

Week 0 / 1

PHY 402 Atomic and Molecular Physics

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These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

0 Administrative affairs

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(ii) Literature:

- Demtröder, *"Atoms, Molecules and Photons"* [DT]
- Brandsen and Joachain, *"Physics of Atoms and Molecules"* [B&J]
- Atkins, Friedman, *"Molecular quantum mechanics"*
- Shankar, *"Principles of quantum mechanics"* [Shankar]
- Griffiths, *"Introduction to quantum mechanics"*
- Sakurai, *"Modern quantum mechanics"*

There is no primary text-book, I collect material from wherever I find it best covered case-by-case.

(iii) Assessment:

- **Surprise Quizzes: 10%** These are "open notes" quizzes, so please always bring yours. Times are random. These will be simple questions on material of maybe the last week's lecture to motivate attendance and continuously keeping on top of the material.
- **Assignments: 20%** I don't mind you working in groups. However, every student must hand in one separate personally handwritten solution. It should be tidy and with commented steps. TA is authorised to deduct marks for messy presentation and blatant copying.
- **Mid-Sem exam: 20%**
- **Final exam: 50%** The exam will try to test understanding of the essential *physics* concepts taught, not maths. For guidance regarding what are the most important concepts look at the quizzes and assignments of this and last year. All exams will be designed to give a significant advantage to those students that solved all assignments by *themselves*.

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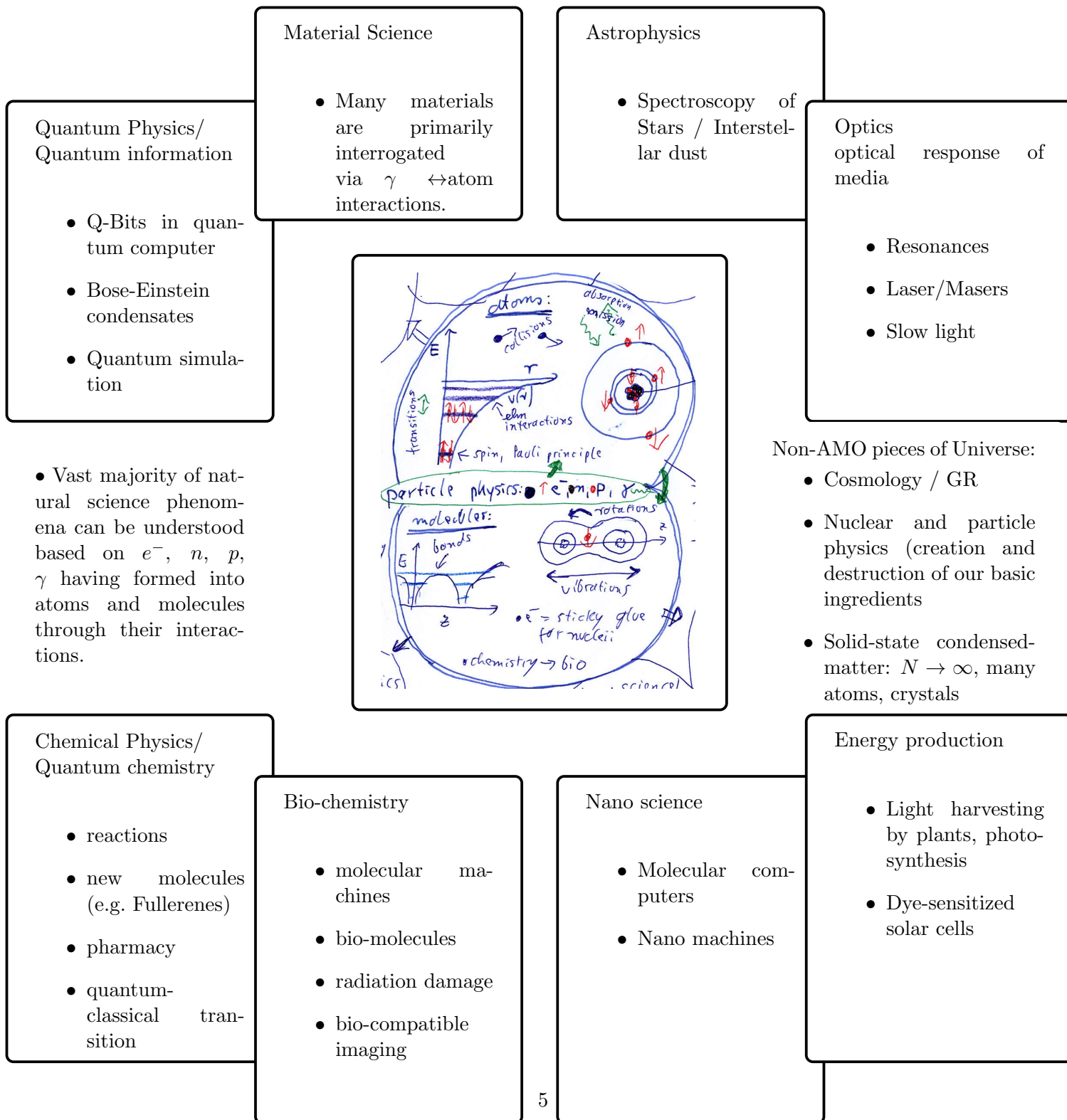
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1 Motivation and Review

1.1 Toolkit for building a universe with life



- You will mostly not have to advance fundamental atomic- or molecular physics itself, we are approaching a complete understanding. Exceptions are very exotic or extreme circumstances, such as U^{89+} .
- However you are likely to need a solid AMO background in many other physics disciplines, and if only to understand standard experimental interrogation techniques for materials or other objects.
- Atoms and basic molecules are fully governed by quantum mechanics: This course will thus fully use your knowledge of QM-I/II to understand how atoms and molecules are built and interact with their surroundings.

Course outline

- 1) Motivation and Review: ~ 1 week
 - Why is AMO compulsory course?, brief review of QM-I/QM-II
- 2) Atoms: $\sim 4-5$ weeks
 - single e^- , Rydberg atoms, fine-/ hyperfine structure, Stark/Zeeaman effect, two and more e^- , periodic table, brief overview of advanced methods (HT, TF, DFT...).
- 3) Interactions of atoms with electromagnetic radiation: $\sim 3-4$ weeks
 - electronic transitions, line shapes and intensities, selection rules, scattering of light, absorption-spontaneous and stimulated emission of photons, Rabi oscillations.
- 4) Molecules: $\sim 4-5$ weeks
 - Born-Oppenheimer approximation, diatomic molecules, rotations and vibrations, polyatomic molecules, chemical bonds, spectroscopy
- 5) Frontiers of modern AMO physics¹: ~ 2 weeks
 - ultra-fast processes, HHG, femtosecond lasers, strong fields, Bose-Einstein condensates, laser cooling and trapping, atomic clocks, quantum simulation

¹time permitting

1.2 Review and Notation

- See QM text-books for much more complete review.
- Please ask *whenever anything* is unclear here, because these concepts are essential for the rest of the course.

1.2.1 Basic concepts of quantum-mechanics

Quantum states: Position space representation of free particle state (matter-wave)

$$\phi_k(\mathbf{r}) = A \exp [i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad \mathbf{r} \in \mathbb{R}^3, \quad \phi \in \mathbb{C}. \quad (1.1)$$

comments:

- Bold face symbols denote vectors, \cdot scalar product.
- Momentum $\mathbf{p} = \hbar \mathbf{k}$
- de-Broglie wavelength

$$\lambda_{\text{dB}} = \frac{\hbar}{|\mathbf{p}|} \quad (1.2)$$

- Frequency and energy

$$\omega_k = \frac{\hbar \mathbf{k}^2}{2m}, \quad E_k = \hbar \omega. \quad (1.3)$$

for a free particle of mass m .

- A : Normalisation factor, such that

$$\int_{\mathcal{V}} d^3\mathbf{r} |\phi_k(\mathbf{r})|^2 = 1, \quad (1.4)$$

where the integral runs over some finite quantisation volume \mathcal{V} .

Operators and Observables: Quantum mechanical *observables* are represented by *Hermitian operators* ($\hat{O} = \hat{O}^\dagger$), e.g.

Hamiltonian operator:

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2, \quad (1.5)$$

Momentum operator:

$$\hat{p} = -i\hbar \nabla_{\mathbf{r}}, \quad (1.6)$$

Reminder on Operators:

- linear mapping $\hat{O} : f \rightarrow g$, for f, g functions $\in \mathcal{H}$, \mathcal{H} Hilbert-space, space of normalizable functions with inner product/ norm.
Example: $(-i\hbar\nabla_{\mathbf{r}})[\exp(-x^2)] \rightarrow i\hbar 2x \exp(-x^2)$
- analogous to matrices, which are linear maps on your common vector spaces, e.g. \mathbb{R}^3 ,
 $M : \mathbf{v} \rightarrow \mathbf{w}$, $M\mathbf{v} = \mathbf{w}$
- in this analogy a function can be thought of as an ∞ -dimensional vector

Energy spectra Energy eigenstates $\phi_k(\mathbf{r})$ satisfy the *time-independent Schrödinger equation* (TISE)

$$\hat{H}\phi_k(\mathbf{r}) = E_k\phi_k(\mathbf{r}). \quad (1.7)$$

comments:

- e.g. $\phi_k(\mathbf{r})$ from Eq. (1.1) and \hat{H} from Eq. (1.5).
- A general quantum state $\Psi(\mathbf{r})$ can be written as *superposition* of eigenstates of the Hamiltonian (or any other Hermitian Operator)

$$\Psi(\mathbf{r}) = \sum_k c_k \phi_k(\mathbf{r}). \quad (1.8)$$

- Probability p_k to find/measure energy E_k is

$$p_k = \left| \int d^3\mathbf{r} \phi_k^*(\mathbf{r}) \Psi(\mathbf{r}) \right|^2 = |c_k|^2. \quad (1.9)$$

- Expectation value / mean value of E in the state $\Psi(\mathbf{r})$:

$$\bar{E} = \langle \hat{H} \rangle = \int d^3\mathbf{r} \Psi^*(\mathbf{r}) \hat{H} \Psi(\mathbf{r}) = \sum_k |c_k|^2 E_k. \quad (1.10)$$

More on states and operators: We can also use *abstract* quantum states (bra/ket) to write

$$\hat{H}|\phi_k\rangle = E_k|\phi_k\rangle \quad (1.11)$$

instead of Eq. (1.7). This leaves out the specification of a basis (or representation) for the quantum state. We can recover the usual **position space representation**

$$\phi_k(\mathbf{r}) = \langle \mathbf{r} | \phi_k \rangle \quad (1.12)$$

and **momentum space representation**

$$\tilde{\phi}_k(\mathbf{p}) = \langle \mathbf{p} | \phi_k \rangle. \quad (1.13)$$

through equally abstract position and momentum space bases $|r\rangle$ and $|p\rangle$.

Importantly, many operators do not commute, for example

$$[\hat{r}, \hat{p}] = \hat{r}\hat{p} - \hat{p}\hat{r} = i\hbar \neq 0. \quad (1.14)$$

In those cases the corresponding observables (here momentum and position) cannot be known (measured) simultaneously.

1.2.2 Orbital angular momentum and Spin

Orbital angular momentum The operator \hat{L} for orbital angular momentum is defined analogous to classical physics

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \quad (1.15)$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \quad (1.16)$$

Eigenstates $|l, m\rangle$ are defined by the angular momentum quantum number l and the one for the z-component m .

$$\hat{\mathbf{L}}^2|l, m\rangle = \hbar^2l(l+1)|l, m\rangle, \quad (1.17)$$

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle. \quad (1.18)$$

Spin Spin \hat{S} is an "abstract" angular momentum. That means it fulfills the angular momentum commutation relations

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k, \quad (1.19)$$

just like Eq. (1.16), but there is no underlying relation Eq. (1.15).

Spin-states $|s, m_s\rangle$ are defined analogously to orbital angular momentum.

$$\hat{\mathbf{S}}^2|s, m_s\rangle = \hbar^2s(s+1)|s, m_s\rangle, \quad (1.20)$$

$$\hat{S}_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle. \quad (1.21)$$

comments:

- The concept of spin arises naturally when doing *relativistic* quantum mechanics for charged particles.
- Most frequently we will encounter spin $s = \frac{1}{2}$ (e.g. electron spin), for which we use the short-hand symbols $|\uparrow\rangle = |s = \frac{1}{2}, m_s = \frac{1}{2}\rangle$ and $|\downarrow\rangle = |s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle$.
- It is frequently helpful to *add* different quantum mechanical angular momenta $\hat{\mathbf{L}}_1$ and $\hat{\mathbf{L}}_2$, such as orbital angular momentum and spin of the same electron, or two different spins, or orbital angular-momenta of two different particles.
- This is called **angular momentum coupling**. We define a total (or coupled) angular momentum operator

$$\hat{\mathbf{J}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 \quad (1.22)$$

(where one of the \hat{L} may in fact be a spin).

- This two-body problem could be described in a **separate / uncoupled basis**:

$$\hat{\mathbf{L}}_n^2 |l_1, m_1; l_2, m_2\rangle = \hbar^2 l_n(l_n + 1) |l_1, m_1; l_2, m_2\rangle, \quad (1.23)$$

$$\hat{L}_{z,n} |l_1, m_1; l_2, m_2\rangle = \hbar m_n |l_1, m_1; l_2, m_2\rangle, \quad n \in \{1, 2\}. \quad (1.24)$$

- Sometime is is advantageous to use a **combined / coupled angular momentum basis**:

$$\hat{\mathbf{J}}^2 |j, l_1, l_2, m_j\rangle = \hbar^2 j(j + 1) |j, l_1, l_2, m_j\rangle, \quad (1.25)$$

$$\hat{J}_z |j, l_1, l_2, m_j\rangle = \hbar m_j |j, l_1, l_2, m_j\rangle, \quad (1.26)$$

where j is the total *angular momentum quantum number*, and m_j the one for its z-component.

- One also finds relations how we can express one basis through the other one:

$$|j, l_1, l_2, m_j\rangle = \sum_{m_1, m_2} C_{l_1, l_2; m_1, m_2}^{j, m_j} |l_1, m_1, l_2, m_2\rangle. \quad (1.27)$$

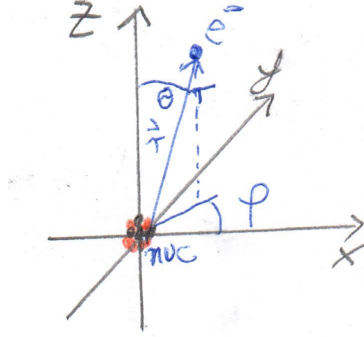
The coefficients $C_{l_1, l_2; m_1, m_2}^{j, m_j}$ are called *Clebsch-Gordan coefficients*. You can find out how to calculate them in your QM textbook or various online apps, e.g. <https://www.volya.net/index.php?id=vc>

- By using the definition Eq. (1.22) and angular momentum algebra, one can find the constraints on quantum numbers $l_1 + l_2 \geq j \geq |l_1 - l_2|$ and $m_j = m_1 + m_2$. This means all Clebsch-Gordan coefficients where these relations are not fulfilled will be equal to zero.

1.2.3 The Hydrogen(ic) atom

- Hydrogen-"ic": Like Hydrogen, but might have larger nuclear charge $q = Z|e|$. For example He^+ , with $Z = 2$.
- Covered in your QM courses, now also logical starting point for AMO course.

- Simplest atom and *only* analytically solvable one.
- Center of mass-frame: 3D problem, $\mathbf{r} \approx$ electron co-ordinate and $m \approx$ electron mass in the following. (reduced mass $m_{\text{red}} = m_e M / (m_e + M) \approx m_e$).



- Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}), \quad V(\mathbf{r}) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}|} \quad (1.28)$$

- Laplacian in 3D spherical co-ordinates r, θ, φ (using $r = |\mathbf{r}|$)

$$\nabla_{\mathbf{r}}^2 = \Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2}}_{= -\hat{\mathbf{L}}^2 / (\hbar^2 r^2)} \quad (1.29)$$

- Solve TISE (1.7) in 3D, using *separation of variables*, find

$$\hat{H} \phi_{nlm}(\mathbf{r}) = E_{nl} \phi_{nlm}(\mathbf{r}) \quad (1.30)$$

with Ansatz

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \underbrace{Y_{lm}(\theta, \varphi)}_{\text{spherical harmonics}} \quad (1.31)$$

- Spherical harmonics fulfill

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi), \quad (1.32)$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) = -i\hbar \frac{\partial}{\partial \varphi} Y_{lm}(\theta, \varphi) = \hbar m Y_{lm}(\theta, \varphi). \quad (1.33)$$

Thus they are the position space representation of angular momentum states, see Eq. (1.25).

Radial Schrödinger equation: Obtained by inserting Eq. (1.31) into Eq. (1.30)

$$\left\{ -\frac{\hbar^2}{2m} \left[\frac{1}{r} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \right] + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}}_{\equiv V_{\text{eff}}(r)} + V(r) \right\} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (1.34)$$

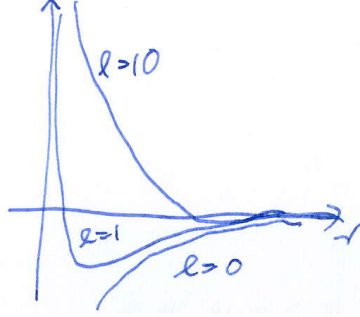


Figure 1.

left: $V_{\text{eff}}(r)$ contains the effect of a centrifugal force pushing the electron outwards, if $l > 0$.

Energy eigenstates of Hydrogen atom

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm} \quad \text{3D wavefunction} \quad (1.35)$$

$$R_{nl}(r) = \mathcal{N}_{nl}e^{-\rho/2}\rho^l L_{n-l-1}^{2l+1}(\rho) \quad \text{radial wavefunction.} \quad (1.36)$$

$$Y_{lm}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos[\theta])e^{im\varphi} \quad \text{angular wavefunction} \quad (1.37)$$

$$\rho = \frac{2Zr}{na_0} \quad \text{scaled radius} \quad (1.38)$$

$$\mathcal{N}_{nl} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \quad \text{normalisation factor} \quad (1.39)$$

$$L_a^b(\rho) \quad \text{generalised/associate Laguerre polynomials} \quad (1.40)$$

$$P_l^m(\cos[\theta]) \quad \text{generalised Legendre polynomial} \quad (1.41)$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e} = \frac{\hbar}{m_e c \alpha} \quad \text{Bohr radius } (\alpha \sim 1/137 \text{ fine-structure constant}). \quad (1.42)$$

Corresponding energy eigenvalues

$$E_{nl} = E_n = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 \hbar^2 n^2} = -Z^2 \frac{\mathcal{R}}{n^2}, \quad (1.43)$$

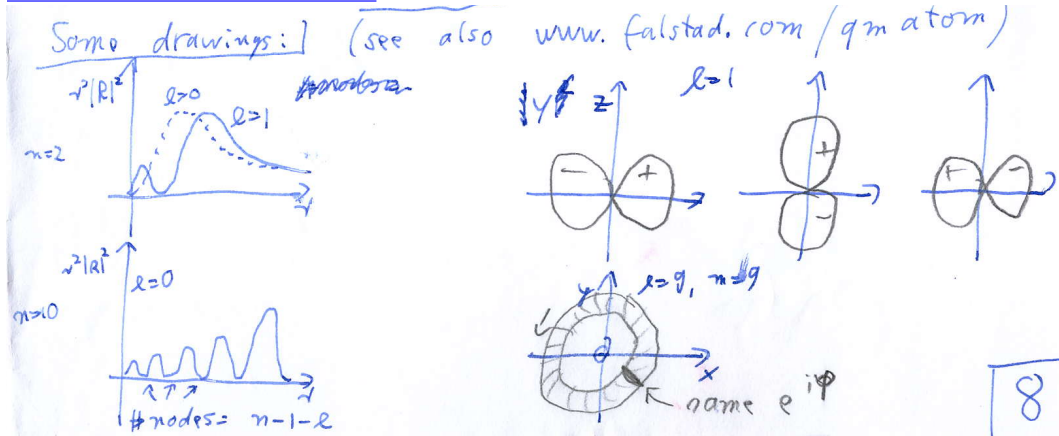
$$\mathcal{R} = \frac{m_e e^4}{8\epsilon_0^2 \hbar^2}, \quad \text{Rydberg constant} \quad (1.44)$$

Integer quantum numbers

- **principal** quantum number $n = 0, 1, 2, \dots \infty$
- **angular momentum** quantum number $l = 0, \dots n - 1$
- **azimuthal** quantum number $m = -l, \dots, l$
- (**electron spin** orientation $m_s = -\frac{1}{2}, \frac{1}{2}$)
- Note, we had earlier allowed quantum numbers nl for the energy, which would be used for

a general central potential $V(r)$. In the case of the Coulomb potential (or any precise $1/r$ form), there is an *accidental degeneracy* due to which energy does not in fact depend on l , see Eq. (1.43).

