2$	2			
2	$2s^2$	$2p^6$	8		
3	$3s^2$	$3p^6$	8		
4	$4s^2$	$3d^{10}$	$4p^6$	18	
5	$5s^2$	$4d^{10}$	$5p^6$	18	
6	$6s^2$	$4f^{14}$	$5d^{10}$	$6p^6$	32
7	$7s^2$	$5f^{14}$	$6d^{10}$	$7p^6$	32

*The electronic configurations
within the periodic table*



*Energy ordering of
subshells inclusive of
nuclear shielding*





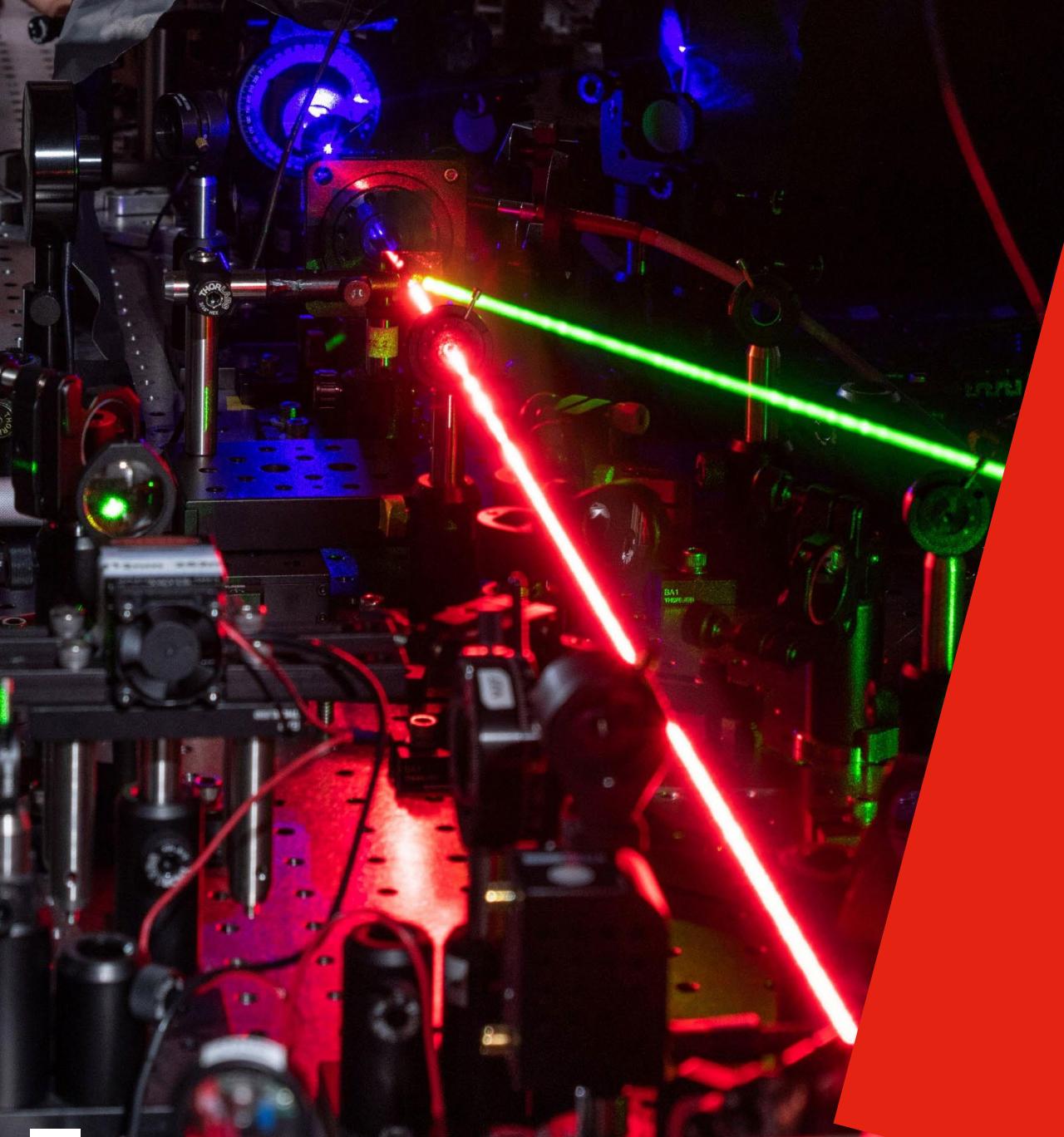
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Summary

Problems

M13.7, M13.12, M13.15

- Symmetrisation
 - The wave functions of identical particles depend on particle type (bosons versus fermions)
 - Wave functions which have separable spin and spatial components have their respective symmetries determined
 - Symmetric wave functions display an “attraction” between particles, and antisymmetric wave functions a “repulsion”
 - Interaction between particles leads to energy splitting dependent on the *direct* and *exchange* integrals
- Multielectron atoms
 - Symmetrisation permits an accurate computation of the energy states of helium
 - The structure of periodic table can be constructed from hydrogenic states and symmetrisation



Radiative transitions

McIntyre Ch. 14 // Foot Ch. 7

Frequency doubling of light; lasers are core to the study of atomic transitions



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Learning outcomes

Week 3, lecture 2

Ch. 14, §1-4 // Throughout:
Radiative transitions

- Dipole transitions in an atom
 - What is laser spectroscopy and how do we do it?
 - Meet and greet a multi-electron atom
 - How to Time-dependently perturb something
 - An important equation: Fermi's golden rule
 - How to make Fermi's golden rule go for dipole interactions
 - The rate equations and coefficients
 - The emergence of selection rules

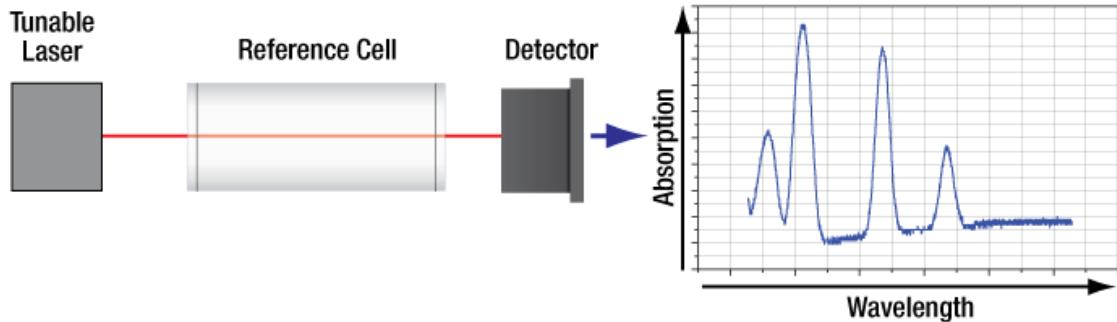
The time is right

To this point, we have studied static systems (without time dependence).

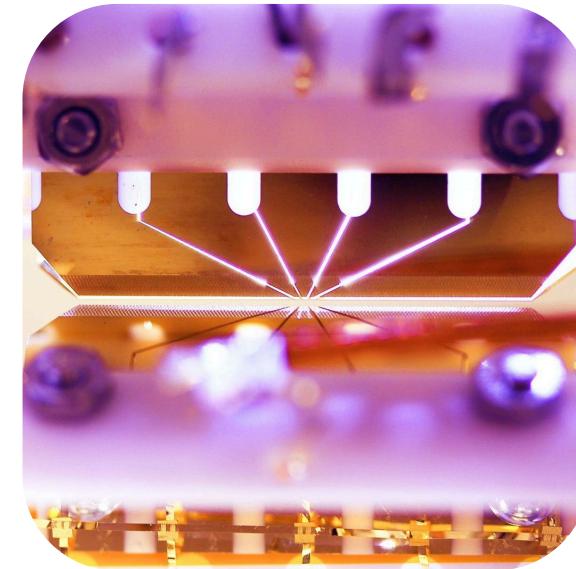
To study transient phenomena, our systems must have time dependence, which we implement via *Time-Dependent Perturbation Theory*

Our main goal is to model and understand transitions between atomic states: how, when, and why?