To leading (non-relativistic) order listed above, Hydrogen energies and spatial wave functions do not depend on spin. In chapter 2 we will see some small corrections due to spin. See also <http://falstad.com/qmatom/>



1.2.4 Quantum dynamics/ time-dependence

Time-dependent Schrödinger equation TDSE

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle. \quad (1.45)$$

- We can always write

$$|\Psi(t)\rangle = \sum_n c_n(t) |\phi_n\rangle, \quad (1.46)$$

where $|\phi_n\rangle$ is any orthonormal basis of our choice, and reduce (1.45) to a set of coupled ODEs for $i\hbar \frac{\partial c_n(t)}{\partial t} = \dots$.

- If the Hamiltonian is actually *time-independent* $\hat{H}(t) = \hat{H} = \text{const}$, we then have

$$|\Psi(t)\rangle = \sum_n c_n(0) \exp\left[-i \frac{E_n}{\hbar} t\right] |\phi_n\rangle, \quad (1.47)$$

where $|\phi_n\rangle$ are the eigenstates from Eq. (1.7) and $c_n(0) = \langle \phi_n | \Psi(0) \rangle$ are fixed by the initial conditions. *Self-test: show this in a few lines from Eq. (1.45) and Eq. (1.7).*

- If the Hamiltonian is fully time-dependent, the solution of Eq. (1.45) is generally difficult. We can use numerical calculations, e.g. based on (1.46), or perturbation theory.

1.2.5 Approximation methods

Time-independent perturbation theory (non-degenerate)

Let

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}', \quad (1.48)$$

where λ is a small parameter and the spectrum (eigenstates and eigenvectors) of \hat{H}_0 is known $\hat{H}_0 |\phi_k^{(0)}\rangle = E_k^{(0)} |\phi_k^{(0)}\rangle$ and *non-degenerate*.

We write the full eigen-energies and eigen-states of (1.48) as

$$\begin{aligned} E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \lambda^3 E_k^{(3)} + \dots \\ |\phi_k\rangle &= |\phi_k^{(0)}\rangle + \lambda |\phi_k^{(1)}\rangle + \lambda^2 |\phi_k^{(2)}\rangle + \lambda^3 |\phi_k^{(3)}\rangle + \dots, \end{aligned} \quad (1.49)$$

insert these expansions into the TISE (1.7) and solve order by order in λ

First order energy correction (non-degenerate PT)

$$E_k^{(1)} = \langle \phi_k^{(0)} | \hat{H}' | \phi_k^{(0)} \rangle. \quad (1.50)$$

- Beware, hidden danger!!: using this if $E_k^{(0)}$ is in fact degenerate gives *wrong results*. (See why in derivation in your QM course).

Time-independent perturbation theory (degenerate)

Let us assume $E_k^{(0)}$ is α -fold degenerate and label the unperturbed degenerate eigenfunctions $|\phi_{kr}^{(0)}\rangle$, for $r = 1, \dots, \alpha$. The perturbation \hat{H}' will in general *break the degeneracy*, yielding new eigenfunctions

$$|\chi_{kr}^{(1)}\rangle = \sum_s c_{ks} |\phi_{ks}^{(0)}\rangle. \quad (1.51)$$

New eigenfunctions and energy shifts are found from

Diagonalisation in degenerate subspace (degenerate PT)

$$\underline{\underline{H'}} \cdot \mathbf{c} = E_{kr}^{(1)} \mathbf{c}, \quad \text{the matrix } \underline{\underline{H'}} \text{ has elements } H'_{us} = \langle \phi_{ku}^{(0)} | \hat{H}' | \phi_{ks}^{(0)} \rangle \quad (1.52)$$

- The vector $\mathbf{c} = [c_{k0}, c_{k1}, \dots, c_{k\alpha}]^T$ (T means "transposed" of the vector) contains the coefficients that give the new eigenvector in Eq. (1.51).
- $\underline{\underline{H'}}$ is the perturbing Hamiltonian in the degenerate subspace.

Time-dependent perturbation theory

Now instead of (1.48) we start from

$$\hat{H}(t) = \hat{H}_0 + \lambda \hat{H}'(t), \quad (1.53)$$

thus assuming the unperturbed Hamiltonian \hat{H}_0 is still time-independent. We modify (1.47) to now include time-dependent weights of each part

$$|\Psi(t)\rangle = \sum_n c_n(t) \exp\left[-i \frac{E_n^{(0)}}{\hbar} t\right] |\phi_n\rangle, \quad (1.54)$$

again with a perturbation expansion

$$c_n(t) = c_n^{(0)} + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \lambda^3 c_n^{(3)}(t) + \dots \quad (1.55)$$

If we assume our system starts in state a , that means $c_n^{(0)} = \delta_{na}$, where δ is the Kronecker delta, then

First order time-dependent perturbation theory coefficients

$$\dot{c}_b^{(0)} = \frac{\partial}{\partial t} c_b^{(0)} = 0, \quad (1.56)$$

$$\dot{c}_b^{(1)} = \frac{\partial}{\partial t} c_b^{(1)} = (i\hbar)^{-1} \int_0^t dt' H'_{ba}(t') \exp[i\omega_{ba}t']. \quad (1.57)$$

- $\omega_{ba} = (E_b^{(0)} - E_a^{(0)})/\hbar$
- $H'_{ba}(t') = \langle \phi_b^{(0)} | \hat{H}'(t') | \phi_a^{(0)} \rangle$

Periodic perturbation

Lets look at a special case of (1.53) that will be important later:

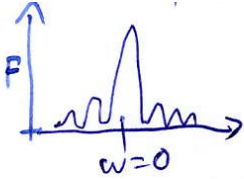
$$\lambda \hat{H}'(t) = \hat{A} \exp[i\omega t] + \hat{A}^\dagger \exp[-i\omega t]. \quad (1.58)$$

We are starting in a (since $c_n^{(0)} = \delta_{na}$ as before), then the transition probability $a \rightarrow b$ to first order PT will be given by

$$\begin{aligned} P_{ba}^{(1)}(t) &= |\lambda c_b^{(1)}(t)|^2 \\ &= \left| A_{ba} \left(\frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} + \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} + \hbar\omega} \right) \right. \\ &\quad \left. + A_{ba}^\dagger \left(\frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} - \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} - \hbar\omega} \right) \right|^2 \end{aligned} \quad (1.59)$$

Here $A_{ba} = \langle \phi_b^{(0)} | \hat{A} | \phi_a^{(0)} \rangle$. Now let us define the **detuning** $\hbar\Delta = |E_b^{(0)} - E_a^{(0)}| - \hbar\omega$, then

- for large detuning $P_{ba}^{(1)}(t) \ll 1$, since A_{ba} small and $P_{ba} \sim \left| \frac{A_{ba}}{\Delta} \right|^2$
- On resonance ($\Delta \approx 0$),
 $P_{ba}^{(1)}(t) = \frac{2}{\hbar^2} |A_{ba}|^2 F(t, \omega_{ba} \mp \omega)$, where the upper sign is in the absorbing case (second term, Eq. (1.59)), and the lower in the emitting case (first term). $F(t, \omega) = 2 \frac{\sin^2[\omega t/2]}{\omega^2}$.



1.2.6 Many particles

For each particle we have to add one set of co-ordinates and quantum numbers to the wave-function. Lets denote with

$$q = \{\mathbf{r}, m_s, \dots\} \quad (1.60)$$

the collection of all such variables. For $N = 2$ particles, we then have to write e.g. energy eigenstates $\phi_k(q_1, q_2)$, where the subscripts on q_j now number the particle j .

An exemplary Hamiltonian for two equal mass particles that interact (with interaction potential U) would be written as

$$\hat{H} = -\frac{\hbar^2}{2m} (\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2) + V(\mathbf{r}_1) + V(\mathbf{r}_2) + U(\mathbf{r}_1, \mathbf{r}_2). \quad (1.61)$$

- Quantum mechanically we *cannot distinguish* identical particles, while classically we might for example via their history, see box 1.
- Thus wave-function must be "equivalent" under exchange of two particles $\bullet 1 \leftrightarrow \bullet 2$ ($q_1 \leftrightarrow q_2$)
- This requirement leads to ...

Symmetry requirements for wave-functions of two indistinguishable particles

$$\Psi(q_1, q_2) = \pm \Psi(q_2, q_1) \quad (1.62)$$

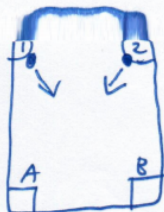
+ for **Bosons** (=integer spin)
 - for **Fermions** (=half-integer spin)

- Allocation to the spins is done in relativistic quantum mechanics (spin-statistics theorem).
- These symmetry properties only matter when particles try to share the *same space* (i.e. $0 < r_1, r_2 < L$, not $0 < r_1 < L$ and $3L < r_2 < 4L$).

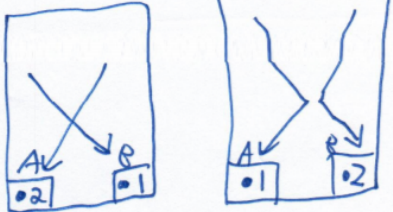
- Leads to
 - Pauli exclusion principle:** Two Fermions cannot be in the same quantum state. (i.e. position $\Psi(\mathbf{r}, \mathbf{r}) = 0$.)
 - Bose enhancement:** Bosons "like to be" in the same quantum state (see chapter 5).

Trajectories of indistinguishable particles (see Shankar p. 260)


Classical identical billiard balls



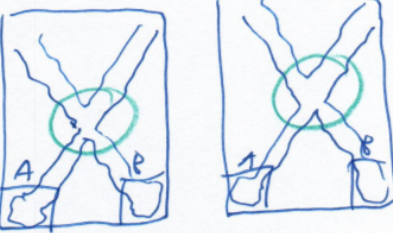
distinguish final states via history/trajectory



Quantum Mechanical



cannot distinguish via history



Box 1:

Week ②

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

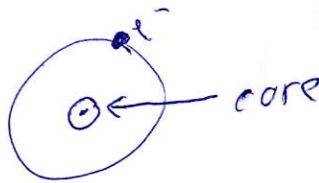
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2 Atoms

2.1 Single (active) electron Atoms

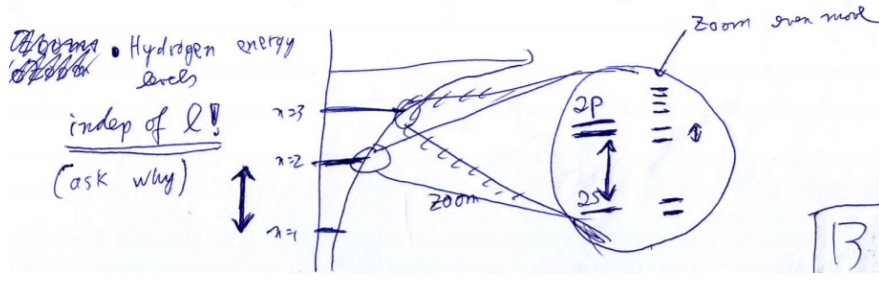
See section (1.2.3) for most basic : Hydrogen atoms

- Directly applies to Hydrogenic *atoms*:
 - deuterium ($pn+e^-$), tritium ($pnn+e^-$) (these are just heavier atoms due to nucleus, but the electron behaves the same).
- Next simplest are Hydrogenic *ions*
 He^+ , Li^{++} etc, here nuclear charge $Z>1$ in section 1.2.3
- Also almost applicable to Rydberg states of Alkali atoms,
 Li , Na , K , Rb , Cs (mainly their single valence electron is important)



Rydberg States ($n \gg 10$)

- In this chapter, we first take a more detailed look at spins, E/ B fields and relativistic corrections. In section 1.2.3 we had just added m_s quantum number without consequences.



2.1.1 Relativistic corrections, effect of spins, fine structure

- Spins arise naturally in *relativistic* Quantum Mechanics, hence they are part of "relativistic corrections".
- Calculations in section 1.2.3 are however fully non-relativistic, i.e. we use $\hat{H} = \frac{p^2}{2m}$ not

$$\hat{H} = \sqrt{p^2c^2 + m_0^2c^4}. \quad (2.1)$$

Fine Structure:

Start from relativistic wave-equation (Dirac Equation), expand for $v \ll c$ (electron velocity much less than speed of light) and get,

$$\hat{H} = \hat{H}_0 + \hat{H}'_{FS}, \quad (2.2)$$

where \hat{H}_0 is same as in section 1.2.3 for Hydrogen and,

$$\hat{H}'_{FS} = \hat{H}'_1 + \hat{H}'_2 + \hat{H}'_3. \quad (2.3)$$

Relativistic Corrections, fine-structure Hamiltonians

$$\hat{H}'_1 = -\frac{p^4}{8m^3c^2} \quad \text{relativistic correction to Kinetic Energy} \quad (2.4)$$

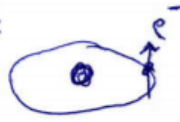
$$\hat{H}'_2 = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad \text{spin-orbit coupling} \quad (2.5)$$

$$\hat{H}'_3 = -\frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \delta(\mathbf{r}) \quad \text{Darwin term} \quad (2.6)$$

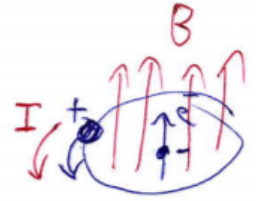
Comment on relativistic correction: Rather than from Dirac equation, \hat{H}'_1 can also be gotten directly by expanding Eq. (2.1) to $\mathcal{O}(p^4)$ and replacing kinetic energy $\hat{T} = \hat{p}^2/(2m)$ accordingly.

Comments on spin orbit coupling!

Atom "cartoon":



Rest
→
frame
of
e⁻



Comment on spin-orbit coupling:

Spin-energy?

- Let us work in the *rest-frame* of the electron, where the proton moves with velocity $-\mathbf{v}$ (where \mathbf{v} is the electron velocity in the lab-frame).
- The electron "sees" a positively charged proton orbiting itself and hence a magnetic field:

$$\mathbf{B} = -\frac{e\mu_0}{4\pi} \frac{\mathbf{v} \times \mathbf{r}}{r^3} \quad \left(\text{from } \mathbf{B} = \frac{\mu_0 q \mathbf{v} \times \hat{\mathbf{r}}}{4\pi r^2}, \text{ see E-dyn.} \right) \quad (2.7)$$

Now we use

$$\hat{H}_{mag} = -\hat{\mu} \cdot \mathbf{B} \quad \text{Energy of spin in magnetic field} \quad (2.8)$$

$$\hat{\mu} = -g_s \mu_b \hat{\mathbf{S}} / \hbar \quad \text{Electron magnetic moment} \quad (2.9)$$

$$\hat{H}_{mag} = +g_s \frac{\mu_b}{\hbar} \mathbf{B} \cdot \hat{\mathbf{S}} \quad \hat{\mu} \sim -\hat{\mathbf{S}} \text{ since } \mathbf{q} < \mathbf{0} \quad (2.10)$$

$$g_s \simeq 2 \quad \text{Gyromagnetic factor} \quad (2.11)$$

$$\mu_B = \frac{e\hbar}{2m_e} \quad \text{Bohr Magneton } e>0 \text{ here} \quad (2.12)$$

and then get:

$$\hat{H}_{mag} = g_s \underbrace{\frac{\mu_b}{\hbar}}_{=\frac{e}{2m_e}} \underbrace{\left(-\frac{\mu_0 e}{4\pi m_e} \frac{\mathbf{p} \times \mathbf{r}}{r^3} \right)}_{=\mathbf{B}} \cdot \hat{\mathbf{S}} \quad (2.13)$$

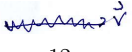
$$\stackrel{\mathbf{L}=\mathbf{r} \times \mathbf{p}}{=} \frac{g_s \mu_0 \epsilon_0}{2m_e^2} \underbrace{\frac{e^2}{4\pi \epsilon_0 r^3}}_{\frac{1}{r} \frac{dV(r)}{dr}} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = 2\hat{H}'_2. \quad (2.14)$$

This is (2.5) up to a factor of two, which is due to the e^- rest frame not being inertial, see Shankar.

Comments on Darwin term:

- Further consequence of relativistic QM is the existence of anti-particles (positrons, e^+). Can

have for time $\Delta E \Delta t \sim \hbar$. Vacuum fluctuations interact with e^- and cause

Zitterbewegung  (Amplitude $\frac{\hbar}{2m_e c} = \frac{\lambda_c}{2}$, freq = $\frac{2m_e c^2}{\hbar}$, where λ_c is the Compton wavelength, 2.4×10^{-12} m).

- Effectively smears out nuclear position, $\delta \rightarrow \emptyset$.
- This is the origin of Darwin term

Calculation of Energy Shift in Perturbation Theory, sketch:

- **term 1:** Relativistic correction: $\Delta E_1 = \langle \phi_{nlm} | \hat{H}'_1 | \phi_{nlm} \rangle$. See B&J book, we can use non-degenerate PT because \hat{H}'_1 is diagonal in l, m .
- **term 2:** We have to rewrite the second term (since \hat{H}'_2 does not commute with $\hat{\mathbf{L}}, \hat{\mathbf{S}}$).

Define Total angular momentum of electron (see section 1.2.2)

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (2.15)$$

New Eigenfunctions $|\phi_{n,l,j,m_j}\rangle$

$$\hat{\mathbf{J}}^2 |\phi\rangle = \hbar^2 j(j+1) |\phi\rangle, \quad (2.16)$$

$$\hat{J}_z |\phi\rangle = \hbar m_j |\phi\rangle. \quad (2.17)$$

With eigenvalues

$$j = \frac{1}{2} \quad (l = 0, s = \frac{1}{2}), \quad (2.18)$$

$$j = l \pm \frac{1}{2} \quad (l > 0, s = \frac{1}{2}). \quad (2.19)$$

For non-relativistic Hydrogen (without (2.4)-(2.6)), the states $|\phi_{nljm_j}\rangle$ are still degenerate in l, j, m_j , energy only depends on n .

Now write:

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (2.20)$$

Now we can again use non-degenerate Perturbation Theory (in coupled basis)

$$\Delta E_2 = \langle \phi_{nljm_j} | \hat{H}'_2 | \phi_{nljm_j} \rangle \quad (2.21)$$

$$= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - l(l+1) - \frac{3}{4} \right]. \quad (2.22)$$

Where $\frac{\hbar^2}{2}$ comes from $\frac{\mathbf{j}^2}{2}$ and we used the short hand $\hat{H}'_2 = \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and,

$$\langle \xi(r) \rangle = \int d^3r \phi_{nljm_j}^*(\mathbf{r}) \xi(\mathbf{r}) \phi_{nljm_j}(\mathbf{r}). \quad (2.23)$$

See B&J for detailed integration and result.

- **term 3:** Darwin term:

$$\Delta E_3 = \langle \phi_{nljm_j} | \hat{H}'_3 | \phi_{nljm_j} \rangle = \frac{\pi \hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} |\phi_{nljm_j}(0)|^2. \quad (2.24)$$

From Eq. (1.36) we see that this shifts $l = 0$ states only (others have $|\phi(0)|^2 = 0$).

Fine structure Energy Shifts: All terms together:

$$E_{n_j} = E_n \left(1 + \frac{(Z\alpha)^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right) \quad (2.25)$$

with E_n from Eq. (1.43).

- Here $\alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} \simeq \frac{1}{137}$ is again the fine structure constant.
- Now degeneracy of energy in j is lifted.
- Note $E_n < 0$, the sign of shift depends on n, j but is mostly towards lower energies.

2.1.2 Lamb-Shift

So far, even when discussing interactions of spins, we always used classical formulae for electric / magnetic fields and interaction potentials.

Fundamentally, electromagnetic-fields and their interactions are due to discrete quanta (photons), as described by *quantum electro-dynamics* (QED).

The resulting vacuum fluctuations of γ , e^+ , e^- cause a further,

Lamb Shift:

$$\Delta E_{\text{Lamb}} = \alpha^5 m_e c^2 \begin{cases} \frac{1}{4n^3} \left[k(n, l) \pm \frac{1}{\pi(j+\frac{1}{2})(l+\frac{1}{2})} \right] & \text{when } l \neq 0, j = l \pm \frac{1}{2} \\ \frac{1}{4n^3} k(n, 0) & \text{when } l = 0 \end{cases} \quad (2.26)$$

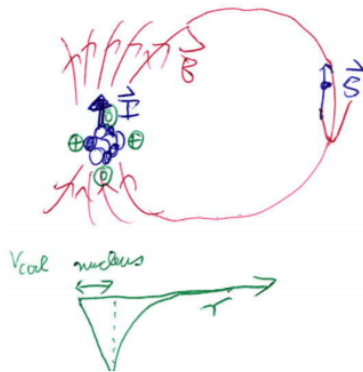
Here $k(n, l) < 0.05$ are small numerical constants.

- This lifts the degeneracy between s and p states (so might cause splitting not only shift)
- The Lamb-Shift or splitting is much *smaller* than the fine-structure splitting, see also section 2.1.4 later.

2.1.3 Hyperfine-structure

Some more details neglected so far that we will consider now:

- Nuclear spin, operator \hat{I} , quantum numbers I, m_I .
- Finite nuclear extension, hence correction to Coulomb potential at very short r (inside the nucleus).
- Due to finite nuclear extension, the nucleus can also have an electric quadrupole moment. However we will not discuss that case here and assume it vanishes, which is true for some nuclei. See Bransden/ Joachain for non-vanishing case.



left: Sketches of nuclear Quadrupole-moment, potential in the nucleus.