Transition theory is a crucial step to arriving at light-atom interactions, and their applications



Spectroscopy is simple to perform



Advanced quantum systems, such as quantum computers, often come down to shining light on an atom

Rubidium 101

Group I element ($Z = 37$) \Rightarrow single valence shell electron: $5s$

Discovered by Kirchhoff and Bunsen in 1861, named from the Latin *rubidus* (deep red)

Convenient for laser spectroscopy due to commercial/industrial laser diode emission at 780 nm

Also, goes boom:



Spectroscopy power couple Gustav Kirchhoff and Robert Bunsen



Rubidium flame



Rubidium in water



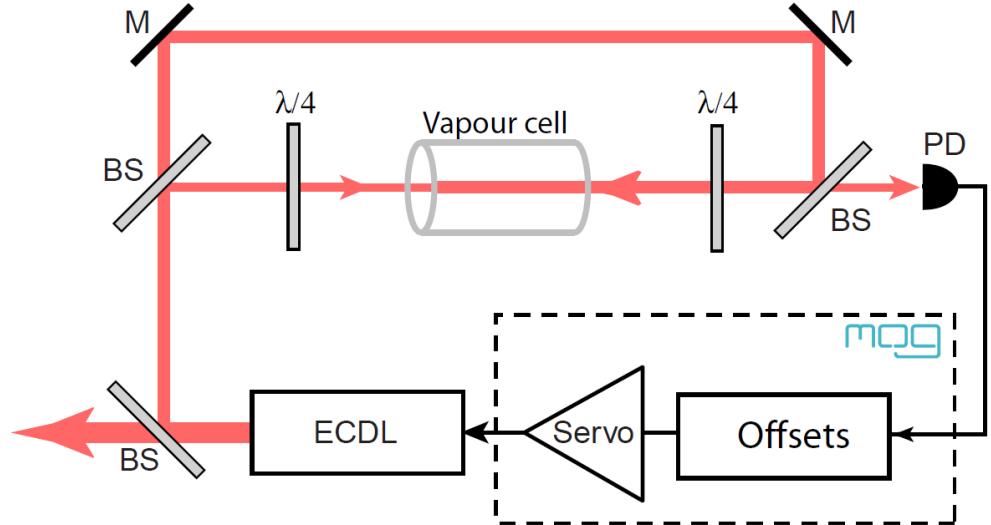
Rubidium metal



An (AlGaAs) laser diode



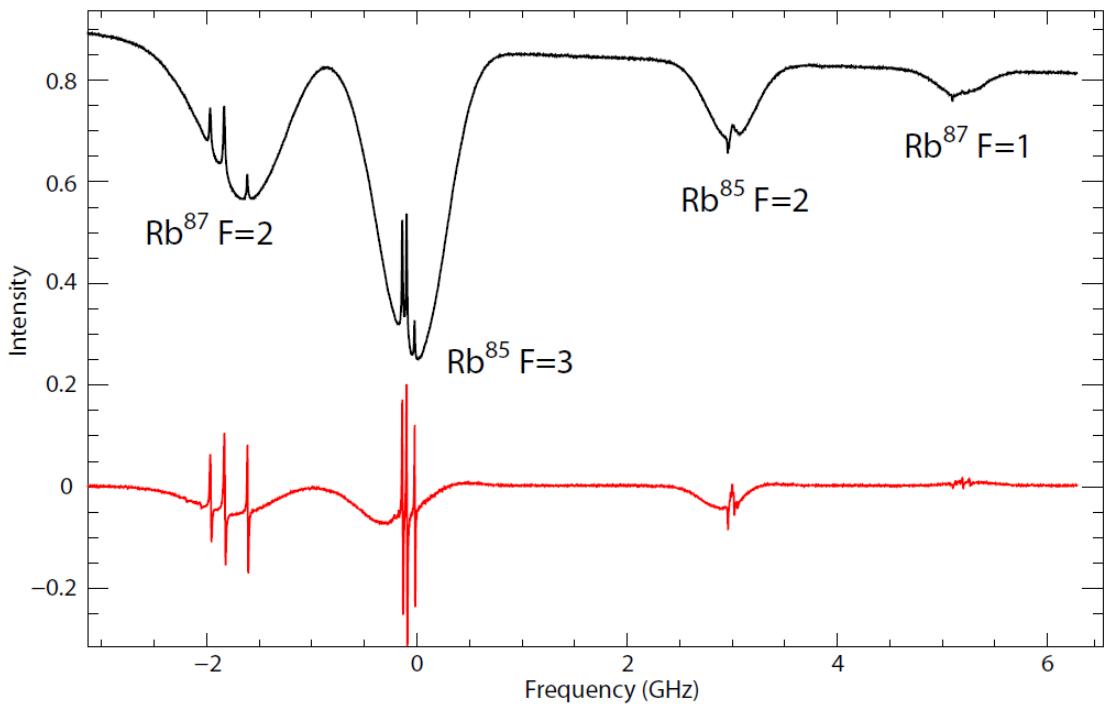
A vapour cell



The setup for (saturated) absorption spectroscopy

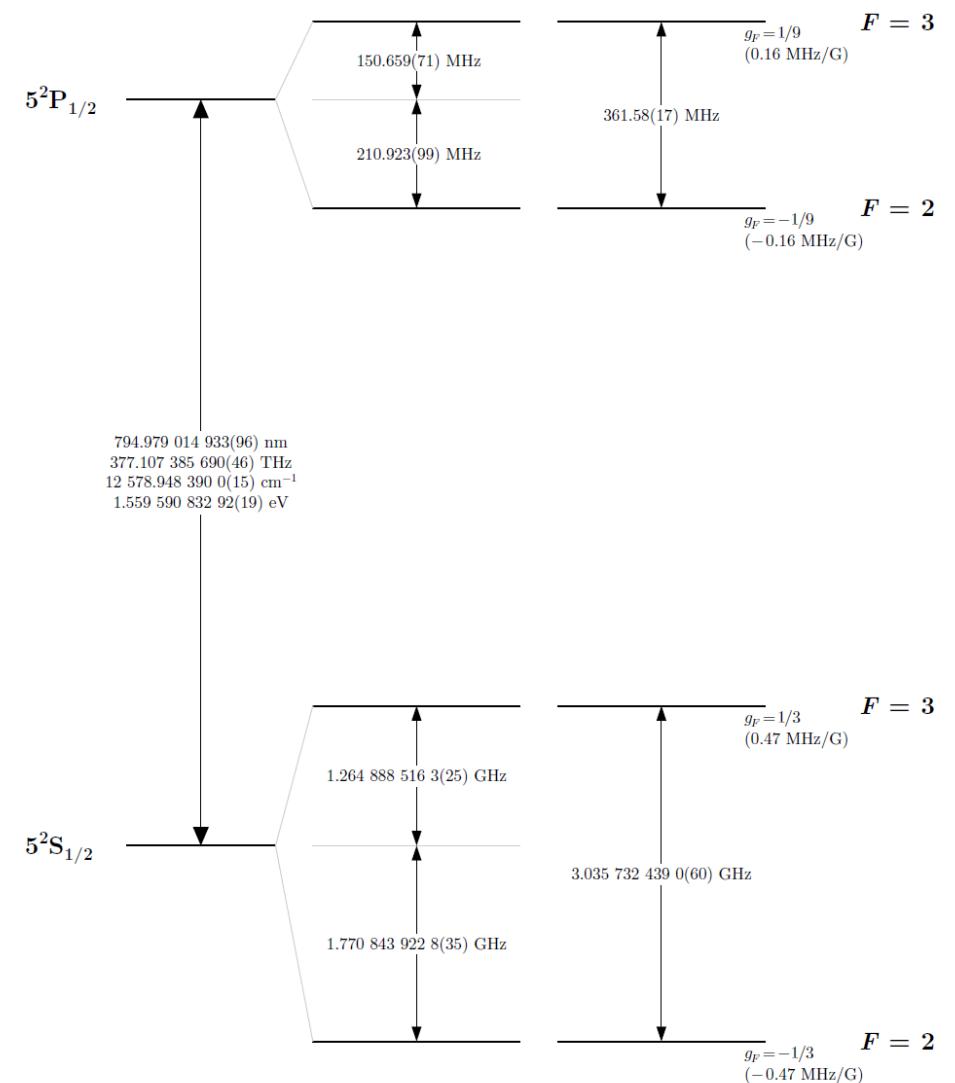
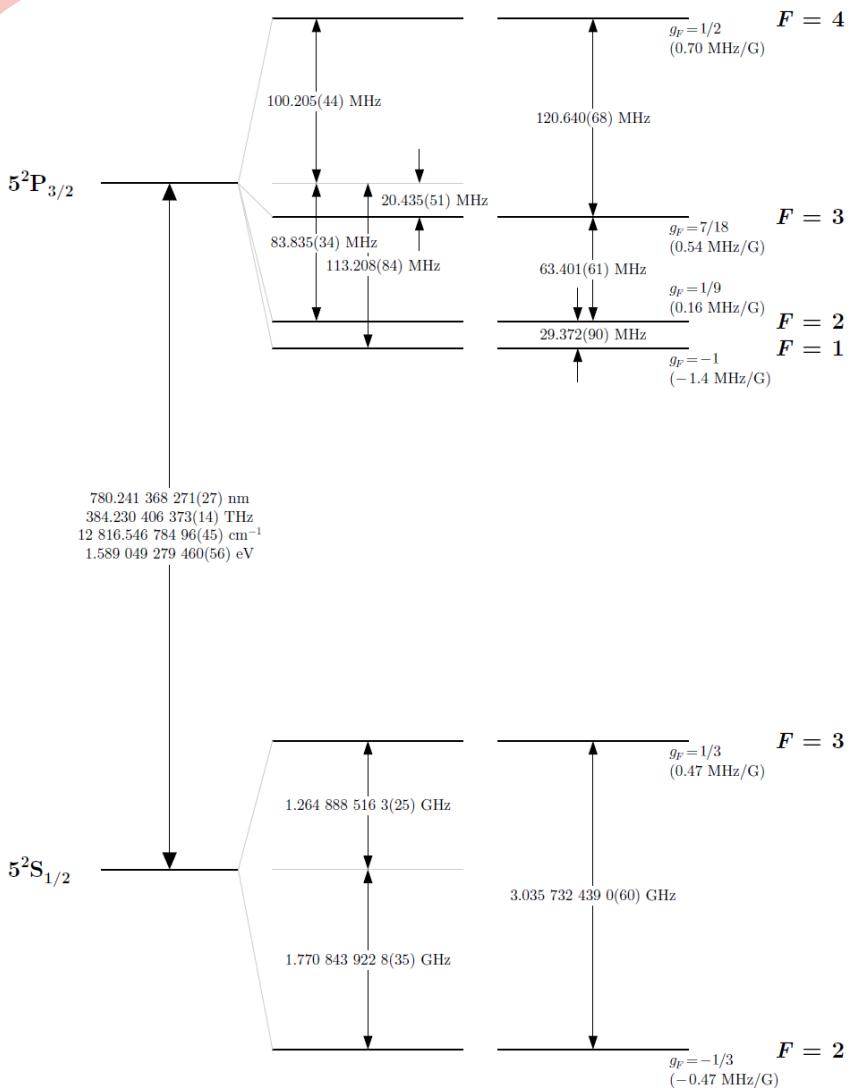