Let us write the Hamiltonian now as

$$\hat{H} = \hat{H}'_0 + \hat{H}'_{HFS}, \quad (2.27)$$

where \hat{H}'_0 already includes fine-structure effects ($\hat{H}'_0 = \hat{H}_0 + \hat{H}'_{FS}$, see Eq. (2.3)).

Hamiltonian of Hyperfine Interactions e.g. $l = 0$ electron, nucleus without quadrupole moment.

$$\hat{H}'_{HFS} = \frac{\mu}{4\pi} \frac{2}{\hbar^2} g_I \mu_B \mu_N \frac{1}{r^3} \left[\hat{\mathbf{L}} \cdot \hat{\mathbf{I}} - \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} + 3 \frac{(\hat{\mathbf{S}} \cdot \hat{\mathbf{r}})(\hat{\mathbf{I}} \cdot \hat{\mathbf{r}})}{r^3} \right] \quad (2.28)$$

- Here g_I is the nuclear g-factor ($g_I = -2 \dots 6$), that means:

- Nuclear magnetic moment $\hat{\mu}_N = g_I \mu_N \hat{\mathbf{I}}/\hbar$, c.f. Eq. (2.9)
- $\mu_N = 5 \times 10^{-27}$ J/T is the nuclear magneton, $\mu_N = (m_e/M_p)\mu_B \sim 5 \times 10^{-4}\mu_B$.
- $\hat{\mathbf{I}}$ is the nuclear angular momentum operator (contains proton and neutron spins and possibly orbital angular momentum of these).
- $\hat{r} = \mathbf{r}/r$.

We can again use perturbation theory. As for fine-structure, it will be useful to change to a coupled spin basis, using

Total Angular Momentum of the atom Is given as the sum of electron- and nuclear angular momenta.

$$\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}} \quad (2.29)$$

As for the other angular momentum operators, eigenstates and eigenvalues are given by

$$\hat{\mathbf{F}}^2|F, m_f\rangle = \hbar^2 F(F+1)|F, m_f\rangle, \quad (2.30)$$

$$\hat{F}_z|F, m_f\rangle = \hbar m_f|F, m_f\rangle, \quad (2.31)$$

with ranges

$$F = |I - J|, \dots, |I + J| \quad (2.32)$$

and

$$m_F = -F, \dots, F. \quad (2.33)$$

Treating Eq. (2.28) and corrections at $r = 0$ using perturbation theory (see book) we find the

Hyperfine energy-shift

$$\Delta E = \frac{\mu_0}{4\pi} 2g_I \mu_B \mu_N \frac{Z^3}{a_0^3 n^3} \left(\frac{m_{\text{red}}}{m_e}\right)^3 \frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} \quad (2.34)$$

$$= \frac{g_I}{2} [m_e c^2] \left(\frac{m_e}{M_p}\right) \frac{\alpha^4 Z^3}{n^3} \left(\frac{m_{\text{red}}}{m_e}\right)^3 \frac{F(F+1) - I(I+1) - j(j+1)}{j(j+1)(2l+1)} \quad (2.35)$$

Note: This uses SI units, BJ book uses atomic units (see later).

- After considering fine structure and Lamb shift, levels are already split according to their different values of j and l , and nuclear spin I is fixed for a given atom.
- Hence 2.34 now causes additional splitting into different allowed values of F in the range,

$$j + I \geq F \geq |j - I| \quad (2.36)$$

- Hyper-fine effects are, as the name suggests, again much smaller than the Lamb-shift, see also section 2.1.4

2.1.4 Hierarchy of level splittings

- Now that we have collected the most important corrections to atomic energy levels, let us estimate their relative strengths.
- We have (for $Z=1$).

$$E_{\text{base}} = -\frac{\alpha^2 [m_e c^2]}{2} \frac{1}{n^2} \sim \alpha^2 \quad (2.37)$$

$$\Delta E_{\text{fine}} = (\alpha)^2 E_{\text{base}} \mathcal{N}_{\text{fine}} \sim \alpha^4 [m_e c^2] \quad (2.38)$$

$$\Delta E_{\text{Lamb}} = \alpha^5 [m_e c^2] \mathcal{N}_{\text{Lamb}} \sim \alpha^5 [m_e c^2] \quad (2.39)$$

$$\Delta E_{\text{hyperfine}} \frac{gI}{2} [m_e c^2] \underbrace{\left(\frac{m_e}{M_p} \right)}_{5 \times 10^{-4}} \frac{\alpha^4}{n^3} \mathcal{N}_{\text{HFS}} \sim (5 \times 10^{-4}) \alpha^4 [m_e c^2] \quad (2.40)$$

from Eq. (1.43), Eq. (2.25), Eq. (2.26), Eq. (2.34), where we have only re-expressed some energy scales in terms of α and $m_e c^2$, and written \mathcal{N} for expressions that depend on quantum numbers and are of $\mathcal{O}(1)$.

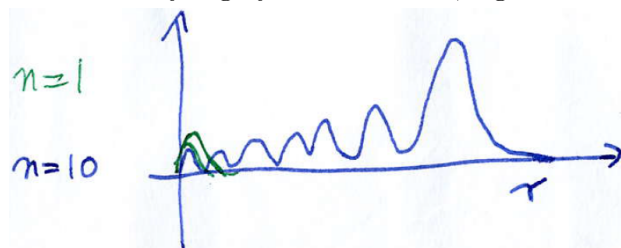
- Since $\alpha \ll 1$ and $5 \times 10^{-4} \ll \alpha$ we see the typical hierarchy already mentioned: Fine Structure > Lamb-Shift > Hyperfine Structure.

2.1.5 Alkali Rydberg atoms

Alkali atoms: Li, Na, K, Rb, Cs have a single valence electron above fully-filled electron shells, as we shall see in section 2.4.

Valence electrons are responsible for chemistry and visible spectra.

Consider very highly excited states, e.g. $n \gg 10$. These are called Rydberg States.



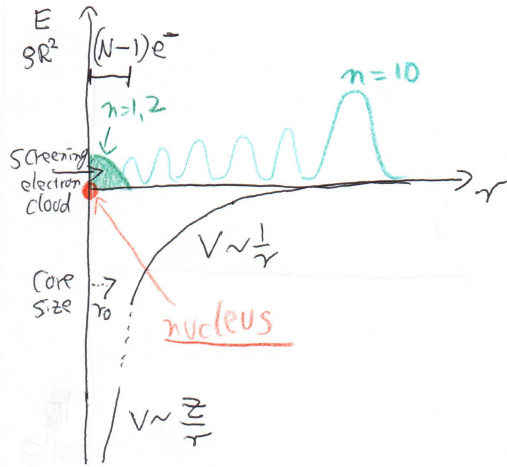
left: Sketch of $n = 1$ versus $n = 10$ radial probability density

Mean electron orbital radius

$$\langle \phi_{nlm} || \hat{\mathbf{r}} || \phi_{nlm} \rangle = a_0 \frac{n^2}{Z} \left(1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right). \quad (2.41)$$

Orbital radius roughly scales like $a_0 n^2$ ($l = 0, Z = 1$).

For, e.g. Li-atom with 3 electrons, two in (1s) and the outer one in (n=60):
 → Valence e^- much further out than others (we call the others + nucleus the atomic core).
 Let N be the number of electrons and Z the nuclear charge. The potential "seen" by the valence electron is as follows:



We can phenomenologically describe this by a modified Coulomb potential

$$V_{\text{eff}} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + U_d(r), \quad (2.42)$$

with $U_d(r) = 0$ for $r > r_0$ (outside the tiny atomic core).

A possible choice is $U_d(r) = -e^2/(4\pi\epsilon_0)[(Z-1)e^{-a_1 r} - r(a_3 + a_4 r)e^{-a_2 r}]$.

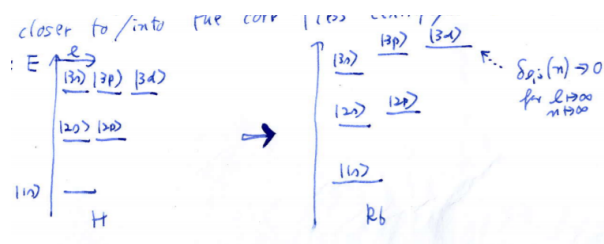
Using this effective potential $V(r) = V_{\text{eff}}$ we can again solve Eq. (1.34) radial SE \Rightarrow get slightly different energies compared to Hydrogen.

Energy levels for Alkali Rydberg atoms ($Z=1$)

$$E = -\frac{R_y}{(n - \delta_{l,j}(n))^2} \quad (2.43)$$

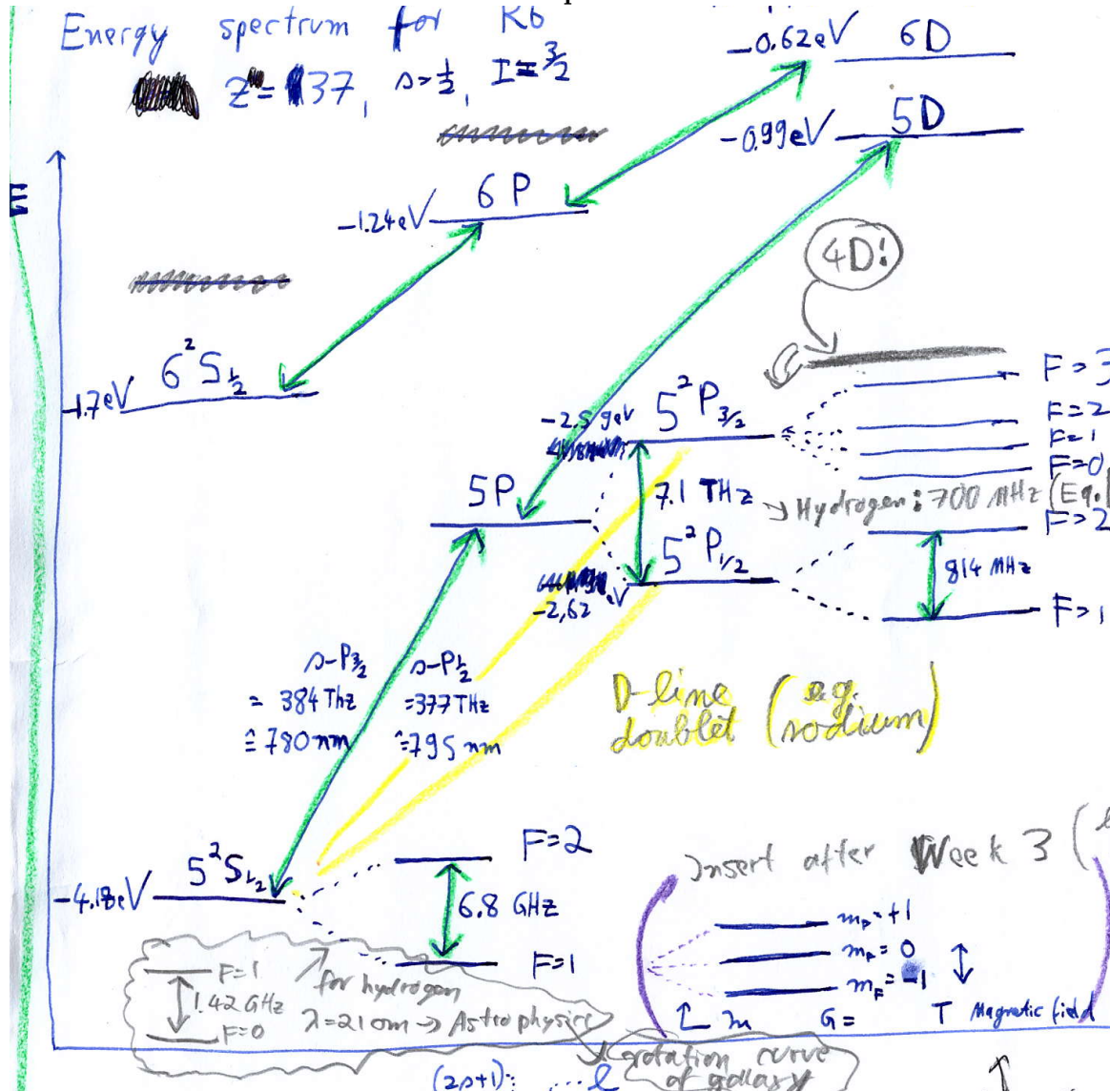
Where $\delta_{l,j}$ includes fine-structure and, $\delta_{l,j} =$ quantum defect (due to $U_d(r)$)

- The lower the l the higher the quantum defect, since $\phi_{n,l,m}(r)$ reaches closer to/ into the core (less centrifugal barrier)



- We will see these features over and over again for multi-electron systems.

Alkali spectra:



top: Energy spectrum for Rb⁸⁷, $Z = 37, s = \frac{1}{2}, I = \frac{3}{2}$

Example 1. • Courtesy Daniel A. Steck <http://www.steck.us/alkalidata/> .

- Spectroscopic Notation $|n^{(2s+1)l_j}\rangle$, e.g. $|5^2s_{1/2}\rangle$ means $|n = 5, s = 1/2, l = 0, j = 1/2\rangle$. Very important to understand literature or exam questions!!!!
- Energy splittings in Hz: $\Delta E = h\nu$. (ν frequency in Hertz).
- Energy splittings in nm: $\nu\lambda = c$.
- also see: <https://www.nist.gov/pml/atomic-spectra-database> .

Week ③

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

2.2 Interaction of one electron atoms with static electric and magnetic fields

Useful for: Probing, trapping, and controlling atoms

Probing fields

2.2.1 The Stark effect: (Electric fields)

Hamiltonian for electron in both electric field of core and external field:

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}}^{\hat{H}_0} + \overbrace{e\mathbf{E}\cdot\mathbf{r}}^{\hat{H}'}. \quad (2.44)$$

- Let us assume $\mathbf{E} = E_0\hat{\mathbf{k}}$ (along z-axis) and constant across atom.
- Hamiltonian (2.44) assumes \mathbf{E} -field strong enough for fine-structure to be negligible.
- TISE Eq. (1.7) can still be fully solved analytically without perturbation theory, exploiting the cylindrical symmetry around the direction of \mathbf{E} and using parabolic coordinates. *see BJ book.*
- Here, we use the approach of perturbation theory, splitting the Hamiltonian into $\hat{H}_0 + \hat{H}'$.

Linear Stark effect:

First order energy shift of a state $|nlm\rangle$ from Eq. (1.50)

$$\Delta E = e\mathbf{E} \cdot \langle\phi_{nlm}|\mathbf{r}|\phi_{nlm}\rangle = 0 \quad \forall nlm. \quad (2.45)$$

- You derived this in assignment 1. The simplest way to show it, is by remembering the symmetry of spherical harmonics under a parity operation: $Y_{lm}(\mathbf{r}) = (-1)^l Y_{lm}(-\mathbf{r})$, thus they are either symmetric or anti-symmetric. Then

$$\begin{aligned}
e\mathbf{E} \cdot \langle \phi_{nlm} | \mathbf{r} | \phi_{nlm} \rangle &= e\mathbf{E} \cdot \int d^3\mathbf{r} |R_{nl}(\mathbf{r})|^2 |Y_{lm}(\mathbf{r})|^2 \mathbf{r} \\
&\stackrel{\tilde{\mathbf{r}} = -\mathbf{r}}{=} e\mathbf{E} \cdot \int d^3\tilde{\mathbf{r}} |R_{nl}(-\tilde{\mathbf{r}})|^2 |Y_{lm}(-\tilde{\mathbf{r}})|^2 (-\tilde{\mathbf{r}}) \\
&= e\mathbf{E} \cdot \int d^3\tilde{\mathbf{r}} |R_{nl}(\tilde{\mathbf{r}})|^2 |(-1)^l Y_{lm}(\tilde{\mathbf{r}})|^2 (-\tilde{\mathbf{r}}) \\
&\stackrel{\text{rename } \tilde{\mathbf{r}} \rightarrow \mathbf{r}}{=} -e\mathbf{E} \cdot \langle \phi_{nlm} | \mathbf{r} | \phi_{nlm} \rangle.
\end{aligned} \tag{2.46}$$

The only way for this to be true is if the integral vanishes.

- Caution: We cannot apply Eq. (1.50) if states are degenerate. So the result that the first order shift $\Delta E = 0$ is valid for $|100\rangle$ only.
- For other state we need to think again, using Eq. (1.52) for degenerate perturbation theory.

So fix $n = n_o$ and write $\langle \phi_{n_o l m} | e\mathbf{E} \cdot \mathbf{r} | \phi_{n_o l' m'} \rangle \rightarrow \underline{\underline{H'}}$ as a matrix.
e.g. for $n_o = 2$, Eq. (1.52) becomes

$$\begin{pmatrix} 0 & 0 & H'_{00} & 0 \\ 0 & 0 & 0 & 0 \\ H'_{00} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} C_{200} \\ C_{21-1} \\ C_{210} \\ C_{211} \end{pmatrix} = E_{n=2}^{(1)} \begin{pmatrix} C_{200} \\ C_{21-1} \\ C_{210} \\ C_{211} \end{pmatrix}. \tag{2.47}$$

(see also later chapter-3, dipole selection rules)

- We can use (2.46) to quickly eliminate all diagonal entries, but have to look now at non-diagonal matrix-elements:

$$\begin{aligned}
e\mathbf{E} \cdot \langle \phi_{n_o l m} | \mathbf{r} | \phi_{n_o l' m'} \rangle &= eE_0 \langle \phi_{n_o l m} | r \cos \theta | \phi_{n_o l' m'} \rangle \\
&= eE_0 \tilde{\mathcal{N}} \int_0^\infty r^2 R_{n_o l}(r) r R_{n_o l'}(r) \underbrace{\int_0^\pi d\theta \sin[\theta] P_l^m(\cos[\theta]) P_{l'}^{m'}(\cos[\theta])}_{\sim \delta_{l(l' \pm 1)}} \underbrace{\int_0^{2\pi} d\varphi e^{i(m'-m)\varphi}}_{\sim \delta_{mm'}},
\end{aligned} \tag{2.48}$$

where \mathcal{N} is just the collection of all normalisation factors from (1.36)-(1.37).

- We now see $eE_0 \langle \phi_{n_o l m} | r \cos \theta | \phi_{n_o l' m'} \rangle \sim \delta_{l'l' \pm 1} \delta_{mm'}$. (obtained by explicit integration or realizing that \hat{H}' is odd under parity, and $[\hat{H}', \hat{L}_z] = 0$)
- The only non-zero matrix element is thus $H'_{00} = eE_0 \langle \phi_{200} | r \cos \theta | \phi_{210} \rangle = -3ea_o E_o$. (*do this explicitly as an exercise, like for assignment 1*)

Linear Stark effect: After diagonalisation, we obtain the following picture

$$(2.49)$$

- Note that the energy shift $|E^{(1)}|$ came about in first order PT and is $\sim E_0$, hence there in fact is a first order (linear) energy shift for degenerate states. *Note: This is an example where the invalid application of degenerate PT clearly gives the wrong result.*

Non-linear Stark effect: For non-degenerate states (in Hydrogen only $|100\rangle$), we have to go to second order perturbation theory to get a non-vanishing Stark effect

$$\Delta E_{100}^{(2)} = \sum_{n \neq 1, l, m} \frac{|\langle \phi_{nlm} | eE_0 z | 100 \rangle|^2}{E_{100} - E_{nlm}}. \quad (2.50)$$

- Technically $|\phi_{nlm}\rangle$ includes continuum (unbound states), let's ignore these for now.
- As in Eq. (2.47), all matrix elements $|\langle \phi_{n10} | eE_0 z | 100 \rangle|^2$ will be non-zero. Also $E_{100} - E_{n10} < 0$ for all n .

We then deduce $\Delta E_{100}^{(2)} < 0$ and $\sim (eE_0)^2 \implies$ quadratic stark effect.

Interpretation of both variants of the Stark effect: Non-degenerate states do not possess any permanent dipole moment (see assignment-1). However, the external field can induce one $\sim E$, which then in turn interacts with the field $\sim E^2$. In contrast, out of degenerate states you can form superpositions (that are also energy eigenstates), which do have a non-vanishing dipole moment, such as $|\Psi\rangle = (|ns0\rangle + |np0\rangle)/\sqrt{2}$, for which you did this in assignment 1. That's why we get a first order shift here.

2.2.2 The Zeeman effect (Magnetic fields)

Hamiltonian for electron in electric field of core and external magnetic field:

$$\hat{H} = \overbrace{\frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - \frac{Ze^2}{4\pi\epsilon_0 r}}^{\text{see electro-dynamics}} + \overbrace{\frac{g_s\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S} + \zeta(r)\mathbf{L} \cdot \mathbf{S}}^{\text{added a in section 2.1.1}}. \quad (2.51)$$

- For interaction of e^- spin \hat{S} with field, see Eq. (2.8).