An optical drive

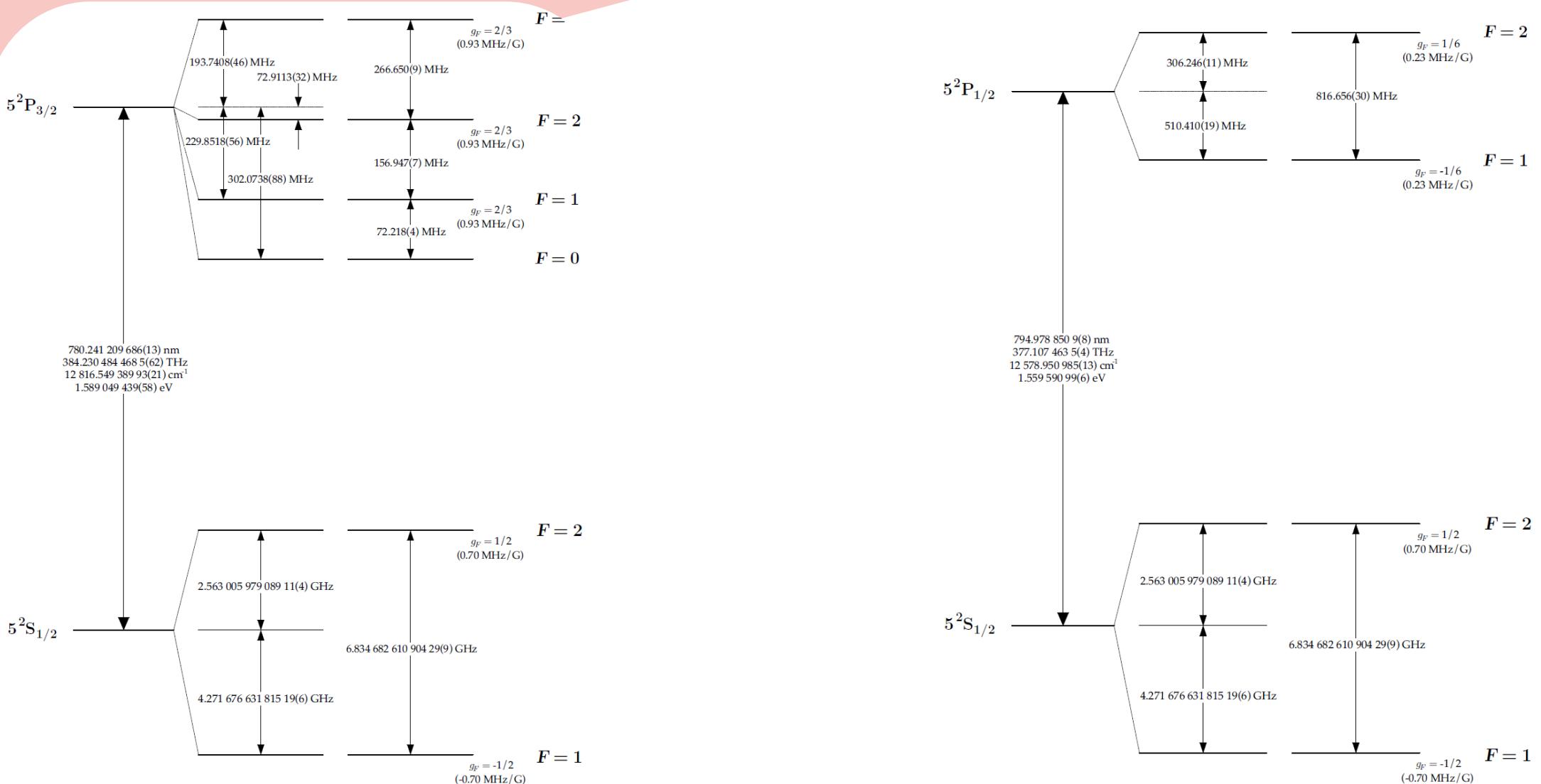


A (saturated)
absorption spectrum
of natural rubidium

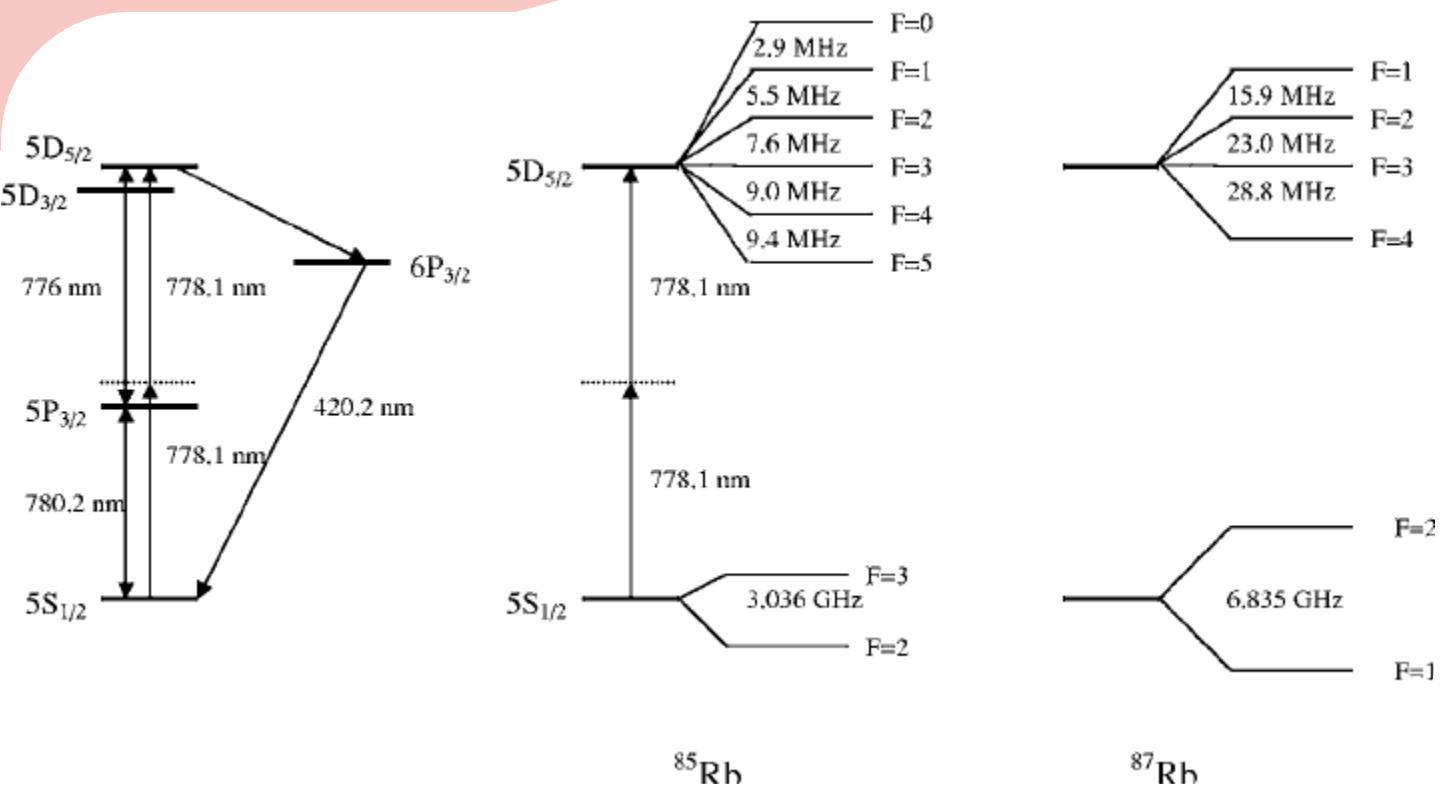
We can compute transitions! ^{85}Rb : $I = 5/2$



^{87}Rb : $I = 3/2$



It gets worse...