Classical vector potential:

$$\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \text{ for a constant B-field.} \quad (2.52)$$

Insert \mathbf{A} , \mathbf{p} and lots of vector calculus (see book)

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m}\nabla^2}^{\hat{H}_a} - \overbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}^{\hat{H}_b} + \overbrace{\zeta(r)\mathbf{L} \cdot \mathbf{S}}^{\hat{H}_c} + \overbrace{\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S})\mathbf{B}}^{\hat{H}_d} + \overbrace{\frac{e^2}{8m}(\mathbf{B} \times \mathbf{r})^2}^{\hat{H}_e}. \quad (2.53)$$

For \hat{H}_c and \hat{H}_d , see Eq. (2.5) and Eq. (2.8) respectively.

Let $\mathbf{B} = B_0\hat{\mathbf{k}}$ (along z -axis).

Now analyze Eq. (2.53) with perturbation theory depending on relative importance of terms $a - e$, which depends on the state to be perturbed $|\phi_{nlm}\rangle$ and the magnetic field strength $|\mathbf{B}|$.

Linear Zeeman effect: (strong B -field)

- Energy due to magnetic field is large compared to fine-structure.

First neglect \hat{H}_c and \hat{H}_e . Then, $\hat{H}_0 = \hat{H}_a + \hat{H}_b + \hat{H}_d$.

The first two just constitute the usual Hydrogen Hamiltonian Eq. (1.28) and the last part

$$\hat{H}_d = \frac{\mu_B}{\hbar}B_0(\hat{L}_z + 2\hat{S}_z)$$

can be expressed in terms of angular momentum z -components (and thus commutes with $\hat{\mathbf{L}}^2$, \hat{S}_z , $\hat{\mathbf{S}}^2$, \hat{S}_z . So, $|\phi_{nlm_l}\rangle \otimes |sm_s\rangle$ of Eq. (1.35) are already eigenfunctions of \hat{H} in Eq. (2.53), solving

$$\hat{H}_0|\phi_{nlm_lsm_s}\rangle = E_{nm_lsm_s}|\phi_{nlm_lsm_s}\rangle.$$

to obtain

Zeeman-shifted energies

$$E_{nm_l m_s} = \overbrace{E_n}^{\text{see Eq. (1.43)}} + \mu_B B_0 (m_l + 2m_s), \quad m_s = \pm \frac{1}{2}. \quad (2.54)$$

Interpretation: \mathbf{L} and \mathbf{S} decouple in B -field and align to it separately.

Paschen-Back effect: (medium B -field)

We now add spin-orbit coupling $\hat{H}' = \hat{H}_c = \zeta(r)\mathbf{L} \cdot \mathbf{S}$ as a perturbation.

- This is for slightly lower fields.

Can use non-degenerate perturbation theory Eq.(1.26) (see book for subtle reasons) to find

$$\Delta E = \langle \phi_{nlm_l m_s} | \hat{H}' | \phi_{nlm_l m_s} \rangle \quad (2.55)$$

$$= \langle \phi_{nlm_l m_s} | \zeta(r) (\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z) | \phi_{nlm_l m_s} \rangle. \quad (2.56)$$

Use

Raising and lowering operators (BJ book 2.185)

$$\begin{aligned} \hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y &\implies \hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2 \\ \hat{L}_y &= -i(\hat{L}_+ - \hat{L}_-)/2 \end{aligned} \quad (2.57)$$

$$\hat{L}_\pm |lm\rangle = \hbar[l(l+1) - m(m \pm 1)]^{1/2} |l(m \pm 1)\rangle$$

to see that the first two terms in Eq. (4.4) vanish and thus

$$\Delta E = \langle \phi_{nlm_l m_s} | \zeta(r) \underbrace{\hat{L}_z \hat{S}_z}_{= \hbar^2 m_l m_s} | \phi_{nlm_l m_s} \rangle = \lambda_{nl} m_l m_s \quad (2.58)$$

with $\lambda_{nl} = \hbar^2 \int_0^\infty dr r^2 [R_{nl}(r)]^2 \zeta(r) = -\frac{\alpha^2 Z^2}{n} \frac{E_n}{[l(l+\frac{1}{2})(l+1)]}$; $l \neq 0$.

- Now shift dependent on l (unlike Eq. (2.54)).

Anomalous Zeeman effect: (weak B -field, most common case)

- The name "anomalous" is historical.
- We now consider

$$\hat{H}_o = \hat{H}_a + \hat{H}_b + \hat{H}_c \text{ with } \hat{H}' = \hat{H}_d \text{ (still neglect } \hat{H}_e)$$

Eigenstates of \hat{H}_o are the same as for fine-structure (section 2.1.1). Can expand total angular momentum states in terms of orbital angular momentum and spin states as section 1.2.2.

$$|j, l, s, m_j\rangle = \sum_{m_l, m_s} \underbrace{\langle l, s, m_l, m_s | j, l, m_j \rangle}_{\equiv C_{l, s; m_l, m_s}^{j, m_j}} |l, s, m_l, m_s\rangle,$$

where $C_{l, s; m_l, m_s}^{j, m_j}$ are **Clebsch-Gordan coefficients** (cgc), see section 1.2.2.

Using the coupled j basis as for fine-structure, let us first evaluate the easy part:

$$\begin{aligned} \Delta E &= \langle \phi_{njl m_j} | \frac{\mu_B}{\hbar} (\hat{J}_z + \hat{S}_z) B_o | \phi_{njl m_j} \rangle \\ &= \mu_B m_j B_o + \frac{\mu_B B_o}{\hbar} \langle \phi_{njl m_j} | \hat{S}_z | \phi_{njl m_j} \rangle. \end{aligned} \quad (2.59)$$

Now we need some cgc, but we only look at $s = \frac{1}{2}$, so $j = l \pm \frac{1}{2}$. Then

$$\begin{aligned} \left| \left(j = l + \frac{1}{2} \right), l, s, m_j \right\rangle &= \sqrt{\frac{l + m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2} \right\rangle \\ &\quad + \sqrt{\frac{l - m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2} \right\rangle \end{aligned} \quad (2.60)$$

and

$$\begin{aligned} \left| \left(j = l - \frac{1}{2} \right), l, s, m_j \right\rangle &= -\sqrt{\frac{l - m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2} \right\rangle \\ &\quad + \sqrt{\frac{l + m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2} \right\rangle. \end{aligned} \quad (2.61)$$

We now use these two expressions in Eq. (2.59) and simplify to get

Anomalous Zeeman shift

$$\Delta E = g \mu_B m_j B_o, \quad (2.62)$$

with Landé g -factor

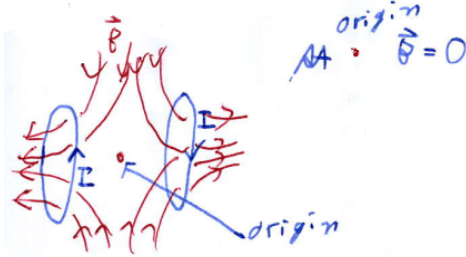
$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$

So the number of split energy levels is now given by the number of different values for m_j .

- Even stronger fields than for Eq. (2.54) \implies Treat \hat{H}_e , even neglect \hat{H}_b (**Landau levels**).
- Even weaker fields than for Eq. (2.62) \implies Consider hyperfine-structure (**Breit-Rabi equation**).

Example-(1) for section section 2.2: Magnetic trapping

Consider double anti-Helmholtz coil (quadrupole trap) with current I .



This is designed to have a local minimum of the magnetic field strength $|\mathbf{B}(\mathbf{x})|$ at the origin. Assume a single atom is in $m_j = \frac{1}{2}$. According to Eq. (2.62) its energy is

$$\Delta E = g_s \mu_B m_j |\mathbf{B}(\mathbf{x})| \quad (2.63)$$

This energy shift increases everywhere from origin \implies atom can be trapped at origin.

Q: Can one magnetically trap $m_j < 0$ states?

Caution: Typical magnetic traps have so weak fields that we need to look at the Zeeman effect of hyperfine-structure, roughly similar to Eq. (2.62) with $m_j \rightarrow m_F$.

Example-(2) for section section 2.2: (see online code "zeeman_effect_of_finestructure.m")

From strong to weak fields: The energy shifts in Eq. (2.54) and Eq. (2.62), valid for different regimes of magnetic field strengths, depend on different quantum numbers. How does the transitions happen for intermediate magnetic fields?

Let us consider hydrogen $|2p\rangle$, with spin we have $2p_{\frac{1}{2}}, p_{\frac{3}{2}}$.

Use coupled basis $A = \{|2p_{\frac{3}{2}}, m_j = \frac{3}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |2p_{\frac{1}{2}}, m_j = \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\}$.

In matrix form

$$\hat{H}_{FS(Fine-Structure)} = \begin{pmatrix} E_{3/2} & 0 & 0 & 0 & 0 & 0 \\ 0 & E_{3/2} & 0 & 0 & 0 & 0 \\ 0 & 0 & E_{3/2} & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{3/2} & 0 & 0 \\ 0 & 0 & 0 & 0 & E_{1/2} & 0 \\ 0 & 0 & 0 & 0 & 0 & E_{1/2} \end{pmatrix}_{Basis-A}$$

The energy terms on the diagonal follow from Eq. (2.25).

Example-(2) contd.: The effect of the magnetic field is easier to capture in the uncoupled basis $B = \{|2p_1, m_l = \frac{1}{2}\rangle, |0, \frac{1}{2}\rangle, |-1, \frac{1}{2}\rangle, |1, -\frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle, |-1, -\frac{1}{2}\rangle\}$, using part d of Hamiltonian Eq. (2.53), which gives

$$\hat{H}_d = \frac{\mu_B B_0}{\hbar} \begin{pmatrix} \hbar(1 + 2 \cdot \frac{1}{2}) & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\hbar \end{pmatrix}_{\text{Basis}-B}.$$

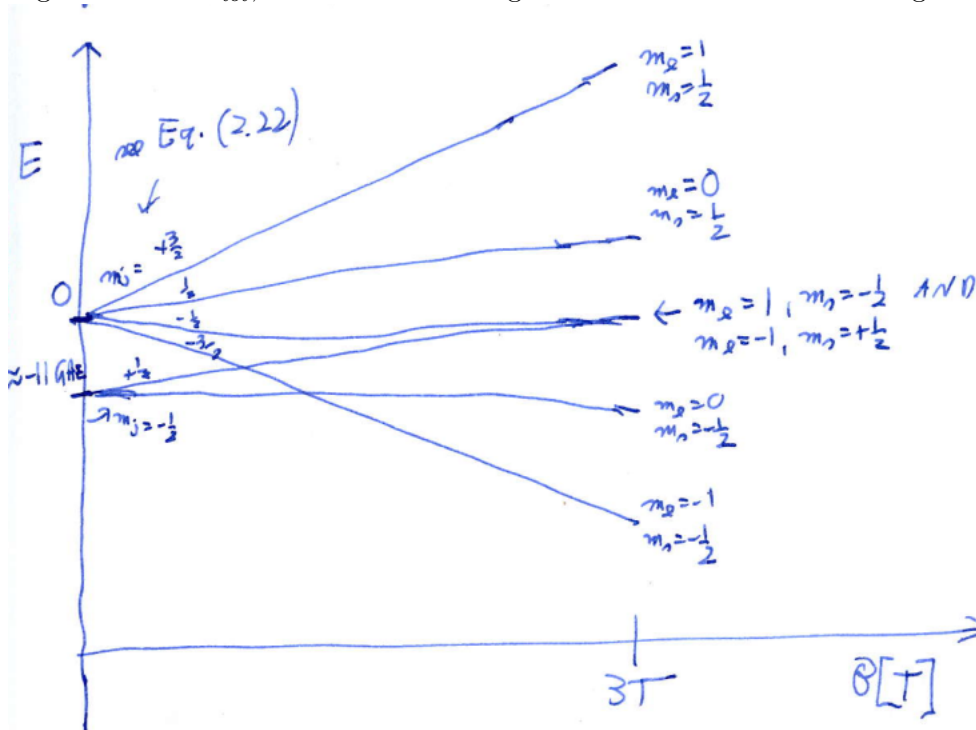
Here the energy terms on the diagonal follow from Eq. (2.53), part d .

To write it all into one matrix we perform a basis transform on the latter part, thus Now,

$$\hat{H}_{tot} = \hat{H}_{fs} + \hat{U}^\dagger \hat{H}_d \hat{U},$$

where \hat{U} is the unitary matrix converting from A to B .

Eigenvalues of \hat{H}_{tot} , from numerical diagonalisation as a function of magnetic field strength:



Week ④

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

2.3 Two Electron Atoms

These include, e.g., $\underbrace{H^-}_{Z=1}$, $\underbrace{He}_{Z=2}$, $\underbrace{Li^+}_{Z=3}$

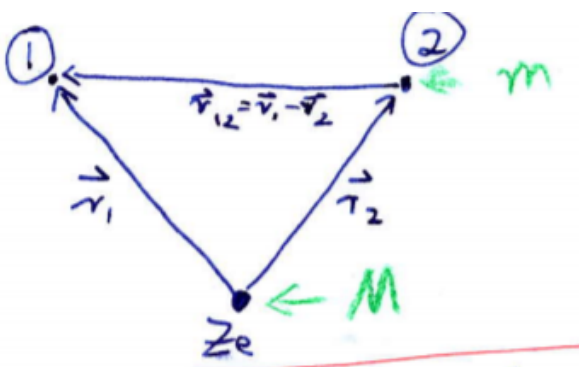
Important because they are the simplest atoms where we see the Pauli Exclusion Principle at work (see Eq. (1.62)) and can introduce essential approximation techniques. We cannot solve any two e^- problems exactly analytically.

2.3.1 The Schrödinger Equation for two-electron atoms

We need co-ordinates for both electrons now, see diagram below.

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \quad (2.64)$$

$$r_1 = |\mathbf{r}_1| \quad (2.65)$$



In terms of these we write the

TISE (see Eq. (1.7)) for the Helium problem

$$\underbrace{\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}_1}^2 - \frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}_2}^2 - \frac{\hbar^2}{M} \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_2} - \frac{Ze^2}{(4\pi\epsilon_0)r_1} - \frac{Ze^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right]}_{\equiv \hat{H}_{hel}} \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \quad (2.66)$$

- $\mu = \frac{m_e M}{m_e + M}$ is reduced mass of the electron, m_e electron mass, M nuclear mass. (We used $\mu = m_e$ for $M \rightarrow \infty$ in section 1.2.3)
- Mass polarisation term $\nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_2}$ comes from separation of centre of mass coordinate. It vanishes for $M \rightarrow \infty$.

From now on, use atomic units:

$$\hbar = 1 \quad \frac{1}{4\pi\epsilon_0} = 1 \quad e = 1 \quad \underbrace{m}_{\text{electron mass}} = 1 \quad (2.67)$$

(then hydrogen energy $E_{nlm} = -\frac{1}{2n^2}$ (see Eq. (1.43)) and $a_0 = 1$)

- The Hamiltonian is symmetric with respect to particle **position** interchange operator

$$P_{12} : \mathbf{r}_1 | \mathbf{r}_2 \longrightarrow \mathbf{r}_2 | \mathbf{r}_1 \quad (2.68)$$

\Rightarrow Also eigen-functions must have this symmetry [=be eigenfunction of P_{12}]

$$\Rightarrow \psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1) \quad (2.69)$$

- Note, this is not the same as the complete particle exchange operation used in writing Bose/Fermi symmetries Eq. (1.62), where we have to swap all properties, not just position.

There are two types of two electron states

Para States, wave functions spatially symmetric:

$$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = \psi_+(\mathbf{r}_2, \mathbf{r}_1) \quad (2.70)$$

Ortho States, wave functions spatially anti-symmetric:

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1) \quad (2.71)$$

2.3.2 Spin Wave functions and Pauli Exclusion Principle

- Now we add electron spin into the picture, it becomes essential now, not jut a small perturbation as for Hydrogen.
- e^- are fermions, total state must be anti-symmetric under $1 \leftrightarrow 2$
- Possible spin states for two electrons are: $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$, see section 1.2.2.
- Useful to move to coupled spin basis, where $\hat{S} = \hat{s}_1 + \hat{s}_2$, see also section 1.2.2.

We find

Spin pair states

$$|S = 0, m_S = 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad \begin{array}{l} \text{Anti-symmetric} \\ \text{spin singlet} \end{array} \quad (2.72)$$

$$|S = 1, m_S = -1\rangle = |\downarrow\downarrow\rangle \quad \text{Symmetric} \quad (2.73)$$

$$|S = 1, m_S = 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad \text{spin triplet} \quad (2.74)$$

$$|S = 1, m_S = 1\rangle = |\uparrow\uparrow\rangle \quad (2.75)$$

Solutions to the helium problem have to satisfy Eq. (2.70)-(2.71) (spatial symmetry) and Eq. (1.62) (total fermionic symmetry). Thus all allowed solutions can be written as

$$\psi(q_1, q_2) = \psi_+(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (\text{Para}) \quad (2.76)$$

$$\psi(q_1, q_2) = \psi_-(\mathbf{r}_1, \mathbf{r}_2) \begin{cases} |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\uparrow\uparrow\rangle \end{cases} \quad (\text{Ortho}) \quad (2.77)$$

- Despite not actually appearing explicitly in the Hamiltonian of (2.66), the total spin dictates which spatial symmetry the solution must have!

2.3.3 Approximate methods for 2 electron groundstate wavefunction

So far we only classified solutions according to spin and spatial symmetry, we yet have to actually determine the symmetric and anti-symmetric eigen functions $\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2)$

Lets split $\hat{H}_{hel} = \hat{H}_0 + \hat{H}'$ again, where (in atomic units, abbreviated a.u.)

$$\hat{H}_0 = -\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} \quad \hat{H}' = \frac{1}{r_{12}} \quad (2.78)$$

Note: Atomic units save a lot of writing!

We see that the unperturbed eigen-problem $\hat{H}_0\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = E^{(0)}\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ is solved by the product Ansatz:

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{nlm}(\mathbf{r}_1)\phi_{n'l'm'}(\mathbf{r}_2), \quad (2.79)$$

$$E^{(0)} = E_{nlm} + E_{n'l'm'}, \quad (2.80)$$

with ϕ_{nlm} and E_{nlm} given by Hydrogen solutions ((1.35) and (1.43)).

- Note, that for every energy $E^{(0)}$, the wavefunctions with swapped indices: $\phi_{n'l'm'}(\mathbf{r}_1)\phi_{nlm}(\mathbf{r}_2)$ are an equally valid solution. This is called \Rightarrow exchange degeneracy.
- This allows us now to construct solutions satisfying Eq. (2.70)-(2.71), namely

Zero'th order approximation for Helium wavefunctions

This is also called independent particle model

$$\psi_{\pm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_{nlm}(\mathbf{r}_1)\phi_{n'l'm'}(\mathbf{r}_2) \pm \phi_{n'l'm'}(\mathbf{r}_1)\phi_{nlm}(\mathbf{r}_2)] \quad (2.81)$$

Where $+$ = Para, and $-$ = Ortho. Only for Para states $\{n', l', m'\} = \{n, l, m\}$ is possible, then $\psi_{+}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{nlm}(\mathbf{r}_1)\phi_{nlm}(\mathbf{r}_2)$.

- Gives ground-state energy of Helium: $E_{100,100}^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{1^2} + \frac{1}{1^2} \right) = -Z^2 \stackrel{\text{He}}{=} -4$
(Para only)

So far we have completely ignored electron-electron interactions in \hat{H}' , let's rectify this now:
PerturbationTheory

Take into account \hat{H}' as in Eq. (1.50), focussing on the ground-state only for now:

$$E^{(1)} = \langle \psi_{\pm}^{(0)} | \hat{H}' | \psi_{\pm}^{(0)} \rangle \quad (2.82)$$

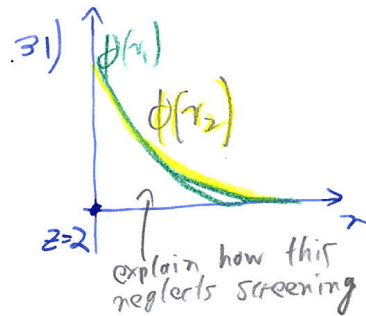
$$\stackrel{\text{Ground}}{=} \int d^3r_1 \int d^3r_2 \underbrace{|\phi_{100}(r_1)|^2}_{\text{Charge density at } \mathbf{r}_1} \frac{1}{|r_1 - r_2|} \underbrace{|\phi_{100}(r_2)|^2}_{\text{Charge density at } \mathbf{r}_2} \quad (2.83)$$

$$\stackrel{\text{See}}{\text{Book}} \dots + \frac{5}{8}Z \quad \text{in a.u.} \quad (2.84)$$

In the second line above we recognize the electro-static interaction energy of the charge densities due to electron 1 and 2.

- Now we have $E^{(0)} + E^{(1)} = -Z^2 + \frac{5}{8}Z = \underbrace{-2.75}_{\text{getting better}}$ ("exact" -2.904)

Variational Method



left: Sketch of helium electron wave-functions with (yellow) and without screening (green).

Look at

$$\psi_+^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{100}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2), \quad (2.85)$$

$$\phi_{100}(\mathbf{r}) \stackrel{\text{a.u.}}{\text{Eq. (1.35)}} \sqrt{\frac{Z^3}{\pi}} \exp[-Zr] \quad (2.86)$$

Now try to improve on this by introducing a screened (or effective) charge $Z \rightarrow Z_{\text{eff}}$. Let us take the trial state

$$\psi_{\text{trial}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{\text{trial}}(\mathbf{r}_1) \phi_{\text{trial}}(\mathbf{r}_2)$$

$$\phi_{\text{trial}}(\mathbf{r}) = \sqrt{\frac{Z_{\text{eff}}^3}{\pi}} \exp[-Z_{\text{eff}}r], \quad (2.87)$$

as guess for the two-electron wave function. We have to find the "best" value of Z_{eff} from variational principle

Variational Principle

- Energy functional

$$E[\phi] = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \quad (2.88)$$

is extremal at an eigenstate ψ_n of \hat{H} , that means

$$\delta E[\psi_n] = 0. \quad (2.89)$$

- The groundstate energy $E_0 \leq E[\phi]$ for any trial state ϕ . Thus the minimal energy we can reach by changing the parameters in our trial state, will be closest to the true ground-state energy.

Variational derivatives:

- δE is a variation of the energy functional: Multiply Eq. (2.88) by $\langle \phi | \phi \rangle$ and take the total derivative wrt. the state

$$\delta E \langle \phi | \phi \rangle + E \langle \delta \phi | \phi \rangle + E \langle \phi | \delta \phi \rangle = \langle \phi | \hat{H} | \delta \phi \rangle + \langle \delta \phi | \hat{H} | \phi \rangle \quad (2.90)$$

(*"How does the energy $E[\phi]$ change for a small variation $\phi + \delta\phi$ around ϕ ?"*)

- Related to functional derivative $\frac{\delta E}{\delta \phi(x)}$ (see books)
- A special variation is $\delta E = \frac{\partial E}{\partial Z_{\text{eff}}} \delta Z_{\text{eff}} \stackrel{!}{=} 0$

To find $\frac{\partial E}{\partial Z_{\text{eff}}}$, we insert Eq. (2.87) into the energy functional Eq. (2.88):

$$E \left[\psi^{(0)}_{\text{trial}} \right] = \langle \psi^{(0)}_{\text{trial}} | \underbrace{\hat{T}_1 + \hat{T}_2 - \frac{Z}{r_1} - \frac{Z}{r_2}}_{\text{see QM1/ standard methods}} + \frac{1}{r_{12}} | \psi^{(0)}_{\text{trial}} \rangle = Z_{\text{eff}}^2 - 2Z Z_{\text{eff}} + \frac{5}{8} Z_{\text{eff}}. \quad (2.91)$$

- The term involving $1/r_{12}$ gives rise to the same integral as in the perturbation theory segment one page above.
- In the expression above, factors Z stem from the Hamiltonian, but factors of Z_{eff} from the trial function.

- $$\frac{\partial E}{\partial Z_{\text{eff}}} = 0 \Leftrightarrow Z_{\text{eff}} = Z - \frac{5}{16} \quad \text{effective charge reduced, as expected} \quad (2.92)$$

- Now ground state energy of Helium $E[\phi_{\text{trial}}] = -\left(Z - \frac{5}{16}\right)^2 \text{ a.u.} = -2.848 \text{ a.u.}$ (even closer to "exact" -2.904)

Screening in the Central Field approximation

Going back to independent particle model/ 0'th order P.T, we can rewrite Hamiltonians as indicated by the vertical arrow below:

\hat{H}_0	\hat{H}'	
$-\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2}$	$\frac{1}{r_{12}}$	
	\Downarrow	
$-\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2} + V(r_1) + V(r_2)$	$\frac{1}{r_{12}} - V(r_1) - V(r_2) - \frac{Z}{r_1} - \frac{Z}{r_2}$	(2.93)

This just constitutes a re-allocation of what we call \hat{H}_0 and what we call \hat{H}' .

See that if we choose the **central field** below for our potential energy,

$$V(r) = -\frac{Z - S}{r} = -\frac{Z_{\text{eff}}}{r} \quad (2.94)$$

with $Z_{\text{eff}} = Z - \frac{5}{16}$ we obtain variational solution as eigenstates in 0'th order PT.²

The re-writing has effectively made \hat{H}' "smaller". S is the screening factor. ($S = \frac{5}{16} = 0.31$ for He)

- This central field concept will be even more useful for $N > 2$ electrons.

2.3.4 Excited States of Two electron atoms

Much of section 2.3.3 can be generalised to excited states.

Let us consider perturbation theory of:

$$\psi_{\pm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_{100}(\mathbf{r}_1) \phi_{nlm}(\mathbf{r}_2) \pm \phi_{nlm}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2)] \quad (2.95)$$

The unperturbed energy is $E^{(0)} = E_{nlm} + E_{100}$. For the perturbed results we find:

First Order excited state with interaction energy

$$E_{\pm}^{(1)} = J \pm K \quad + = \text{para}, - = \text{ortho}, (\text{ortho not possible for ground state}) \quad (2.96)$$

$$J = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\phi_{100}(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\phi_{nlm}(\mathbf{r}_2)|^2 \quad \text{Coulomb (direct) integral} \quad (2.97)$$

$$K = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \phi_{100}^*(\mathbf{r}_1) \phi_{nlm}^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{100}(\mathbf{r}_2) \phi_{nlm}(\mathbf{r}_1) \quad \text{Exchange integral} \quad (2.98)$$

- Using $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2} \hat{\mathbf{S}}^2 - \frac{3}{4}$, we can express the energies as

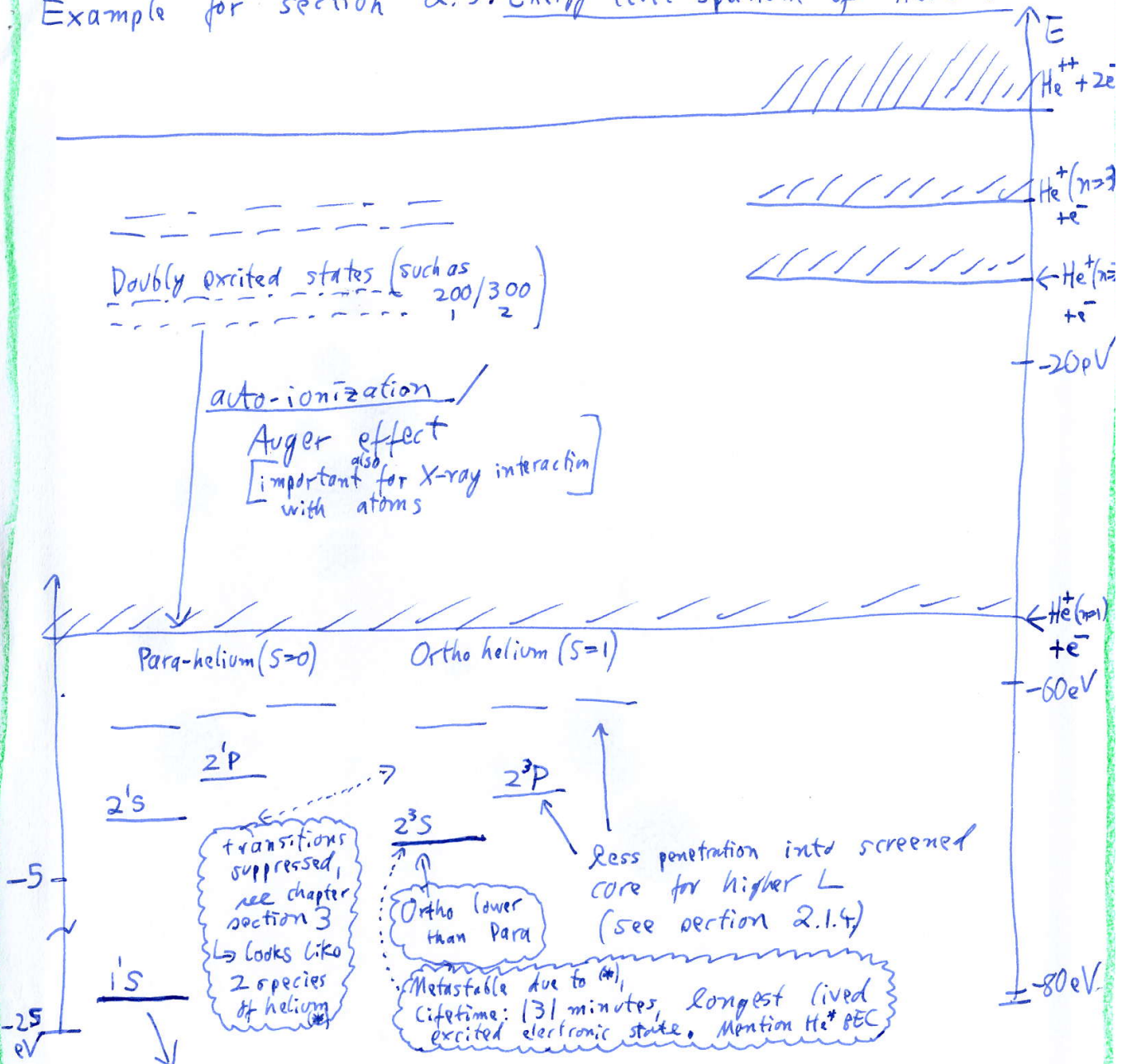
$E_{\pm}^{(1)} = J - \frac{1}{2} \left(1 + 4 \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \right) K \Rightarrow$ spin dependence of energy. Note that the energy became spin dependent because of the required allocation (2.76)-(2.77) of spatial symmetry to total electron spin.

- When evaluating integrals we find that $J > 0$ (*see BJ book*). It also turns out that J, K depend on n, l , hence ($J \rightarrow J_{nl}, K \rightarrow K_{nl}$).
- Usually also $K > 0 \Rightarrow$ Thus the ortho state ($S = 1$) has a lower energy.

All that we have learnt so far (and some more) enters the energy level diagram of helium on the next page:

²Finding eigenstates of the newly arranged \hat{H}_0 in (2.93) proceeds as we did for finding Eq. (2.81), except in the solution we have to replace everywhere $Z \rightarrow Z_{\text{eff}}$. Thus we obtain the solution (2.87).

Example for section 2.3: Energy level spectrum of Helium



Helium groundstate, ionization potential including fine structure etc...

theory (f.d.c): $24.586812487292 \text{ eV} \pm 6 \cdot 10^{-6} \text{ eV}$

expt. : $24.5868274589038 \text{ eV} \pm 1.8 \cdot 10^{-5} \text{ eV}$

(QM seems to work)

Week ⑤

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

2.4 Many-electron atoms

- Already cannot solve the two electron problem exactly. The variational approach also becomes too hard for large numbers of electrons. Now, the central field approximation will be very useful.

Many-electron (N) Schrödinger equation:

$$\hat{H}\psi(q_1, q_2, \dots, q_N) = E\psi(q_1, q_2, \dots, q_N)$$

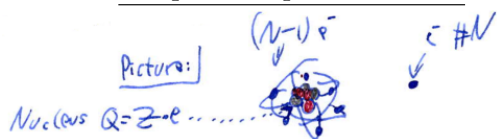
$$q_k = \{m_{sk}, \mathbf{r}_k\} \text{ (spin and position variables)}$$

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right) + \sum_{i < j=1}^N \frac{1}{r_{ij}} \text{ (in atomic units)} \quad (2.99)$$

- Eq. (2.4) constitutes a PDE, for a wavefunction with $3N$ spatial plus 2^N discrete co-ordinates \implies very impossible to solve directly.
- This problem generically arises in quantum-many-body-physics.
- Unlike two electron case, $\hat{H}' = \sum_{i < j=1}^N 1/r_{ij}$ generally is not small due to many terms in the sum.

2.4.1 Central field approximation

Now the independent-particle model and central field approximation become indispensable:



left: When considering a selected electron, the most important effect of other $(N - 1)$ electrons is collectively screening the nuclear charge, which however still leaves the potential for the N th electron spherically symmetric (to a good approximation).

Similar to our treatment of Helium, we write for this radial potential felt by electron number i

$$V(\mathbf{r}_i) = -\frac{Z}{|\mathbf{r}_i|} + S(|\mathbf{r}_i|) \quad (\text{Now screening is } r\text{-dependent}). \quad (2.100)$$

We now re-write Eq.(2.99), ignoring spin for now

$$\hat{H}_c = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_i) \right) = \sum_{i=1}^N \hat{h}_i \quad (2.101)$$

$$\hat{H}' = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z}{r_i} + V(\mathbf{r}_i) \right) = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(\mathbf{r}_i) \quad (2.102)$$

such that $\hat{H} = \hat{H}_c + \hat{H}'$ (just re-writing).

- \hat{H}_c is central field Hamiltonian.
- Expect eigenfunctions of \hat{H}_c to be better than those of $\hat{H}_o = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - Z/r_i \right)$.
- Challenge is to find out suitable $S(\mathbf{r}_i)$ or $V(\mathbf{r}_i)$.

Central field Schrödinger equation

$$\hat{H}_c \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_c \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2.103)$$

can be solved using

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = u_{a_1}(\mathbf{r}_1) u_{a_2}(\mathbf{r}_2) \dots u_{a_N}(\mathbf{r}_N); \quad a_i \equiv \{n_i l_i m_i\} \quad (2.104)$$

where,

$$\left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_i) \right) u_{a_i}(\mathbf{r}_i) = E_i u_{a_i}(\mathbf{r}_i), \quad E_c = \sum_i E_i. \quad (2.105)$$

The functions $u_{n_i l_i m_i}(\mathbf{r}_i)$ are called central-field orbitals.

- Exercise: Show directly that (2.104) is a solution for (2.103).

- To actually find the central field orbitals, as for hydrogen states, we write $u_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$ with Y_{lm} exact same as for H (spherical harmonics), but R_{nl} determined from the radial equation:

$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{nl}(r) + \underbrace{V(r)}_{\neq} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (2.106)$$

potential used for Hydrogen
due to screening

- Now we can use the following iterative procedure:
 - (i) Solve (2.106) with some *trial* $V(\mathbf{r}_i)$ to determine the $u_{a_i}(\mathbf{r}_i)$.
 - (ii) Use the obtained $u_{a_i}(\mathbf{r}_i)$ to infer the electron charge distributions.
 - (iii) Use the charge distribution to infer the screened potential $V(\mathbf{r}_i)$ with usual electro-statics methods.
 - (iv) Loop back to step (i) using the updated screened potential $V(\mathbf{r}_i)$.
 - (v) Repeat iteration until nothing changes any more.
- We will see one method that formalises this later.
- However we can learn a lot without doing the actual iteration, from two known limits:

$$V(r) \rightarrow -\frac{Z}{r} \quad (\text{for } r \mapsto 0), \quad (2.107)$$

here the electron is closer to the nucleus than all others, so no screening can take place, and

$$V(r) \rightarrow -\frac{Z - (N - 1)}{r} \quad (\text{for } r \mapsto \infty), \quad (2.108)$$

here all $N - 1$ other electrons are closer to the nucleus and screen its charge as much as possible.

2.4.2 Spin and Pauli-exclusion principle

- Product states $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = u_{a_1}(\mathbf{r}_1) \dots u_{a_N}(\mathbf{r}_N)$ do not in general satisfy the anti-symmetry requirements of Eq. (1.62) for fermions, and we have not yet included spin ($\mathbf{r}_N \rightarrow q_N$, see Eq.(2.99)).

Introduce spin-orbitals:

$$\underbrace{u_{nlm_l m_s}(q)}_{\equiv \alpha} = u_{nlm_l}(\mathbf{r}) |\chi\rangle_{m_s} = R_{nl}(r) Y(\theta, \phi) |\chi\rangle_{m_s} \quad (2.109)$$

with

$$|\chi\rangle_{+\frac{1}{2}} = |\uparrow\rangle, \quad |\chi\rangle_{-\frac{1}{2}} = |\downarrow\rangle.$$

In terms of these, a valid fermionic N -electron total wavefunction is given by a Slater-determinant

$$\psi_c(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ u_\alpha(q_N) & \cdots & \cdots & u_\nu(q_N) \end{vmatrix} \quad (2.110)$$

Reminder: For matrix $A = \{a_{ij}\}$, the determinant $\det A = |A| = \sum_{\substack{\sigma \in S_N \\ \text{Permutations}}} \text{sgn}(\sigma) \prod_{i=1}^N a_{i\sigma_i}$.

- We see that this enforces antisymmetry, since determinant changes sign when we exchange two rows (*math course*).
- Also, if for any indices $\alpha = \beta \implies \det = 0$. (Since, it also changes sign if we exchange two columns. This means there can never be two electrons in the same spin-orbital.)
- Set of electron quantum numbers $[\alpha, \beta, \dots, \nu]$ in (2.110) is called electron-configuration.
- Let us define also

$$\begin{aligned} \text{the } \underline{\text{total angular momentum}} \text{ of all electrons} & \quad \mathbf{J}_{tot} = \sum_{i=1}^N \mathbf{J}_i \\ \text{the } \underline{\text{total orbital angular momentum}} \text{ of electrons} & \quad \mathbf{L}_{tot} = \sum_{i=1}^N \mathbf{L}_i \\ \text{the } \underline{\text{total spin}} \text{ of electrons} & \quad \mathbf{S}_{tot} = \sum_{i=1}^N \mathbf{S}_i \end{aligned} \quad (2.111)$$

- Note that $[\hat{H}_c, \mathbf{L}_{tot}] = 0$, $[\hat{H}_c, \hat{S}_{tot}] = 0$ for the central field Hamiltonian \hat{H}_c in Eq.(2.101).

\implies We can in principle write all many electron eigenstates also as eigenstates of \hat{L}_{tot} , \hat{S}_{tot} . However, note, the the Slater determinant (2.110) is not yet in general an eigenstate of \hat{L}_{tot} , \hat{S}_{tot} .

Atomic terms A state of multi-electron atoms with well defined quantum numbers for the total angular momenta J for \mathbf{J}_{tot} , L for \mathbf{L}_{tot} and S for \mathbf{S}_{tot} is called term, denoted with a term symbol

$$^{2S+1}L_J, \quad (2.112)$$

c.f. Example p. 24.

2.4.3 Ground state energetic ordering and periodic table

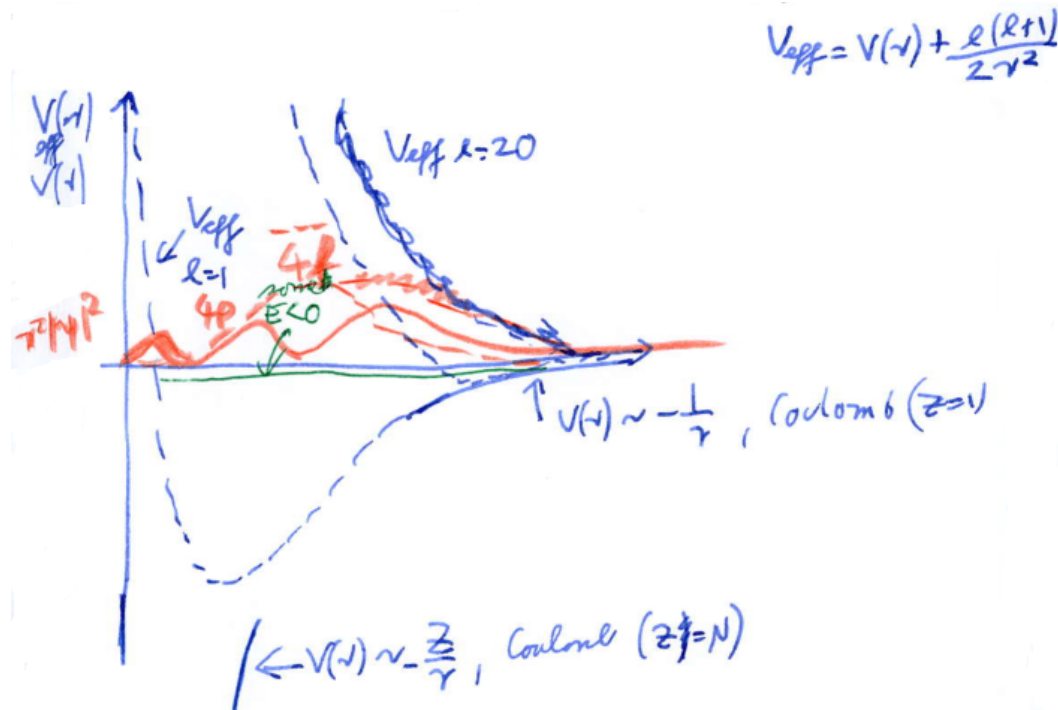
- So far we have not really solved the many-electron-atom problem since we did not yet calculate $S(\mathbf{r})$. But, most essential properties of all atoms, incorporated into the periodic table, can be understood already now, based on some $V(\mathbf{r})$ with properties (2.107)-(2.108).