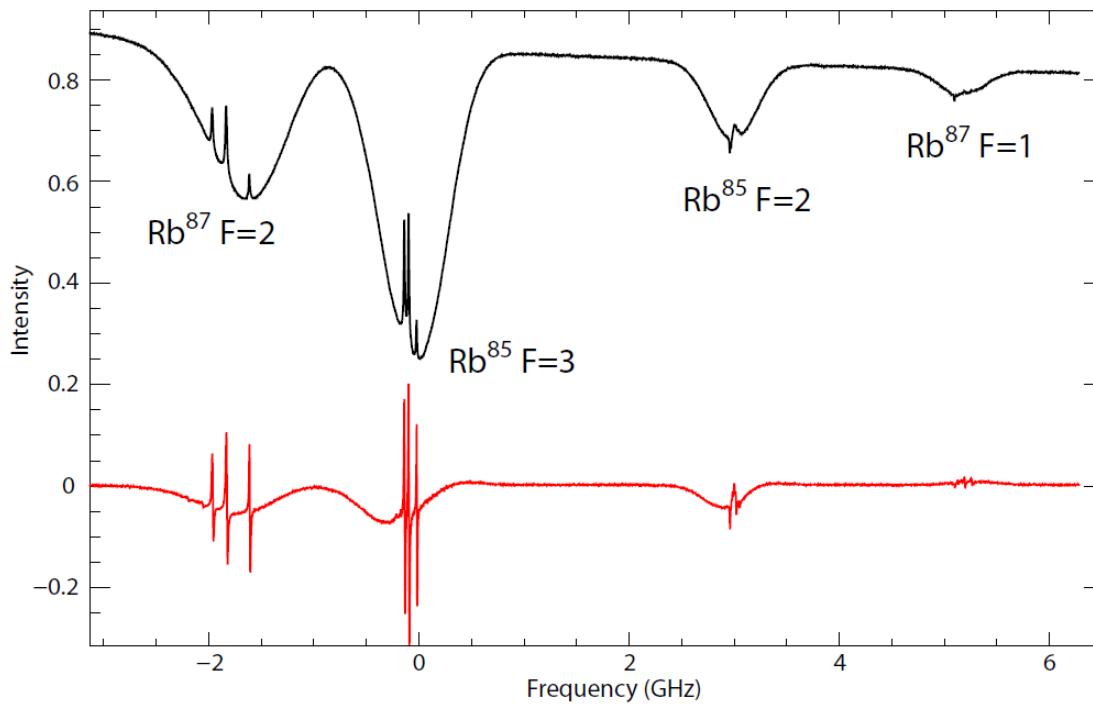
Two-photon excitation pathways in rubidium



420 nm light produced from excitation to the 5D state

TL;DR

In short: there are lots of transitions, and impressively, we can predict the frequency of these transitions, but (currently) not the intensity



In order to precisely manipulate atoms, we need to understand how they respond to light, or more generally, time-varying electromagnetic fields



Transition probability

The system we model is as follows:

- System initially in state $|i\rangle$
- A (time-dependent) perturbation is turned on at $t = 0$
- We measure the probability that the system is in a final state $|f\rangle$ at some later time

Using time-dependent perturbation theory, one obtains the result

$$c_k(t) = \frac{1}{i\hbar} \int_0^t \langle k | H'(t') | i \rangle e^{i(E_k - E_i)t'/\hbar} dt'$$

which gives the expansion coefficient $c_k(t)$ for the eigenstate $|k\rangle$ subject to the evolution under the perturbation $H'(t)$, given the starting state $|i\rangle$.

To find the probability that the system is in a particular final state $|f\rangle$ at a later time:

$$\mathcal{P}_{i \rightarrow f}(t) = \frac{1}{\hbar^2} \left| \int_0^t \langle f | H'(t') | i \rangle e^{\frac{i(E_f - E_i)t'}{\hbar}} dt' \right|^2$$



This is a Fourier transform, meaning the result is the Fourier coefficient of the perturbation $H'(t)$ at so-called Bohr frequency, $\omega_{ki} = \frac{E_k - E_i}{\hbar}$.

This means that if the perturbation has a component at the frequency corresponding to the energy difference between states, the probability of transition will be non-zero.



Transition rates

We define the transition rate as the probability of transition per unit time, which we can obtain by differentiating the probability

$$R_{i \rightarrow f} = \frac{d}{dt} \mathcal{P}_{i \rightarrow f}(t)$$

which in the case of periodic perturbations gives *Fermi's golden rule*:

$$R_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |V_{fi}|^2 g(E_f)$$

where $g(E)$ is the density of states V_{fi} is common notation for the matrix element $\langle f | V(\mathbf{r}) | i \rangle$ for the perturbing potential



Enrico Fermi in 1943



Enrico's slide rule

The electric dipole interaction

The interaction between an atom and an electromagnetic field can be effectively modelled through the electric dipole interaction.

The electric dipole moment of the atom is $\mathbf{d} = -e\mathbf{r}$ and the associated Hamiltonian is

$$H' = -\mathbf{d} \cdot \mathbf{E}$$

where we have an electric field

$$\begin{aligned}\mathbf{E}(t) &= 2\epsilon_0 \hat{\epsilon} \cos(\omega t) \\ &= \epsilon_0 \hat{\epsilon} (e^{i\omega t} + e^{-i\omega t})\end{aligned}$$

with $\hat{\epsilon}$ specifying the polarisation vector.

We identify this interaction as a periodic perturbation with potential $V = -\mathbf{d} \cdot \hat{\epsilon} \epsilon_0 = e\epsilon_0 \hat{\epsilon} \cdot \mathbf{r}$, meaning Fermi's golden rule can then be applied, giving

$$R_{i \rightarrow f} = \frac{2\pi e^2 \epsilon_0^2}{\hbar^2} |\hat{\epsilon} \cdot \langle f | \mathbf{r} | i \rangle|^2 \delta(\omega_{fi} - \omega)$$

We are able to ignore the magnetic interaction, as it is weaker by a factor of α

We also make the *electric dipole approximation*, which assumes that the atom sees a uniform electric field across its distribution.

The density of states for an infinitely sharp energy level is represented by a Dirac delta function

The Einstein model

The Einstein model is constructed around a two-level atom in thermal equilibrium with blackbody radiation at temperature $T \Rightarrow$ broadband excitation

The energy density per unit volume of radiation is

$$u = \varepsilon_0 \mathcal{E}^2 = 4\varepsilon_0 \mathcal{E}_0^2 \cos^2(\omega t)$$

which is related to the energy per unit volume per unit angular frequency

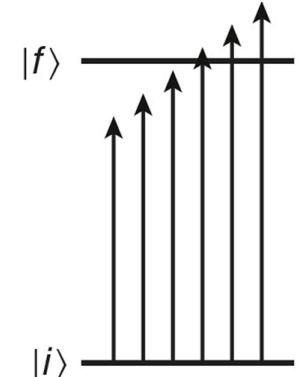
$$u_{RMS} = \rho(\omega) d\omega$$

The transition rate is then

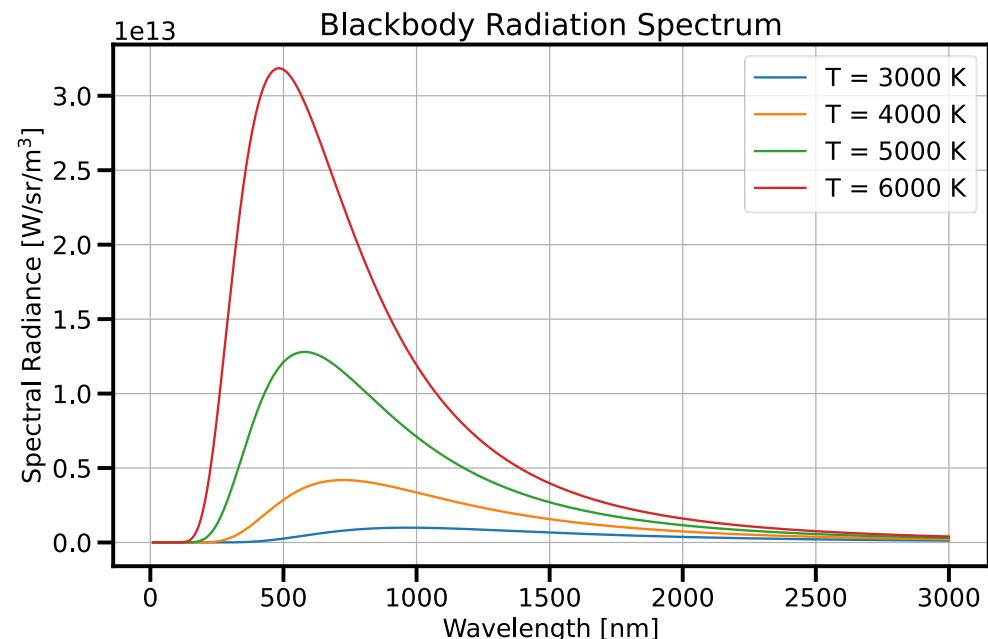
$$\begin{aligned} R_{i \rightarrow f} &= \frac{\pi^2 e^2}{\varepsilon_0 \hbar^2} |\hat{\varepsilon} \cdot \langle f | \mathbf{r} | i \rangle|^2 \int_0^\infty \delta(\omega_{fi} - \omega) d\omega \\ &= \frac{\pi^2 e^2}{\varepsilon_0 \hbar^2} \rho(\omega_{fi}) |\hat{\varepsilon} \cdot \langle f | \mathbf{r} | i \rangle|^2 \end{aligned}$$