Angular momentum versus screening ($N = Z$ atoms):

Revisit Eq.(2.106):

$$-\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} \right) R_{nl}(r) + \underline{V(r)} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (2.113)$$

We can again combine the underlined pieces into an effective potential $V_{\text{eff}} = V(r) + \frac{l(l+1)}{2r^2}$ that includes the centrifugal barrier due to angular momentum (as in section 1.2.3).



- The centrifugal potential $l(l+1)/2r^2$ pushes the wavefunction further out (to larger r), the higher the value of l .
- All higher l -states thus feel the unscreened and stronger $-Z/r$ potential less than lower l states thus energy typically increases with l .
- Energy E_i in Eq.(2.105) depends on n, l of all electrons (but not their m_l, m_s while we ignore fine and hyperfine structure).
 \implies electrons with the same n, l are said to belong to the same sub-shell and are also called equivalent electrons.

- For a given selection of the two numbers (n, l) , there are $2(2l + 1)$ equivalent electrons (size of shell).
- To build the periodic table, we fill shells starting from low energies.

See table 8.3, Fig 8.1 of the book BJ, also follow <https://ptable.com/>

- $4s$ states fill before $3d$ (because $3d$ has so much centrifugal potential) †.
- **Filled sub-shells always have zero total spin and zero total angular momentum.** This is because we have to fill *all possible* m_l, m_s and at the same time maintain fermionic total anti-symmetry.
- Still reminiscent of the situation in Hydrogen, the binding energy of the outer electron jumps up (becomes much less negative) whenever $n \rightarrow n+1$, this gives periodic recurrence of chemical properties, mainly determined by outermost (valence) electron and how easily it is lost.
- The confusing middle part of the periodic table (transition metals) exists due to $3d \leftrightarrow 4s$ swap in the energy ordering (see † above) (This happens again for higher energy states $4d \leftrightarrow 5s, 4f \leftrightarrow 5d$).
- Note that all chemical variety in the world around us is due to the Pauli exclusion principle. Without it, any atom with varying nuclear charge Z would be just in a configuration $(1s)^Z$, thus all atoms would behave chemically very similar.

2.4.4 Approximation methods for many-electron systems

Thomas-Fermi theory: Assume electrons are (i) degenerate Fermi gas, (ii) numerous, (iii) can be treated in WKB/semi-classical approximation \implies Obtain electron charge density $\rho(\mathbf{r})$ and from that $V(\mathbf{r})$ (screened potential). Not very accurate, but interesting conceptually and useful in e.g. ultra-cold gases (also Bosons, *see Chapter-V*). Precursor to:

Density-functional theory: (Based on theorem by Hohenberg and Kohn)

For an N -electron system with ground-state wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, the ground-state electron density is

$$\rho(\mathbf{r}) = \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \cdots \int d^3\mathbf{r}_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2. \quad (2.114)$$

Then,

- (a) every observable is uniquely determined by $\rho(\mathbf{r})$.
- (b) there exists a functional $I[\rho]$ such that for a given potential $U(\mathbf{r})$ (felt by all e^-), ground state energy is minimum of

$$E_o[\rho] = I[\rho] + \int d^3\mathbf{r} U(\mathbf{r})\rho(\mathbf{r}), \text{ for } \int d^3\mathbf{r} \rho(\mathbf{r}) = N.$$

- Useless unless we know $I[\rho]$. By now many "good" choices for $I[\rho]$ are available.
- Very successful method for quantum-chemistry/ material science.

Hartree-Fock method and the self-consistent field:

Idea: (i) Calculate $u_{nlm}(\mathbf{r})$ as in (2.105) using trial $V(\mathbf{r})$.

(ii) Calculate electron charge density $\rho(\mathbf{r}) = -e \sum |u_{nlm}(\mathbf{r})|^2$, this gives screening $V'(\mathbf{r})$.

(iii) Re-calculate $u'_{nlm}(\mathbf{r})$ with new $V'(\mathbf{r})$, iterate until converged.

(iv) In practice, this is all embedded in a many-body variational method, so won't directly recognize ρ, V .

Now, a sketch of derivation:

Use natural splitting of Hamiltonian (2.99)

$$\hat{H}_1 = \sum_{i=1}^N \hat{h}_i, \quad \hat{h}_i = -\frac{\nabla_{\mathbf{r}_i}^2}{2} - \frac{Z}{r_i}, \quad \hat{H}_2 = \sum_{i<j=1}^N \frac{1}{r_{ij}}, \quad \hat{H} = \hat{H}_1 + \hat{H}_2$$

from variational principle (2.89), the true ground-state energy E_0 fulfills

$$E_0 \leq E[\phi] = \langle \phi | \hat{H} | \phi \rangle, \quad (2.115)$$

but now ϕ is a many-electron Slater-determinant as in (2.110). Let us re-write

$$\phi(q_1, \dots, q_N) = \sqrt{N!} \mathcal{A} \phi_H(q_1, \dots, q_N) \quad (2.116)$$

with Hartree function:

$$\phi_H(q_1, \dots, q_N) = u_\alpha(q_1) u_\beta(q_2) \dots u_\nu(q_N). \quad (2.117)$$

$u_\alpha(q_i)$ etc. are again spin-orbitals, with form yet to be determined. We also used the anti-symmetrisation operator

$$\mathcal{A} \dots = \frac{1}{N!} \sum_{\mathcal{P}} (-1)^P \mathcal{P}[\dots] \quad (2.118)$$

Here the sum runs over all possible permutations \mathcal{P} of the set of integers $1 \dots N$, P is the sign of the permutation, and $\mathcal{P}[\dots]$ tells us to permute coordinates that occur within the brackets according to \mathcal{P} , i.e. $u_\alpha(q_1) u_\beta(q_2) \rightarrow u_\alpha(q_{\mathcal{P}[1]}) u_\beta(q_{\mathcal{P}[2]})$.

We now have to evaluate $E[\phi] = \langle \phi | \hat{H}_1 | \phi \rangle + \langle \phi | \hat{H}_2 | \phi \rangle$ for a Slater-determinant. We will use $[\hat{H}_i, \mathcal{A}] = 0$ (both \hat{H}_k are symmetric under all particle label swaps) and $\mathcal{A}^2 = \mathcal{A}$ (\mathcal{A} is a projector, if the expression in \dots is already anti-symmetrised, anti-symmetrising it again does nothing).

Now:

$$\begin{aligned} \langle \phi | \hat{H}_1 | \phi \rangle &\stackrel{\text{Eq. (2.116)}}{=} N! \langle \phi_H | \mathcal{A} \hat{H}_1 \mathcal{A} | \phi_H \rangle \stackrel{[\hat{H}_i, \mathcal{A}] = 0}{=} N! \langle \phi_H | \hat{H}_1 \mathcal{A}^2 | \phi_H \rangle \\ &\stackrel{\mathcal{A} \text{ is projector}}{=} N! \langle \phi_H | \hat{H}_1 \mathcal{A} | \phi_H \rangle \stackrel{\text{Eq. (2.118)}}{=} \sum_{i=1}^N \sum_{\mathcal{P}} (-1)^P \langle \phi_H | \hat{h}_i \mathcal{P} | \phi_H \rangle \end{aligned}$$

Now we can check that:

$$\langle \phi_H | \hat{h}_i \mathcal{P} | \phi_H \rangle = \begin{cases} \langle \phi_H | \hat{h}_i | \phi_H \rangle & ; \text{if } \mathcal{P} = \text{identity} \\ 0 & ; \text{else} \end{cases} \quad (2.119)$$

To see this explicitly expand the many-body scalar product as in the next step.

$$\begin{aligned} \langle \phi | \hat{H}_1 | \phi \rangle &= \sum_{i=1}^N \langle \phi_H | \hat{h}_i | \phi_H \rangle \\ &\stackrel{\text{Eq. (2.117)}}{=} \sum_{i=1}^N \int dq_1 \int dq_2 \underbrace{\dots}_{\text{No } i} \int dq_N \left(u_\alpha^*(q_1) u_\alpha(q_1) \right) \left(u_\kappa^*(q_{i-1}) u_\kappa(q_{i-1}) \right) \left(u_\eta^*(q_{i+1}) u_\eta(q_{i+1}) \right) \\ &\quad \left(u_\nu^*(q_N) u_\nu(q_N) \right) \left[\int dq_i \left(u_\lambda^*(q_i) \hat{h}_i u_\lambda(q_i) \right) \right] \\ &\stackrel{\text{all orbitals orthonormal}}{=} \sum_{i=1}^N \langle u_{\lambda_i}(q_i) | \hat{h}_i | u_{\lambda_i}(q_i) \rangle \equiv \sum_{i=1}^N I_{\lambda_i}; \quad \text{using an index vector } \vec{\lambda} = [\alpha, \beta, \dots, \nu]. \end{aligned}$$

The I_{λ_i} can be thought of as non-interacting energy of electron number i being in the spin-orbital $u_{\lambda_i}(q_i)$.

Similarly:

$$\begin{aligned} \langle \phi | \hat{H}_2 | \phi \rangle &= \sum_{i < j} \sum_{\mathcal{P}} (-1)^P \underbrace{\left\langle \phi_H \left| \frac{1}{r_{ij}} \mathcal{P} \right| \phi_H \right\rangle}_{\text{whenever } \mathcal{P} \text{ "touches" any index } \neq i, j \text{ this is } = 0} \\ &\stackrel{\text{only allowed permutation}}{=} \sum_{i < j} \left\langle \phi_H \left| \frac{1}{r_{ij}} (1 - \mathcal{P}_{ij}) \right| \phi_H \right\rangle \\ &\stackrel{\text{as above}}{=} \sum_{\substack{\lambda, \mu \\ (\text{Pairs})}} \underbrace{\left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\lambda(q_i) u_\mu(q_j) \right\rangle}_{\equiv \mathcal{J}_{\lambda\mu}} - \underbrace{\left\langle u_\lambda(q_i) u_\mu(q_j) \left| \frac{1}{r_{ij}} \right| u_\mu(q_i) u_\lambda(q_j) \right\rangle}_{\equiv \mathcal{K}_{\lambda\mu}} \\ &\quad \text{direct term, compare Eq. (2.97)} \quad \text{exchange term, compare Eq. (2.98)} \end{aligned}$$

In the second line, the only allowed permutations that don't give zero in the scalar product, is the identity (giving the 1), and \mathcal{P}_{ij} which flips $i \leftrightarrow j$.

- All together, we have now obtained a much simpler looking energy functional

$$E[\phi] = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda\mu} [\mathcal{J}_{\lambda\mu} - \mathcal{K}_{\lambda\mu}]. \quad (2.120)$$

That consists of single particle energies I_{λ} and interaction energies J and K . The 1/2 just avoids double counting of pairs.

- Now, in a more complex variational principle than used for Helium, we vary all the $u_\lambda(q_i)$ themselves:

$$\delta E - \underbrace{\sum_\lambda E_\lambda}_{\text{Lagrange-multiplier}} \delta \langle u_\lambda | u_\lambda \rangle = 0. \quad (2.121)$$

(see math and book)

The Lagrange multipliers implement the constraint $\langle u_\lambda | u_\lambda \rangle = \delta_{\lambda\mu}$.

From variation $\delta u_\lambda(q_i)$ we obtain (see books)

Hartree-Fock equations:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right] u_\lambda(q_i) + \left[\sum_\mu \int dq_j u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j) \right] u_\lambda(q_i) - \left[\sum_\mu \int dq_j u_\mu^*(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i). \quad (2.122)$$

- Set of integer-differential, coupled equations for N spin orbitals $u_\lambda(q_i)$.
- Lagrange-multipliers E_λ take role of energy eigenvalues.
- We can define a direct potential

$$V^{(d)}(q_i) = \sum_\mu \int dq_j u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j)$$

and exchange potential (operator)

$$V^{(ex)}(q_i)[f] = \sum_\mu \left[\int dq_j u_\mu^*(q_j) \frac{1}{r_{ij}} f(q_j) \right] u_\mu(q_i)$$

such that

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} + \underbrace{V^{(d)} - V^{(ex)}}_{\equiv V(q_i)} \right] u_\lambda(q_i) = E_\lambda u_\lambda(q_i). \quad (2.123)$$

Comparison with Eq.(2.103), $V(q_i)$ takes the role of central field here.

- For atoms with filled subshells, can show that $V(q_i)$ is indeed spherically symmetric. Otherwise not, but derivations are small.
- Solve (2.122) by iteration: Start with some trial solution $u_\lambda^{(0)}(q_i)$ (e.g. the one for Hydrogen or guessed $V(q_i)$). Then find solution of

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right] u_\lambda^{(1)}(q_i) + \left[\sum_\mu \int dq_j u_\mu^{*(0)}(q_j) \frac{1}{r_{ij}} u_\mu^{(0)}(q_j) \right] u_\lambda^{(1)}(q_i) - \left[\sum_\mu \int dq_j u_\mu^{*(0)}(q_j) \frac{1}{r_{ij}} u_\lambda^{(0)}(q_j) \right] u_\mu^{(1)}(q_i) = E_\lambda u_\lambda^{(1)}(q_i). \quad (2.124)$$

etc. until $u_\lambda^{(n)}(q_i)$ is converged.

Example-(1) for section 2.4: Radial electron density in Neon

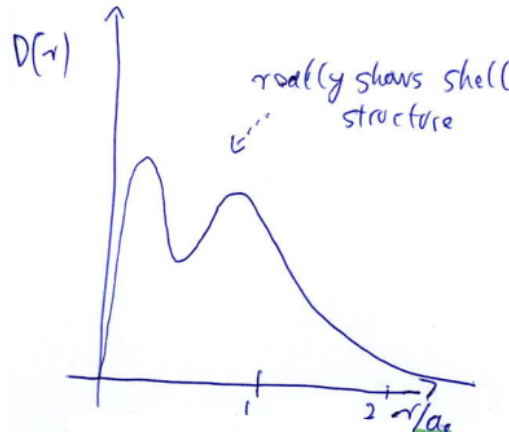
Define radial electron density

$$D(r) = r^2 \int \underbrace{d\Omega}_{\text{angles}} \rho(r) = \sum_{nl} \underbrace{g_{nl}}_{\substack{\# \text{ of equivalent electrons} \\ \text{in subshell } (nl)}} |\rho_{nl}(r)|^2. \quad (2.125)$$

Neon configuration $(1s)^2(2s)^2(2p)^6$, thus

$$D(r) = 2|P_{1s}(r)|^2 + 2|P_{2s}(r)|^2 + 6|P_{2p}(r)|^2.$$

which can be obtained via Eq. (2.122). The result is



2.4.5 Corrections to the central field. L-S/J-J coupling

There are two important correction terms to the central field picture discussed so far:

$$\hat{H}_1 = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z}{r_i} + V(\mathbf{r}_i) \right), \quad (2.126)$$

$$\hat{H}_2 = \sum_{i=1}^N \zeta_i(r) \hat{L}_i \cdot \hat{S}_i. \quad (2.127)$$

First is non-central field part of Hamiltonian, which we had listed as \hat{H}' in Eq. (2.102). Second spin-orbit coupling for each electron (c.f. Eq. (2.5)), the most important of relativistic corrections neglected in Eq. (2.99).

Which one is more important depends on Z .

L-S coupling (or Russell-Sanders coupling): : *Warning: L-S coupling means sth. very different from the words “spin-orbit coupling”!!*

L-S coupling is used for small or intermediate Z , in this case

$$|\hat{H}_1| \gg |\hat{H}_2| \text{ (nontrivial to link this to “small } Z\text{”).}$$

- First consider only \hat{H}_1 . \hat{H} commutes with \mathbf{J}_{tot} , \mathbf{L}_{tot} , \mathbf{S}_{tot} , see section 2.4.2.
- Determining which quantum numbers J , L , S are possible for a given state is nontrivial due to Pauli-exclusion principle⁰. Energy level with given fixed values of L , S is called a term.

Hund’s rules: For ground states:

- the term with the largest possible S for a given configuration has the lowest energy; energy then goes up as S goes down.
- for a given S , the term with maximum L has the lowest energy.

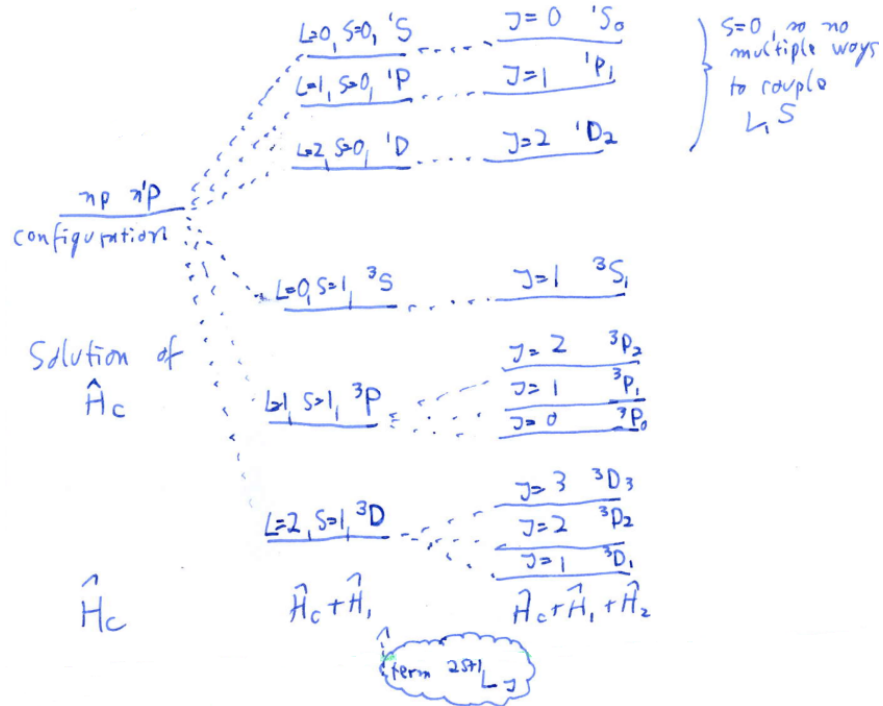
- So far we considered \hat{H}_1 only. Now we can add \hat{H}_2 as perturbation \rightarrow Fine-structure.
- Now each term with fixed L , S splits into separate J -components, which form a multiplett.
- Landé interval rule:

$$E(J) - E(J - 1) = \bar{A} \times J, \text{ within one } \underline{\text{multiplett}}, \quad (2.128)$$

where \bar{A} is a constant. One finds $\bar{A} > 0$ for less than half filled shells, so that the ground-state has the lowest allowed J . However, $\bar{A} < 0$ for more than half filled shells, so that the ground-state then has the hightest allowed J .

⁰e.g. see section 4, helium ground-state can be only $L = 0$, not $L = 1$

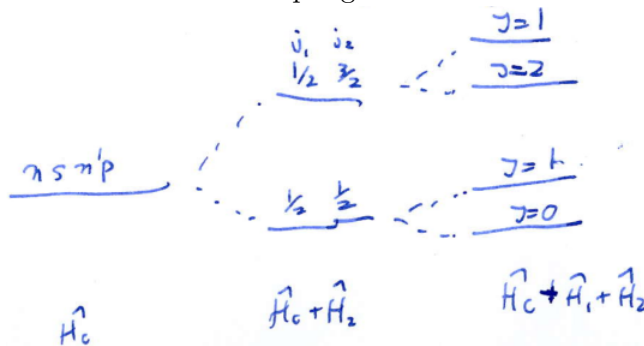
Example-(2) for section 2.5: L-S coupling and fine-structure for two electrons



J-J coupling: This takes place for large Z ($Z \approx 80$), then we have $|\hat{H}_2| \gg |\hat{H}_1|$.

- First: $\hat{H}_c + \hat{H}_2 = \sum_{i=1}^N \hat{h}_i \rightarrow$ for each electron separately couple spin and angular momentum to j_k , giving orbitals u_{nljm_j} (based on $\hat{J}_i = \hat{L}_i + \hat{S}_i$).
- Second: We only then consider $\hat{H}_c + \hat{H}_2 + \hat{H}_1$ and have to label our many-electron state with $\hat{J} = \sum_{i=1}^N \hat{J}_i$, only labelled by J .

Example-(3) for section 2.5: J - J coupling



Week ⑥

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

3 Interaction of Atoms with Electromagnetic Radiation

So far we had looked at what is called atomic structure, i.e. their energy levels and electron states, without any time dependence. Now we will begin to look at dynamics, in particular how to get from one energy level to another.

3.1 Atomic Transitions

3.1.1 Electromagnetic fields and charged particles

Unlike section 2.2 on static fields, we now want to simultaneously consider time-dependent \mathbf{E} and \mathbf{B} fields such as they occur within an electromagnetic wave.

It is often convenient to,

Express fields via potentials

$$\begin{aligned}\mathbf{E}(\mathbf{r}, t) &= -\nabla\varphi(\mathbf{r}, t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}, t) & \varphi &= \text{Scalar Potential} & (3.1) \\ \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) & \mathbf{A} &= \text{Vector Potential}\end{aligned}$$

Warning: Make sure in the following not to confuse \mathbf{E} with an energy or φ with a wave function, it should be obvious from context what they are!