*Blackbody emission
is broadband*



*Broadband excitation
for a two-level atom*



*Blackbody spectra for different
temperatures*

Einstein *B* coefficient

Blackbody radiation is isotropic with a random polarisation vector \Rightarrow average over all $\hat{\varepsilon}$:

$$\begin{aligned}\langle |\hat{\varepsilon} \cdot \hat{\mathbf{r}}|^2 \rangle &= \frac{1}{4\pi} \int |\hat{\varepsilon} \cdot \hat{\mathbf{r}}|^2 d\Omega \\ &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \cos^2(\theta) \sin(\theta) d\theta d\phi = \frac{1}{3}\end{aligned}$$

So

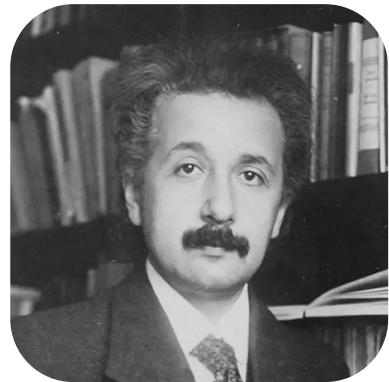
$$R_{i \rightarrow f} = \frac{\pi^2 e^2}{3\varepsilon_0 \hbar^2} |\langle f | \mathbf{r} | i \rangle|^2 \rho(\omega_{fi}) \equiv B_{if} \rho(\omega_{fi})$$

where B_{if} is the Einstein *B* coefficient.

This coefficient gives us the probability per unit time that an atom will absorb or emit a photon.

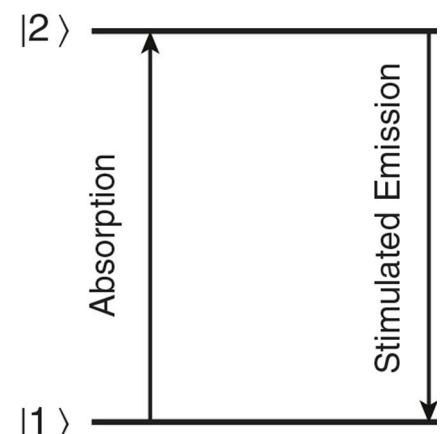
For states $|1\rangle$ and $|2\rangle$ with energies E_1 and E_2 , the radiation induces:

- A transition from $|1\rangle \rightarrow |2\rangle$ - absorption
- A transition from $|2\rangle \rightarrow |1\rangle$ - stimulated emission



Einstein in 1916

The Einstein *B* coefficient is the same if we swap $|i\rangle$ and $|f\rangle$, and the energy density $\rho(\omega_{fi}) = \rho(\omega_{if})$ so $R_{i \rightarrow f} = R_{f \rightarrow i}$



Einstein model of absorption and emission

Spontaneity

Discussion:

Einstein argued that beyond absorption and stimulated emission, a third process must exist. What might this process be, and why must it exist?



Einstein A coefficient

Incorporating spontaneous decay, the *rate* equation for state $|1\rangle$ ($|2\rangle$) with N_1 (N_2) atoms is

$$\frac{dN_1}{dt} = -N_1 B_{12}\rho(\omega_{21}) + N_2 B_{21}\rho(\omega_{21}) + N_2 A_{21}$$

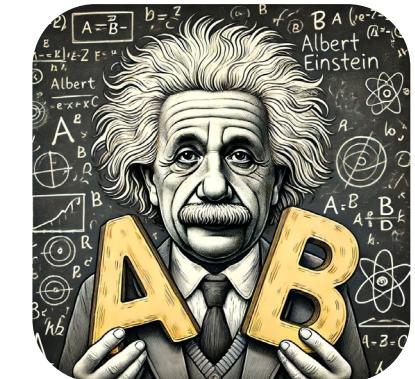
Abs $|1\rangle \rightarrow |2\rangle$ Stim $|2\rangle \rightarrow |1\rangle$ Spont $|2\rangle \rightarrow |1\rangle$

and

$$\frac{dN_2}{dt} = +N_1 B_{12}\rho(\omega_{21}) - N_2 B_{21}\rho(\omega_{21}) - N_2 A_{21}$$

which when solved for the steady state gives

$$A_{21} = \frac{e^2 \omega_{21}^3}{3\pi\epsilon_0\hbar c^3} |\langle 2|\mathbf{r}|1\rangle|^2$$



Requires Planck blackbody radiation formula

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

With no field:

$$\frac{dN_2}{dt} = -N_2 A_{21} \Rightarrow N_2(t) = N_2(0)e^{-A_{21}t}$$

meaning the excited state population decays with lifetime τ , where

$$\tau = \frac{1}{A_{21}}$$

The finite state lifetime enforces a limit on the energy uncertainty

$$\Delta E = \hbar/\Delta t = \hbar/\tau = \hbar A_{21}$$

We have an expression for the spontaneous emission rate, but not a physical mechanism to underpin its existence; to properly develop this requires a study of quantum electrodynamics.

Tick tick

The second is defined by the hyperfine splitting of the ground state of Caesium, the frequency of the transition is (exactly) 9,192,631,770 Hz

More ticks are better, correct?

The *linewidth* of a transition is

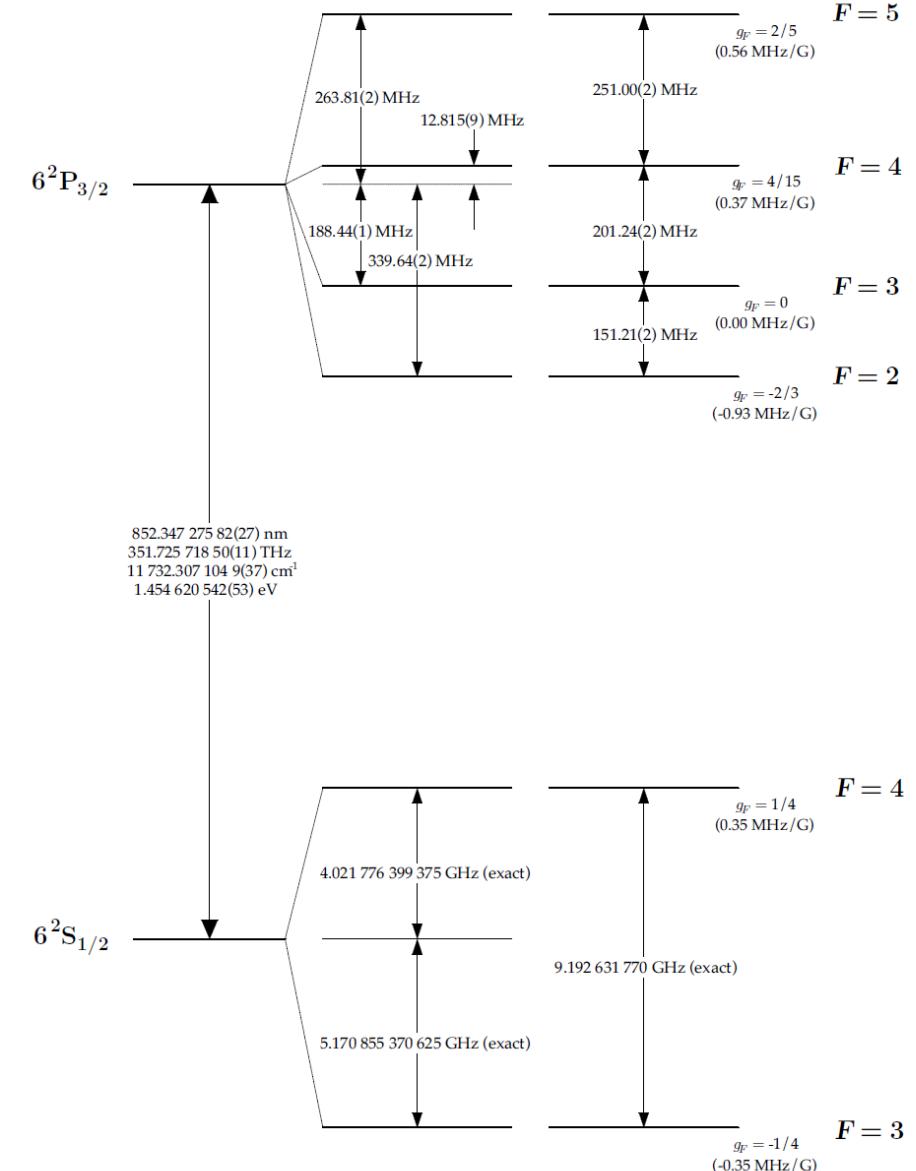
$$\Delta\nu \approx 1/2\pi\tau$$

For Caesium:

- Hyperfine transition lifetime: 30 μ s
- Optical transition ($6S_{1/2} \rightarrow 6P_{3/2}$) lifetime: 30 ns

How to make a better clock?

- Use *forbidden* optical transitions, e.g. strontium ($^1S_0 - ^3P_0$) has frequency ≈ 4.29 THz and lifetime ≈ 145 s



Energy-level structure of caesium

Monochromatic excitation

We now consider a monochromatic field exciting an atom

The density of states $g(E)$ can be calculated as the Fourier transform of the emitted field; for an exponentially decaying excited state, the density of states is

$$g(E) = \frac{\hbar A_{21}/2\pi}{(E - \hbar\omega_{21})^2 + \left(\frac{\hbar A_{21}}{2}\right)^2}$$

and Fermi's golden rule gives

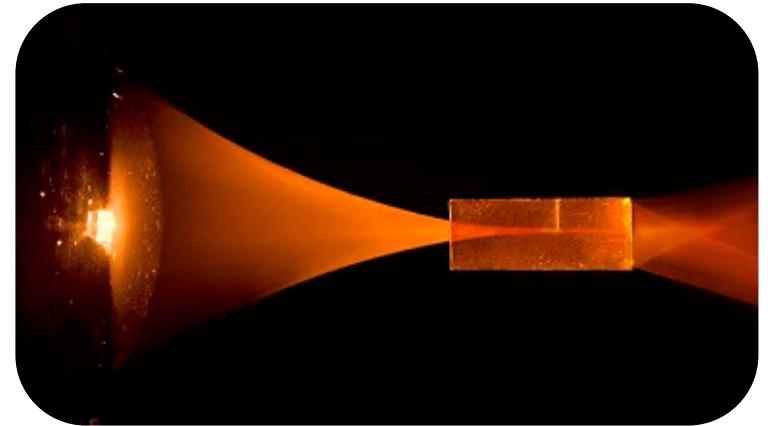
$$R_{1 \rightarrow 2} = \frac{2\pi e^2 \mathcal{E}_0^2}{\hbar^2} |\hat{\epsilon} \cdot \langle 2 | \mathbf{r} | 1 \rangle|^2 f(\omega)$$

or expressed in terms of the Einstein B coefficient:

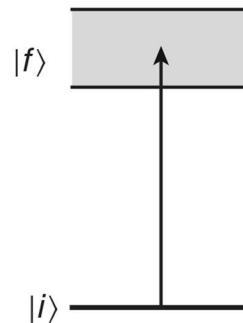
$$R_{1 \rightarrow 2} = 6\mathcal{E}_0 \mathcal{E}_0^2 B_{21} f(\omega)$$

If we then have a laser field with intensity $I = 2c\mathcal{E}_0 \mathcal{E}_0^2$, the rate is

$$R_{1 \rightarrow 2} = 3 \frac{I}{c} B_{21} f(\omega)$$



A monochromatic light field



All excited states have an energy spread

$g(E)$ is a Lorentzian, and it is convenient to consider its related frequency Lorentzian

$$f(\omega) = \frac{A_{21}/2\pi}{(\omega - \omega_{21})^2 + \left(\frac{A_{21}}{2}\right)^2}$$

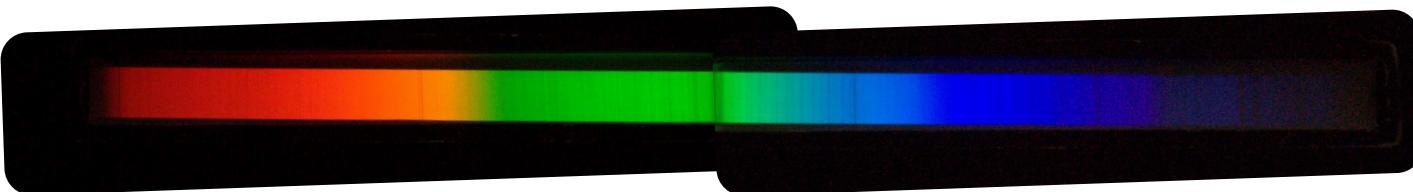


What does this mean?

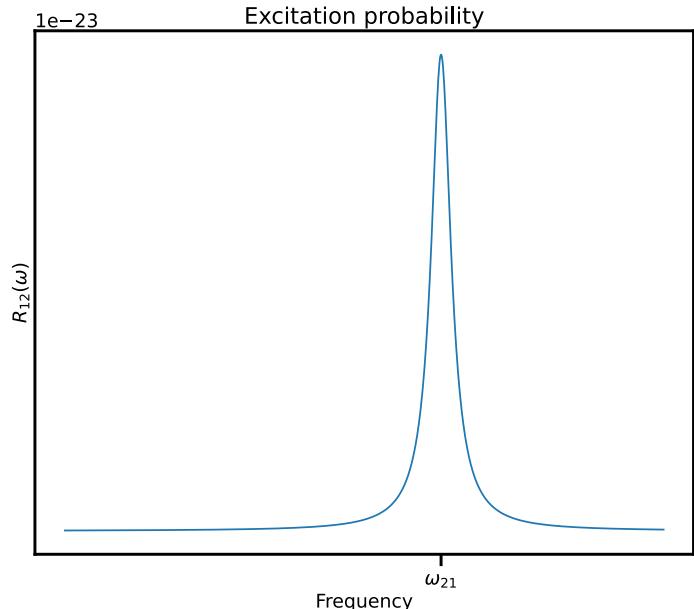
This result tells us that the excitation probability rate has a Lorentzian frequency dependence, with a FWHM of the spontaneous decay rate A_{21}

This is resonance: the origin of spectral lines!

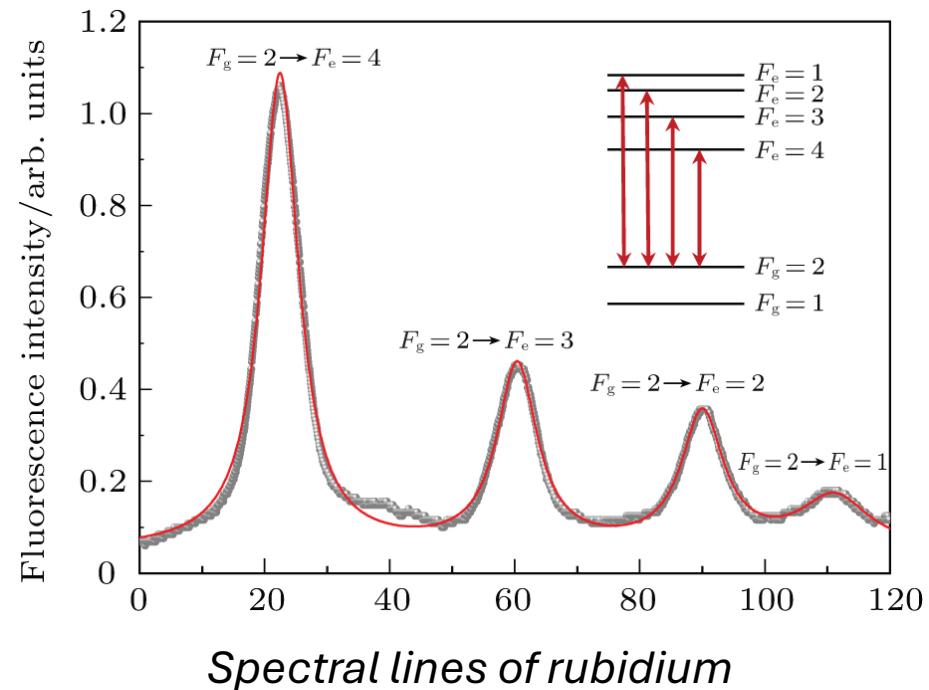
- Are spectral lines actually Lorentzian?