Potentials are not unique, they can be changed via a

Gauge Transformation

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi(\mathbf{r}, t) \qquad \varphi \rightarrow \varphi - \frac{\partial}{\partial t}\chi(\mathbf{r}, t) \qquad (3.2)$$

where, $\chi(\mathbf{r}, t) \in \mathbb{R}$ is any differentiable function

We now use this freedom to choose the

Coulomb Gauge

$$\nabla \cdot \mathbf{A} = 0 \text{ and } \varphi = 0. \qquad (3.3)$$

We can show from Maxwell's equations the

Wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0, \qquad (3.4)$$

with the following solution which represents an electro-magnetic wave-packet

$$\mathbf{A}(\mathbf{r}, t) = \int_0^\infty A_0(\omega) \boldsymbol{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega) d\omega. \qquad (3.5)$$

here $A_0(\omega)$ is the spectral Amplitude, $\boldsymbol{\epsilon} \in \mathbb{C}^3$ is the polarisation vector, $\omega = |\mathbf{k}|c$ as usual and δ_ω is the phase of frequency component ω .

- For a laser we would have $\delta_\omega = \text{fixed } \forall \omega$, e.g.=0
- For incoherent radiation: δ_ω is random for all ω .
- For a simple spectral distribution, imagine a narrow Gaussian centered on a central frequency ω_0 such as $A_0(\omega) = \bar{A} \exp[-(\omega - \omega_0)^2/\sigma_\omega^2]$.

Hamiltonian for charged electron in radiation field

$$\hat{H} = \frac{1}{2m} (\hat{p} + e\mathbf{A})^2 - \frac{Ze^2}{(4\pi\epsilon)r} \qquad (3.6)$$

Insert $\hat{p} = -i\hbar\nabla$ and using $\nabla \cdot (\mathbf{A} \cdot \dots) = \mathbf{A} \cdot (\nabla \cdot \dots) + \underbrace{(\nabla \cdot \mathbf{A})}_{=0} \dots$ we get the

Atom-Radiation Hamiltonian

$$\hat{H}(t) = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon)r}}_{=\hat{H}_0} - \underbrace{i\hbar\frac{e}{m}\mathbf{A}(\mathbf{r},t)\cdot\nabla + \frac{e^2}{2m}(\mathbf{A}(\mathbf{r},t))^2}_{=\hat{H}'(t)} \quad (3.7)$$

- This is written in the form (1.53) for time dependent perturbation theory
- it seems to depend on the gauge, but gauges just change inconsequential spatial phase of wavefunction, so any dependence cancels (see book)
- can neglect \mathbf{A}^2 term (and will do from now) except in very strong fields

3.1.2 Transition Rates

Assume we start in the specific atomic state $|\phi_a\rangle = |\phi_{n_a l_a m_a}\rangle$. (a is thus a short-hand index for all quantum numbers n_a, l_a, m_a).

Solving the TDSE $i\hbar\partial|\psi(t)\rangle/\partial t = \hat{H}(t)|\psi(t)\rangle$ for state vector $|\psi(t)\rangle = \sum_k c_k(t)|k\rangle$ is in general too hard. Hence, we use TDPT (see section 1.2.5) in order to find the amplitude for transition from state a to another state b : $|\phi_a\rangle \rightarrow |\phi_b\rangle$.

$$c_b^{(1)}(t) = (i\hbar)^{-1} \int_0^t H'_{ba}(t') \exp(i\omega_{ba}t') dt' \quad \text{where,} \quad (3.8)$$

$$\omega_{ba} = \frac{(E_b - E_a)}{\hbar} \quad (3.9)$$

We thus need the matrix-element

$$H'_{ba}(t') = \langle\phi_b|H'(t')|\phi_a\rangle \quad (3.10)$$

$$= -i\hbar\frac{e}{m} \int_0^\infty d\omega A_0(\omega) \boldsymbol{\epsilon} \cdot \langle\phi_b|\frac{1}{2}(e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t+i\delta_\omega} + e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t-i\delta_\omega})\nabla|\phi_a\rangle \quad (3.11)$$

Insert Eq. (3.11) into Eq. (3.8):

$$c_b^{(1)}(t) = -\frac{e}{2m} \int_0^\infty d\omega A_0(\omega) \left[e^{i\delta_\omega} \langle\phi_b|e^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\epsilon}\cdot\nabla|\phi_a\rangle \int_0^t dt' e^{i(\omega_{ba}-\omega)t'} \right. \\ \left. + e^{-i\delta_\omega} \langle\phi_b|e^{-i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\epsilon}\cdot\nabla|\phi_a\rangle \int_0^t dt' e^{i(\omega_{ba}+\omega)t'} \right] \quad (3.12)$$

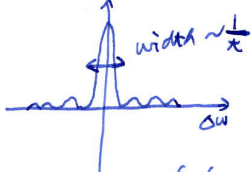
We can explicitly solve the time-integrals,

$$I \equiv \int_0^t dt' e^{i(\omega_{ba}\pm\omega)t'} = \frac{e^{i(\overbrace{\omega_{ba}\pm\omega}^{\equiv\Delta\omega})t} - 1}{i(\omega_{ba}\pm\omega)} \quad (3.13)$$

We see,

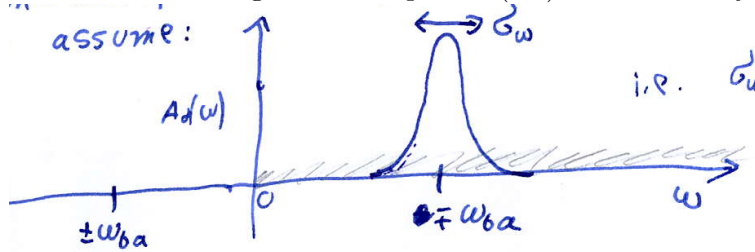
$$|I|^2 = \left| \frac{e^{i(\Delta\omega t')} - 1}{i\Delta\omega} \right|^2 = \left| e^{\frac{i(\Delta\omega t')}{2}} \frac{\left(e^{\frac{i(\Delta\omega t')}{2}} - e^{-\frac{i(\Delta\omega t')}{2}} \right)}{i\Delta\omega} \right|^2 = 4 \frac{\sin^2 \left(\frac{\Delta\omega t}{2} \right)}{\Delta\omega^2} = 2F(\Delta\omega), \quad (3.14)$$

where the function F was defined in section 1.2.5.



left: Plot of $F(\Delta\omega)$

We see that the r.h.s. of 3.12 is only significant for $\Delta\omega = \omega_{ba} \pm \omega = 0 \Rightarrow \omega = -\omega_{ba}$ or $\omega = +\omega_{ba}$. Now our electromagnetic wave-packet (3.4) contains many different frequencies ω .



left: For simplicity we assume a wavepacket as on the left, i.e. with $\sigma_\omega \ll |\omega_{ba}|$ and $\omega_0 > 0$.

We can then have two cases:

- $E_b > E_a \Rightarrow \omega_{ba} > 0 \Rightarrow \omega_{ba} - \omega$ term in Eq. (3.12) will contribute
- $E_b < E_a \Rightarrow \omega_{ba} < 0 \Rightarrow \omega_{ba} + \omega$ term in Eq. (3.12) will contribute

These two cases give rise to:

Absorption $E_b > E_a$:

Neglect second term in Eq. (3.12) and write,

$$|c_b^{(1)}(t)|^2 = \frac{1}{4} \left(\frac{e}{m} \right)^2 \left| \int_0^\infty d\omega A_0(\omega) M_{ba} \left[\frac{e^{i(\omega_{ba}-\omega)t} - 1}{i(\omega_{ba} - \omega)} \right] e^{i\delta\omega} \right|^2 \quad (3.15)$$

with,

Matrix Element

$$M_{ba}(\omega) = \langle \phi_b | \exp(i\mathbf{k} \cdot \mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla | \phi_a \rangle. \quad (3.16)$$

- Note, some other definitions might include the electric charge e into the matrix element.
- We write $M_{ba}(\omega)$ since the ME depends on ω through $\omega = \mathbf{k}c$.
- To obtain $|c_b^{(1)}(t)|$ we have to evaluate $|\int_0^\infty d\omega z(\omega)|^2 = \int_0^\infty d\omega \int_0^\infty d\omega' z^*(\omega)z(\omega')$, in which $z^*(\omega)z(\omega')$ contains a term $e^{-i(\delta_\omega - \delta_{\omega'})}$.
- Since we assume random $\delta_\omega, \delta_{\omega'}$ for (incoherent light) this part is on average zero unless $\omega = \omega'$.
- Using this we can simplify:

$$|c_b^{(1)}(t)|^2 = \frac{1}{4} \left(\frac{e}{m}\right)^2 \int_0^\infty d\omega \underbrace{|A_0(\omega)|^2}_{\text{approx } |A_0(\omega)|^2 = |A_0(\omega_{ba})|^2} |M_{ba}(\omega)|^2 \underbrace{\left| \frac{e^{i(\omega_{ba}-\omega)t} - 1}{i(\omega_{ba} - \omega)} \right|^2}_{=2F(t, \omega - \omega_{ba}) \text{ sharply peaked around } \omega = \omega_{ba}}$$
(3.17)

$$|c_b^{(1)}(t)|^2 = \frac{1}{2} \left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2 \underbrace{\int_{-\infty}^\infty F(t, \Delta\omega) d\omega}_{\substack{j_0^\infty \Rightarrow j_{-\infty}^\infty \\ =\pi t}}$$
(3.18)

So Probability $P_b = |c_b^{(1)}(t)|^2$ to be in state b increases linearly in time, $P_b = W_{ba}t$, with

Transition rate for absorption (integrated over ω)

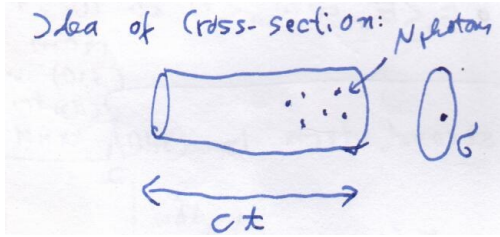
$$W_{ba} = \frac{\pi e^2}{2m} A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2$$

$$= \frac{4\pi^2}{m^2 c^2} \frac{e^2}{(4\pi\epsilon_0)} \frac{I(\omega_{ba})}{\omega_{ba}^2} |M_{ba}(\omega_{ba})|^2$$
(3.19)

- second line uses intensity at ω

$$I(\omega) = \frac{1}{2} \epsilon_0 c \omega^2 A_0^2(\omega)$$
(3.20)

- so, most importantly, the rate is proportional to light intensity and matrix element $|M_{ba}(\omega_{ba})|^2$
- We can remove the intensity dependence of the absorption process by defining the



left:

Absorption cross section:

$$\sigma_{ab} = \hbar\omega W_{ba}/I(\omega_{ba}) \quad (3.21)$$

The intensity is $I = \hbar\omega N_{\text{photons}}c$

Stimulated Emission $E_a > E_b$:

Through the same steps as above, we obtain the same expression for the transition rate (see book).

- If we have a thermal distribution of atoms at temperature T , the number of atoms in state a or b is given by $N_{a,b} \sim \exp\left(-\frac{E_{a,b}}{k_b T}\right)$ respectively, so there are more atoms in the lower energy state and it is thus more likely to absorb light (despite the same rates for absorption and emission)
- The principle of a Laser relies on population inversion, which means $N_b > N_a$ even though $E_b > E_a$. In that case stimulated emission can become more likely than absorption.

Spontaneous Emission:

In QED, the vector potential for absorption (**emission**) of a single photon from an N photon state, has the form:

$$\mathbf{A} = \boldsymbol{\epsilon} \left[\frac{2[N(\omega)+1]\hbar}{V\epsilon_0\omega} \right]^{\frac{1}{2}} \frac{1}{2} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)]. \quad (3.22)$$

- Importantly the **+1** is only there for emission, not for absorption. V is the quantisation volume.
- One can see that absorption gives the same result as (3.19) [N and V go into the factor $I(\omega)$].
- However emission would be the same only if we replace $N(\omega) + 1 \rightarrow N(\omega)$.
- The piece **+1** is related to spontaneous emission, it takes place even without any external field (light), due to vacuum fluctuations of the electro-magnetic field.

3.2 Selection Rules

Rates depend most critically on matrix-element

$$M_{ba}(\omega) = \langle \phi_b | \exp(i\mathbf{k} \cdot \mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla | \phi_a \rangle \quad \text{where,} \quad (3.23)$$

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 1 + (i\mathbf{k} \cdot \mathbf{r}) + \frac{1}{2!}(i\mathbf{k} \cdot \mathbf{r})^2 + \dots \quad (3.24)$$

For wavelength much larger than atomic size (r_0), we have that $|\mathbf{k} \cdot \mathbf{r}| \lesssim 2\pi \frac{r_0}{\lambda} \ll 1$ at all locations \mathbf{r} with non-vanishing electron density, i.e. $\phi_{a/b}(\mathbf{r}) \neq 0$. Thus we can replace the exp by 1. This is called the dipole approximation. Then we define the

Matrix-element in the dipole approximation

$$M_{ba}^D = \epsilon \cdot \langle \phi_b | \nabla | \phi_a \rangle \quad (3.25)$$

To see more clearly why we use the name “dipole-approximation”, let us utilize:

$$\hat{\mathbf{p}} = m \frac{m}{\hbar} [\hat{H}_0, \hat{\mathbf{r}}], \text{ with } \quad \hat{\mathbf{p}} = -i\hbar \nabla \text{ and } \quad \nabla = -\frac{m}{\hbar^2} [\hat{H}_0, \mathbf{r}] \quad (3.26)$$

↓

$$\begin{aligned} M_{ba}^D &= \boldsymbol{\epsilon} \cdot \frac{-m}{\hbar^2} \langle \phi_b | (\hat{H}_0 \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{H}_0) | \phi_a \rangle \\ &= -\frac{\omega_{ba} m}{\hbar} \boldsymbol{\epsilon} \cdot \langle \phi_b | \mathbf{r} | \phi_a \rangle \end{aligned}$$

To reach this we had to also remember $\hat{H}_0 = \hat{\mathbf{p}}^2/2m + V(\hat{\mathbf{r}})$ and $[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}$. We call the result

Matrix-Element in length form

$$M_{ba}^D = \frac{m\omega_{ba}}{\hbar e} \boldsymbol{\epsilon} \cdot \mathbf{D}_{ba} \quad \text{where} \quad \mathbf{D}_{ba} = \langle \phi_b | (-e\hat{\mathbf{r}}) | \phi_a \rangle \quad (3.27)$$

with transition dipole moment vector operator \mathbf{D}_{ba} .

“Dipole-approximation” thus implies that only the dipole-moment of the electronic charge distribution is taken into account for interactions with the light.

If \mathbf{D}_{ba} does not vanish between two states $|\phi_a\rangle$ and $|\phi_b\rangle$, the transition between these states is called electric dipole allowed (E_1). Even if \mathbf{D}_{ba} vanishes, M_{ba} might not vanish due to higher order terms in $\exp(i\mathbf{k} \cdot \mathbf{r})$, e.g. $i(\mathbf{k} \cdot \mathbf{r})$ which gives rise to magnetic dipole (M_1) and electric quadrupole (E_2) transitions. These M_{ba} are however much smaller than non-vanishing \mathbf{D}_{ba} .

Let us thus now consider when M_{ba} can be nonzero, which depends on the transition dipole moment \mathbf{D}_{ba} and the polarisation vector $\boldsymbol{\epsilon}$. Let us first look at \mathbf{D}_{ba} in detail:

Elementary symmetry considerations:

$$|\phi_a\rangle = |\phi_{n_a l_a m_a}\rangle \implies R_{n_a l_a}(r) Y_{l_a m_a}(\theta, \varphi) \quad (3.28)$$

From Eq. (1.35) we can obtain the transformation law of the wavefunction for $\mathbf{r} \rightarrow \mathbf{r}' = -\mathbf{r}$. In polar co-ordinates ($r, \theta, \varphi \rightarrow r, \theta \rightarrow \pi - \theta, \varphi \rightarrow \varphi + \pi$), hence we deduce $\phi(\mathbf{r}) \rightarrow (-1)^{l_a} \phi(\mathbf{r})$ where the

Factor under space inversion $(-1)^{l_a}$ is called parity of the state $|\phi_a\rangle$.

Thus $\mathbf{D}_{ba} = -e \int d^3\mathbf{r} \phi_b^*(\mathbf{r}) \mathbf{r} \phi_a(\mathbf{r})$ transforms like

$$\mathbf{D}_{ba} \rightarrow \mathbf{D}_{ba} (-1)^{l_a + l_b + 1}. \quad (3.29)$$

where we have used $\int d^3\mathbf{r} = \int d^3(-\mathbf{r})$. \implies We need $l_a + l_b + 1 = \text{even}$, otherwise \mathbf{D}_{ba} has to vanish. \implies dipole ME connects only states of opposite parity, independent of $\boldsymbol{\epsilon}$.

Full Calculation

We can write $\boldsymbol{\epsilon} \cdot \mathbf{D}_{\mathbf{b}\mathbf{a}} = (-e)\langle\phi_b|\boldsymbol{\epsilon} \cdot \mathbf{r}|\phi_a\rangle$ and,

$$\boldsymbol{\epsilon} \cdot \mathbf{r} = \begin{pmatrix} \epsilon_x \\ \epsilon_y \\ \epsilon_z \end{pmatrix} \begin{pmatrix} r \sin \theta \cos \phi \\ r \sin \theta \sin \phi \\ r \cos \theta \end{pmatrix} = -\frac{1}{\sqrt{2}} \underbrace{(\epsilon_x + i\epsilon_y)}_{\epsilon_1} \underbrace{\left[\frac{r \sin \theta e^{i\varphi}}{\sqrt{2}} \right]}_{\equiv r_1} + \frac{1}{\sqrt{2}} \underbrace{(\epsilon_x - i\epsilon_y)}_{\epsilon_{-1}} \underbrace{\left[\frac{r \sin \theta e^{-i\varphi}}{\sqrt{2}} \right]}_{\equiv r_{-1}} + \underbrace{\epsilon_z}_{\epsilon_0} \underbrace{r \cos \theta}_{r_0}, \quad (3.30)$$

where we have used so called ‘‘spherical components’’ r_q $q \in \{1, 0, -1\}$ of the vector \mathbf{r} .

Then an explicit integration gives:

$$\langle\phi_b|r_1|\phi_a\rangle \neq 0 \quad \text{if} \quad l_b = l_a \pm 1 \quad m_b = m_a + 1 \quad (3.31)$$

$$\langle\phi_b|r_{-1}|\phi_a\rangle \neq 0 \quad l_b = l_a \pm 1 \quad m_b = m_a - 1 \quad (3.32)$$

$$\langle\phi_b|r_0|\phi_a\rangle \neq 0 \quad l_b = l_a \pm 1 \quad m_b = m_a \quad (3.33)$$

Now if only some polarisation components $\epsilon_{-1,0,1}$ are non zero, we can select specific cases, and obtain:

Dipole Selection rules for absorption: Assuming light propagates along the \hat{k} direction (quantisation axis).

linearly polarized light (π transition)	$l_b = l_a \pm 1$	
only $\epsilon_0 \neq 0$	$m_b = m_a$	(3.34)

left handed circularly polarized light ($\sigma+$ transition),	$l_b = l_a \pm 1$	
only $\epsilon_1 \neq 0$	$m_b = m_a + 1$	(3.35)

right handed circularly polarized light ($\sigma-$ transition),	$l_b = l_a \pm 1$	
only $\epsilon_{-1} \neq 0$	$m_b = m_a - 1$	(3.36)

unpolarized or any other polarization direction	$l_b = l_a \pm 1$	
random mixture of $\boldsymbol{\epsilon}$ or all $\epsilon_k \neq 0$	$m_b = m_a, m_a \pm 1$	(3.37)

- $\sigma+$ means photon spin \parallel quantisation axis, $\sigma-$ opposite.
- Rules for emission have swapped signs for $m_b = m_a \pm 1$.
- If the light is propagating in the $-\hat{k}$ direction, the allocation between σ_{\pm} and left- / right- is swapped.

3.2.1 More on Spontaneous Emission

Using the QED vector potential \mathbf{A} (3.22) we can derive a rate ,

$$W_{ba}^S = \frac{4\pi^2}{m^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{\hbar}{V\omega_{ba}} |M_{ba}|^2 \delta(\omega - \omega_{ba}) \quad (3.38)$$

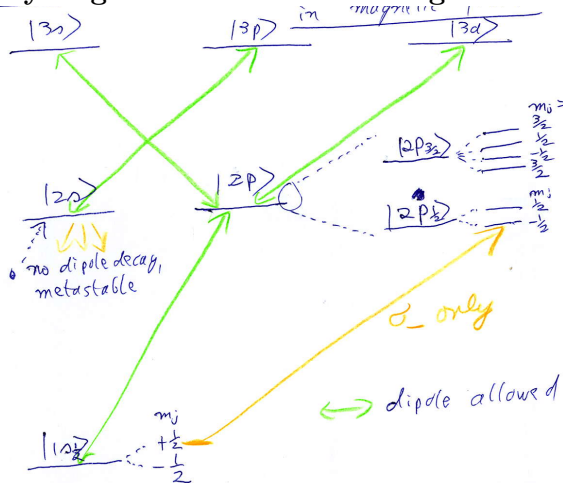
for the emission of a given photon with energy ω . To find the total spontaneous emission rate, we integrate over all possible photon states (momenta/ wave-vectors \mathbf{k})

Total spontaneous emission rate

$$W_{ba}^{S,TOT} = \frac{4\alpha}{3c^2} \omega_{ba}^3 |\langle \phi_b | \mathbf{r} | \phi_a \rangle|^2 \quad (3.39)$$

- we have used the dipole-approximation
- Important is the ω_{ba}^3 dependence: decay will always be dominantly to the state of the lowest energy that is accessible via dipole selection rules.
- The same selection rules apply for absorption, emission, and stimulated emission. \implies states that cannot decay via dipole-allowed transitions have comparatively longer lifetimes. These are called metastable.