A solar spectrum from the heliostat experiment



Frequency dependence of the excitation rate



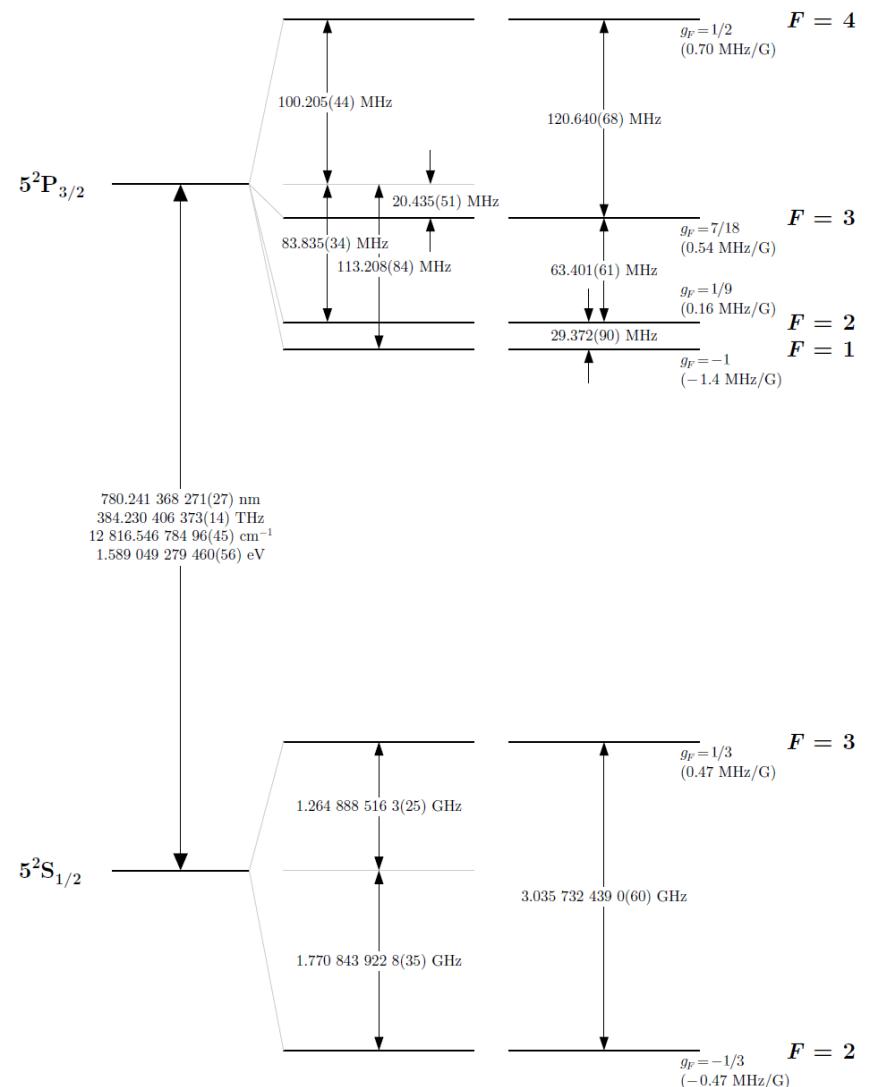
Spectral lines of rubidium

How are we looking?

We now have expressions to calculate transition rates

Discussion:

How many absorption lines would you expect to see?



Energy levels of the $5S_{1/2}$ and $5P_{3/2}$ states in Rb-85



Selection rules

Einstein A and B coefficients depend on the matrix element
 $\langle f | \hat{\varepsilon} \cdot \mathbf{r} | i \rangle$

Recall that this is under the electric dipole approximation

$$\langle f | \hat{\varepsilon} \cdot \mathbf{r} | i \rangle = \hat{\varepsilon} \cdot \langle f | r \hat{\mathbf{r}} | i \rangle$$

$$= \int_0^\infty r^2 dr \int d\Omega R_{n_f \ell_f}^*(r) Y_{\ell_f}^{m_f *}(\theta, \phi) \hat{\varepsilon} \cdot \hat{\mathbf{r}} r R_{n_i \ell_i}(r) Y_\ell^{m_i}(\theta, \phi)$$

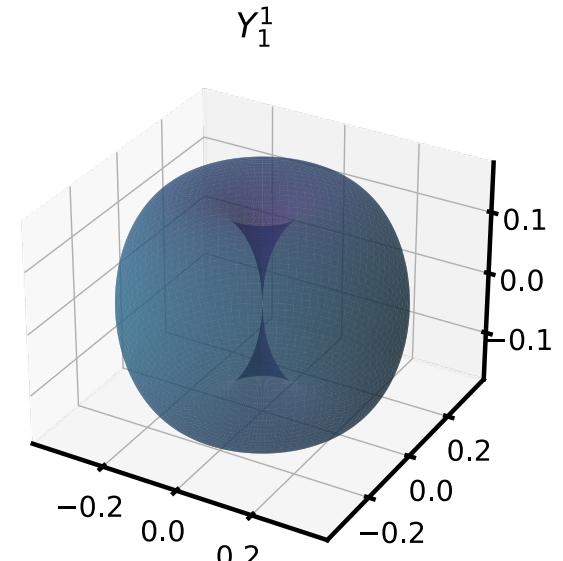
$$= \int_0^\infty R_{n_f \ell_f}^*(r) R_{n_i \ell_i}(r) r^3 dr \int Y_{\ell_f}^{m_f *}(\theta, \phi) \hat{\varepsilon} \cdot \hat{\mathbf{r}} Y_\ell^{m_i}(\theta, \phi) d\Omega$$

Only depends on r and is system specific

Angular component is independent of the system

$$\hat{\varepsilon} \cdot \hat{\mathbf{r}} = \varepsilon_x \sin(\theta) \cos(\phi) + \varepsilon_y \sin(\theta) \sin(\phi) + \varepsilon_z \cos(\theta)$$

$$= \sqrt{\frac{4\pi}{3}} \left(\varepsilon_z Y_1^0(\theta, \phi) + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^1(\theta, \phi) + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} Y_1^{-1}(\theta, \phi) \right)$$



Spherical harmonic $Y_1^1(\theta, \phi)$

Note that only harmonics of order 1 appear here

The return of Clebsch-Gordan coefficients

Computation of the angular integral becomes sum of three integrals of the form

$$\int Y_{\ell_f}^{m_f *}(\theta, \phi) Y_1^m(\theta, \phi) Y_{\ell_i}^{m_i}(\theta, \phi) d\Omega$$

where $m = -1, 0, 1$.

We have seen that a *coupled* state can be expressed in terms of *uncoupled* states using the Clebsch-Gordan coefficients

⇒ This means that one spherical harmonic can be decomposed into a product of pairs of other spherical harmonics!

Explicitly:

$$\int Y_{\ell_f}^{m_f *}(\theta, \phi) Y_1^m(\theta, \phi) Y_{\ell_i}^{m_i}(\theta, \phi) d\Omega = \left[\frac{2(2\ell_i + 1)}{4\pi(2\ell_f + 1)} \right]^{1/2} \langle \ell_i 1 m_i m | \ell_f m_f \rangle \langle \ell_i 1 0 0 | \ell_f 0 \rangle$$

Clebsch-Gordan
coefficient

E1 selection rules

* and ensuring even parity with respect to spatial symmetry



We saw that only certain values of quantum numbers for coupled angular momenta are allowed for given uncoupled angular momentum numbers

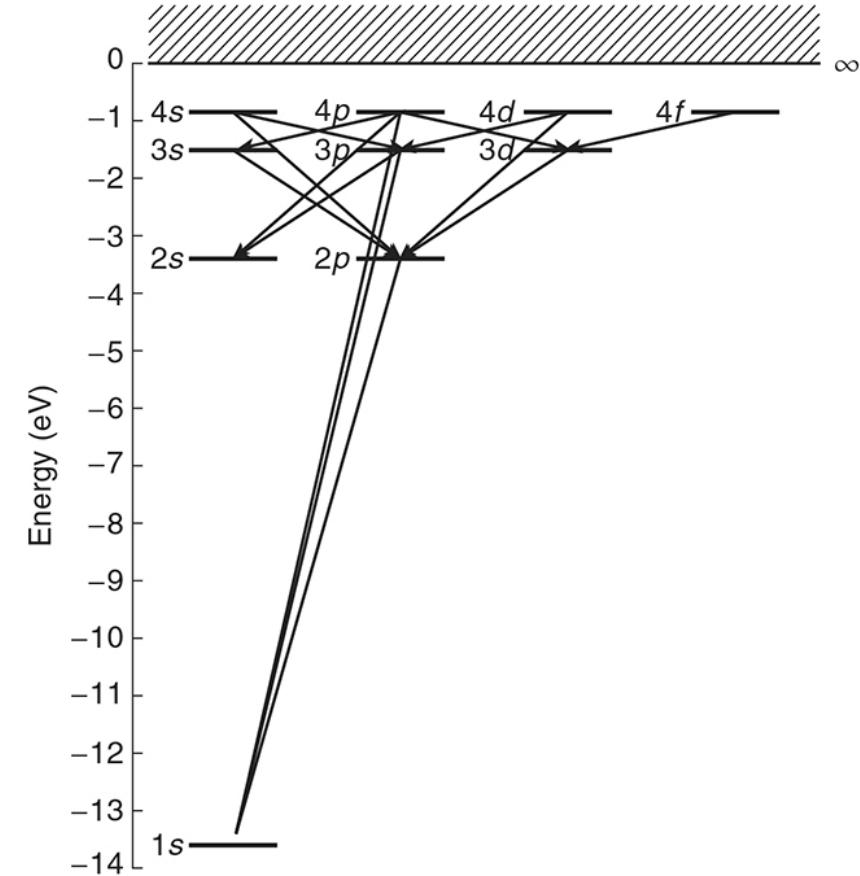
$\langle \ell_i \ 1 \ m_i \ m | \ell_f \ m_f \rangle$ characterises the addition of uncoupled momenta $j_1 = \ell_1$ and $j_1 = 1$ to the coupled momentum $j = \ell_f$

By enforcing the rules of adding angular momentum*, the only non-zero values of the integral are:

$$\Delta\ell = \pm 1$$
$$\Delta m = 0, \pm 1$$

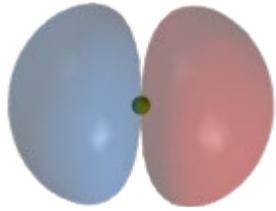
which are the **selection rules** for electric dipole ($E1$) transitions.

Transitions which cannot occur are called *forbidden* transitions

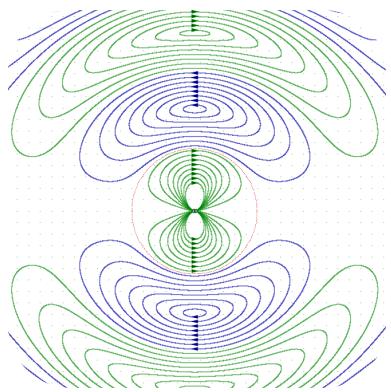
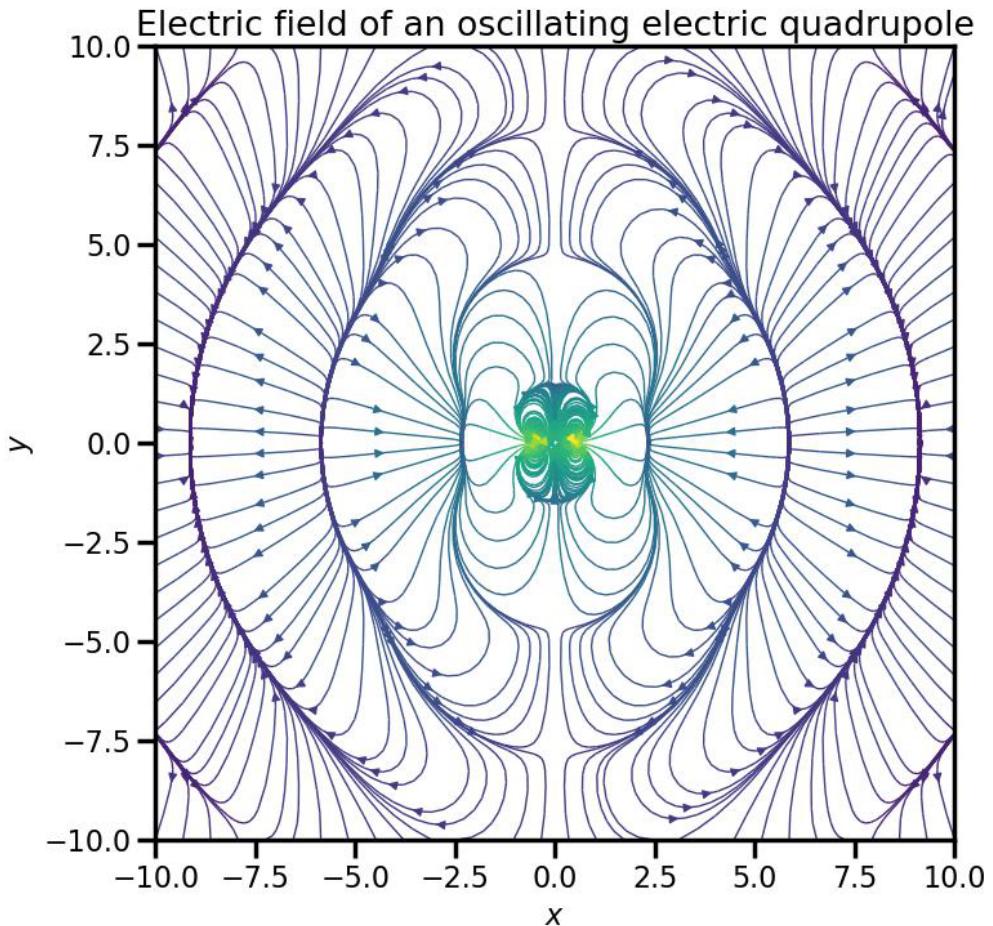
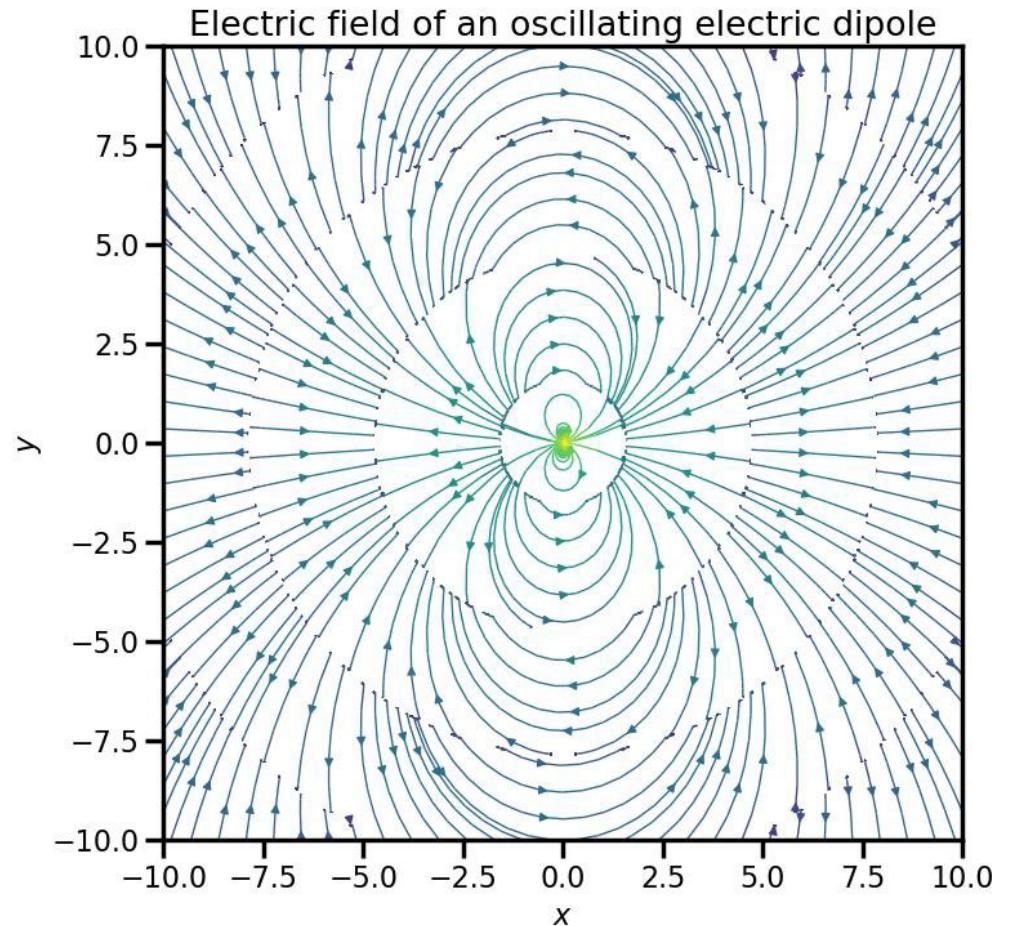


Allowed electric dipole decay pathways in hydrogen

Visualising electric dipole transitions



The $2p$ and $1s$ states



But what are selection rules?

Discussion:

We have done a bunch of maths which pop out seemingly arbitrary rules for transitions between states. What is the physical origin of selection rules, and what are their consequences?



Photons stealing the show

Consider the emission from the $2p \rightarrow 1s$ state. What are the possible transitions? What conditions do these transitions impose on the emissions?



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Summary

Problems

M14.3, M14.7 M14.10,

- Time-dependent perturbation theory
 - Probability amplitudes can be propagated in time
 - Periodic perturbations give rise to Fermi's golden rule: $R_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |V_{fi}|^2 g(E_f)$
- The Einstein coefficients
 - Describe the probability of absorption, spontaneous, and stimulated emission of radiation by atoms
 - $A_{21} = \frac{e^2 \omega_{21}^3}{3\pi\epsilon_0\hbar c^3} |\langle 2|\mathbf{r}|1\rangle|^2$
 - $B_{12} = \frac{\pi^2 e^2}{3\epsilon_0\hbar^2} |\langle 2|\mathbf{r}|1\rangle|^2$
- Radiative transitions
 - Excited states have a finite lifetime due to spontaneous emission
 - Selection rules exist for transitions, and act to conserve angular momentum