Hydrogen transitions in a magnetic field:



left: Hydrogen level diagram

- Dipole radiation does not couple to spin, \implies all selection rules can be translated to j-basis (e.g. $\Delta m = 0 \implies \Delta m_j = 0$). It is a bit more tricky for the j quantum number (Even though Δl is not possible, $\Delta j = 0$ is possible, since e.g. $(l = 1, s = \frac{1}{2})$ and $(l = 2, s = \frac{1}{2})$ both have $j = \frac{3}{2}$).
- Hydrogen $|2s\rangle$ state metastable.
- Transition $|1s\rangle \rightarrow |3s\rangle$ can only happen via E_2 , M_1 or via a two-step process such as $|1s\rangle \rightarrow |2p\rangle \rightarrow |3s\rangle$ (e.g. using two lasers).

Week 7

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

3.3 Rabi-Oscillations

- Consider again the Hamiltonian (3.7) $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$, neglecting the \mathbf{A}^2 term. For this section we choose a simpler vector potential

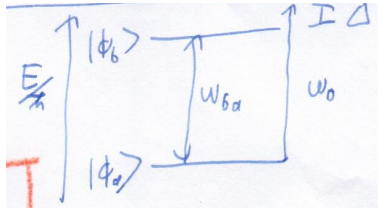
$$\mathbf{A}(\mathbf{r}, t) = A_0 \boldsymbol{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega_0 t) \quad (3.40)$$

In terms of the more complicated expression (3.5), this could be monochromatic/narrow band laser which thus has $\delta_\omega \equiv 0$ and $A_0(\omega)$ sharply peaked around $\omega = \omega_0$.

From (3.1), we have

$$\mathbf{E}(\mathbf{r}, t) = \underbrace{\omega_0 A_0 \boldsymbol{\epsilon}}_{\mathbf{E}_0} \sin(\mathbf{k} \cdot \mathbf{r} - \omega_0 t) \quad (3.41)$$

for the Electric field.



left: Two level atom with laser coupling

For simplicity consider only two atomic states $|\phi_a\rangle, |\phi_b\rangle$ with $\omega_{ba} \approx \omega_0$, and introduce the

Detuning $\Delta = \omega_0 - \omega_{ba}$, the difference between laser and atomic transition frequency.

We want to determine the full time evolution of the atom, which we can write as

$$|\psi(t)\rangle = c_a(t) e^{-\frac{i}{\hbar} E_a t} |\phi_a\rangle + c_b(t) e^{-\frac{i}{\hbar} E_b t} |\phi_b\rangle, \quad (3.42)$$

thanks to our restriction to just two atomic states. For writing the TDSE (1.45) we nextly require

all possible matrix elements of \hat{H} with states $|\phi_{a/b}\rangle$. These are:

$$\langle\phi_a|\hat{H}_0|\phi_a\rangle = E_a, \quad \langle\phi_b|\hat{H}_0|\phi_b\rangle = E_b, \quad (3.43)$$

$$\langle\phi_b|\hat{H}'(t)|\phi_a\rangle \stackrel{\text{Eq. (3.7)}}{=} -i\hbar\frac{A_0e}{m}\langle\phi_b|\boldsymbol{\epsilon}\cos(\mathbf{k}\cdot\mathbf{r}-\omega_0t)\cdot\nabla|\phi_a\rangle \quad (3.44)$$

$$= -i\hbar\frac{A_0e}{2m}\langle\phi_b|\boldsymbol{\epsilon}\left(\underbrace{e^{i\mathbf{k}\cdot\mathbf{r}}}_{\approx 1}e^{-i\omega_0t} + \underbrace{e^{-i\mathbf{k}\cdot\mathbf{r}}}_{\approx 1}e^{i\omega_0t}\right)\cdot\nabla|\phi_a\rangle \quad (\text{dipole approximation})$$

$$= -i\hbar\frac{A_0e}{2m}(e^{-i\omega_0t} + e^{i\omega_0t})\boldsymbol{\epsilon}\cdot\langle\phi_b|\nabla|\phi_a\rangle$$

$$\stackrel{\text{Eq. (3.27)}}{=} -i\frac{A_0\omega_{ba}}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\boldsymbol{\epsilon}\cdot\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle$$

$$\approx -\frac{i}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\mathbf{E}_0\cdot\underbrace{\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle}_{\substack{\text{atomic} \\ \text{transition dipole}}} \quad (3.45)$$

Now rewrite TDSE (1.45) as matrix equation

$$i\hbar\begin{pmatrix}\dot{c}_a(t) \\ \dot{c}_b(t)\end{pmatrix} = \begin{pmatrix}o & \tilde{H}_{ab} \\ \tilde{H}_{ab}^* & 0\end{pmatrix}\begin{pmatrix}c_a(t) \\ c_b(t)\end{pmatrix} \quad (3.46)$$

where,

$$\tilde{H}_{ab} = \frac{i}{2}(e^{-i\omega_0t} + e^{i\omega_0t})\mathbf{E}_0\cdot\langle\phi_b|(-e\hat{\mathbf{r}})|\phi_a\rangle e^{\frac{i}{\hbar}(E_a-E_b)t}, \quad (3.47)$$

which we further re-write with two steps:

- We see complex exponentials such as $e^{-i\overbrace{(\omega_0 + \omega_{ba})}^{\approx 2\omega_0, \text{ large}}}t$ and also $e^{i\overbrace{(\omega_0 - \omega_{ba})}^{= \Delta, \text{ small}}}t$. We neglect the fast oscillating exponential, assuming the complex number averages to zero. This is called the rotating wave approximation.
- We define the

Rabi-frequency as

$$\hbar\Omega = \langle\phi_b|\mathbf{d}\cdot\mathbf{E}_0|\phi_a\rangle \quad (3.48)$$

where, $\mathbf{d} = -e\hat{\mathbf{r}}$. This describes the strength with which atoms undergo a transition from $|\phi_a\rangle$ to $|\phi_b\rangle$ and is not to be confused with the laser frequency ω_0 or transition frequency ω_{ab} .

We can then re-write our matrix equation:

$$i\hbar\begin{pmatrix}\dot{c}_a(t) \\ \dot{c}_b(t)\end{pmatrix} = \begin{pmatrix}o & i\frac{\hbar\Omega}{2}e^{-i\Delta t} \\ -i\frac{\hbar\Omega}{2}e^{i\Delta t} & 0\end{pmatrix}\begin{pmatrix}c_a(t) \\ c_b(t)\end{pmatrix}, \quad (3.49)$$

and finally redefine $\tilde{c}_b(t) = ie^{-i\Delta t}c_b(t)$ and $\tilde{c}_a(t) = c_a(t)$, to reach

Effective SE and Hamiltonian for two-level atom in dipole and rotating-wave approximation

$$i \begin{pmatrix} \dot{\tilde{c}}_a(t) \\ \dot{\tilde{c}}_b(t) \end{pmatrix} = \underbrace{\begin{pmatrix} 0 & \frac{\Omega}{2} \\ \frac{\Omega}{2} & -\Delta \end{pmatrix}}_{\hat{H}_{\text{eff}}} \begin{pmatrix} \tilde{c}_a(t) \\ \tilde{c}_b(t) \end{pmatrix}. \quad (3.50)$$

Can solve with standard methods [exercise], using eigensystem of \hat{H}_{eff} . For the initial condition $\tilde{c}_a(0) = 1$, $\tilde{c}_b(0) = 0$, i.e. an atom in state a , we find

$$\begin{aligned} \tilde{c}_a(t) &= e^{i\frac{\Delta t}{2}} \left\{ \cos\left(\frac{t\Omega_{\text{eff}}}{2}\right) - i\frac{\Delta}{\Omega_{\text{eff}}} \sin\left(\frac{t\Omega_{\text{eff}}}{2}\right) \right\}, \\ \tilde{c}_b(t) &= -i\frac{\Omega}{\Omega_{\text{eff}}} e^{i\frac{\Delta t}{2}} \sin\left(\frac{t\Omega_{\text{eff}}}{2}\right). \end{aligned} \quad (3.51)$$

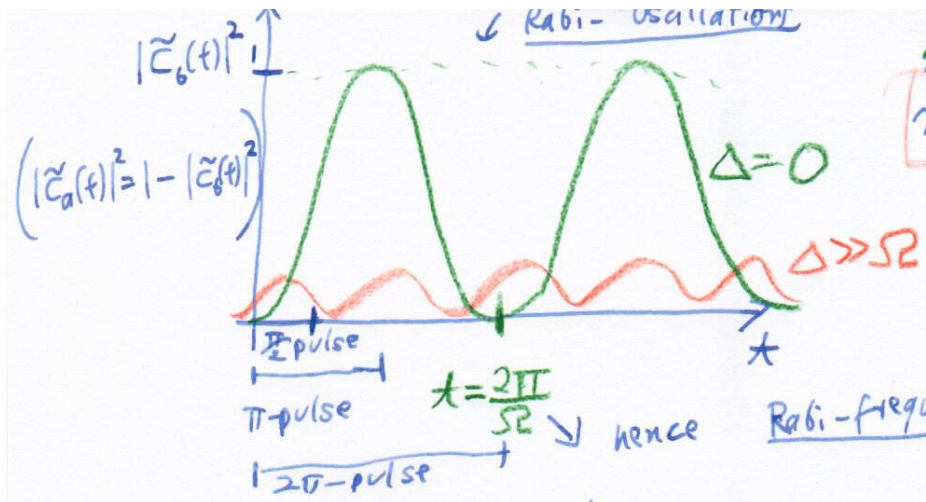
with $\Omega_{\text{eff}} = \sqrt{\Omega^2 + \Delta^2}$.

These are the ubiquitous

Rabi-oscillations:

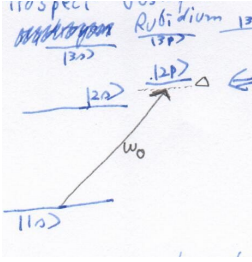
$$n_b(t) = |\tilde{c}_b(t)|^2 = \frac{\Omega^2}{\Omega_{\text{eff}}^2} \sin^2\left(\frac{\Omega_{\text{eff}}}{2} t\right) \quad (3.52)$$

where, $\Omega_{\text{eff}} = \sqrt{\Delta^2 + \Omega^2}$.



On resonance, $\Delta = 0$, the atom undergoes oscillations between states $|\phi_a\rangle$ and $|\phi_b\rangle$ with the Rabi frequency.

- For large detuning $\Delta \gg \Omega$, the probability to reach the state $|\phi_b\rangle$ remains small: $n_b(t)|_{\text{max}} = \Omega^2/\Omega_{\text{eff}}^2 \approx (\Omega/\Delta)^2 \ll 1$. This often in retrospect justifies our initial approximation to consider only two atomic states, see diagram below.



left: Rubidium level diagram with laser light at frequency ω_0 that is near-resonant with $|1s\rangle \rightarrow |2p\rangle$. This means however that it is far-off resonant with any other transition (e.g. $|2s\rangle \rightarrow |2p\rangle$). According to the arguments above other states than $|2p\rangle$ will thus not become populated.

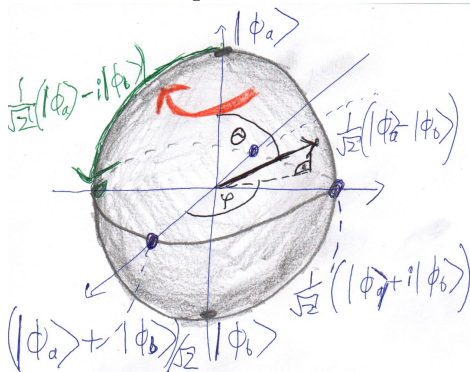
- The system of two laser coupled electronic states in an atom realizes a coherent two-level system as long as we ignore spontaneous decay. To discuss manipulations of this system, we use

Nomenclature for Rabi pulses: Suppose we apply the laser coupling only for a duration T . The indicated effects are for resonant pulses with $\Delta = 0$.

$$\begin{aligned}
 \pi/2 \text{ pulse} &\Leftrightarrow T = \frac{\pi}{2\Omega} & |\Psi(t=0)\rangle &= |\phi_a\rangle \rightarrow \frac{1}{\sqrt{2}}(|\phi_a\rangle - i|\tilde{\phi}\rangle), \\
 \pi \text{ pulse} &\Leftrightarrow T = \pi\frac{1}{\Omega} & |\phi_a\rangle &\rightarrow -i|\tilde{\phi}_b\rangle, \\
 2\pi \text{ pulse} &\Leftrightarrow T = 2\pi\frac{1}{\Omega} & |\phi_a\rangle &\rightarrow -|\phi_a\rangle.
 \end{aligned} \tag{3.53}$$

Bloch-sphere representation: The most general two-state superposition has the form $|\Psi\rangle = \cos[\theta/2]|\phi_a\rangle + e^{i\varphi}\sin[\theta/2]|\phi_b\rangle$ where $0 \leq \theta \leq \pi$ and $0 \leq \varphi \leq 2\pi$ are simply some parametrisation of the superposition^(*). However we can now also view θ and φ as the usual angles in spherical polar coordinates. This allows us to visualize any such superposition as a point on the surface of the Bloch sphere shown below.

From Eq. (3.51) we can also understand the simplest types of time evolution: For a resonant pulse starting in $|\phi_a\rangle$ with $\Delta = 0$ we identify $\theta = t\Omega$ (green arrow). For uncoupled states $\Omega = 0$ with different energies $\Delta E \neq 0$, we see $\varphi = \Delta E t/2$ (red arrow). More generally evolution due to any unitary operator \hat{U} in the space $|\phi_{a/b}\rangle$ corresponds to a specific rotation on the Bloch sphere.



left: Visualisation of states and dynamics on Bloch sphere.

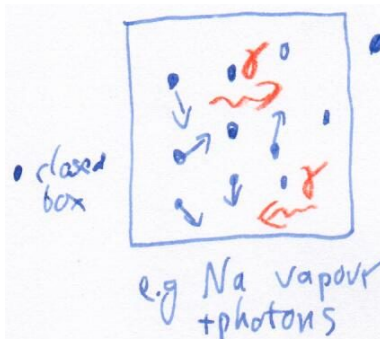
Bloch-sphere representation contd.:

The visualisation can be extended to include spontaneous decay (optical Bloch equations).

(*) Originally $|\Psi\rangle = c_1|\phi_a\rangle + c_2|\phi_b\rangle$ with $c_1, c_2 \in \mathbb{C}$ contained 4 real numbers. Due to the constraint $1 = |c_1|^2 + |c_2|^2$ we reduce one of those, one more can be removed since the overall phase of the state is irrelevant.

3.4 Spectral Lines

3.4.1 Thermal gas of atoms



left: Consider a box with atomic vapor and photons in equilibrium at temperature T

- Again let's consider two atomic levels $|\phi_{a/b}\rangle$ only, with $E_b > E_a$. In thermal equilibrium atoms are found in both states with some probability, let the number of atoms in a be N_a . Photons can thus take part in a statistical mix of stimulated emission, absorption and spontaneous emission.
- The number of atoms making the transition $a \rightarrow b$ per unit time is³

$$\dot{N}_{ba} = B_{ba}N_a\rho(\omega_{ba}), \quad (3.54)$$

where B_{ba} is the Einstein coefficient for absorption and $\rho(\omega_{ba})$ is the energy density in the radiation field (of the photons) at frequency ω_{ba} .

- For the reverse transition

$$\dot{N}_{ab} = A_{ab}N_b + B_{ab}N_b\rho(\omega_{ba}), \quad (3.55)$$

where A_{ab} is the Einstein coefficient for spontaneous emission and B_{ab} the Einstein coefficient for stimulated emission.

- In thermal equilibrium we must have $\dot{N}_{ab} = \dot{N}_{ba}$ and also

$$\frac{N_a}{N_b} = \exp[-(E_a - E_b)/(k_B T)] = \exp[\hbar\omega_{ba}/(k_B T)]. \quad (3.56)$$

³It is logical that \dot{N}_{ba} must be $\sim N_a$. We know from Eq. (3.19) that it must be $\sim \rho(\omega_{ba})$. Finally we just give the remaining proportionality constant the name B_{ba} .

We can use these relations to get an expression for the radiation density

$$\rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba} \exp[\hbar\omega_{ba}/(k_B T)] - B_{ab}} \quad (3.57)$$

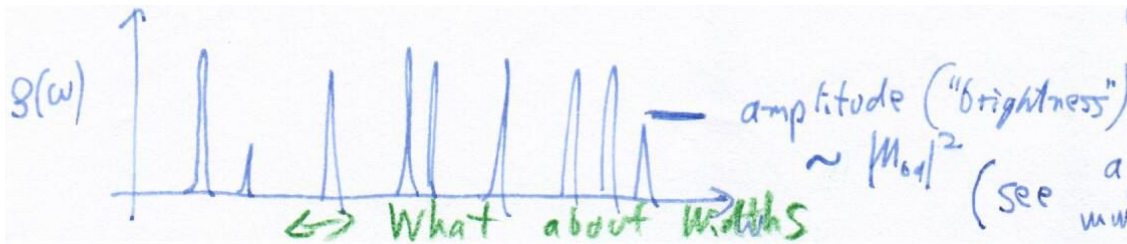
By requiring that (3.57) is identical with Planck's law from thermodynamics, we can deduce that

$$B_{ba} = B_{ab}, \quad (3.58)$$

$$A_{ab} = \left(\frac{\hbar\omega_{ba}^3}{\pi c^3} \right) B_{ab}. \quad (3.59)$$

This argument, due to Einstein, gives some link between stimulated and spontaneous emission without even solving the atomic physics problem. The result is consistent with the detailed calculations in section 3.1.2. There, from Eq. (3.19) we can write $B_{ba} = W_{ba}/[I(\omega_{ba})/c] \sim |M_{ba}|^2$, where the factor in square brackets is the energy density.

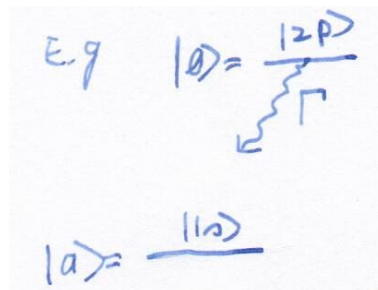
From Eq. (3.57) we also infer that there are photons in the box at equilibrium, at all frequencies belonging to any transition between two states a, b . This would look like:



top: From the picture of a gas in the box in thermal equilibrium above, we would also expect that in the radiation spectrum, all transitions frequencies for allowed transitions between atomic levels are present. Their amplitude (“brightness”) will be determined by $|M_{ba}|^2$. For a tabulation of experimental data on allowed transition frequencies and their strength (matrix elements), see www.nist.gov/pml/atomic-spectra-database .

- The remaining question regarding a spectrum such as above is, what sets the width and shape of the spectral lines?

3.4.2 Line shapes



left: As discussed in section 3.1.2 atomic excited states decay via spontaneous emission

A calculation of the corresponding decay rate, based on Eq. (3.22) and (3.39) gives for example a spontaneous decay rate $\Gamma_{2p \rightarrow 1s} = \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{h} = 6.2710^8 Z^4 s^{-1}$. Does the emission really only go into the mode with the resonance frequency $\omega = \omega_{ab}$?

A rigorous QED approach: would be to calculate the amplitude for the process $|b, \text{no photons}\rangle \rightarrow |a, \text{one photon with frequency } \omega, \text{polarisation } \epsilon \text{ and momentum } \mathbf{p}\rangle$, then integrate over all possible ϵ, \mathbf{p} to reach the rate as a function of ω .

We follow a simpler, semi-classical approach. Assume a single atom in an excited state $|\phi_b\rangle$ starts emitting light at time t , while returning to the ground-state $|\phi_a\rangle$ with a rate Γ . Ignoring the vector character of the light, the emitted field strength for $t \geq 0$ will look like:

$$E(t) = E_0 \left(e^{[-\Gamma t/2]} e^{i\omega_{ba}t} + c.c. \right), \tag{3.60}$$

while $E(t) = 0$ for $t < 0$. We took into account that the field intensity must be proportional to the probability of the atom actually remaining in $|\phi_b\rangle$, which drops as $e^{[-\Gamma t]}$.

Now we do the Fourier transform of Eq. (3.60) to find the frequency spectrum via

$$E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(\omega) e^{i\omega t} d\omega, \tag{3.61}$$

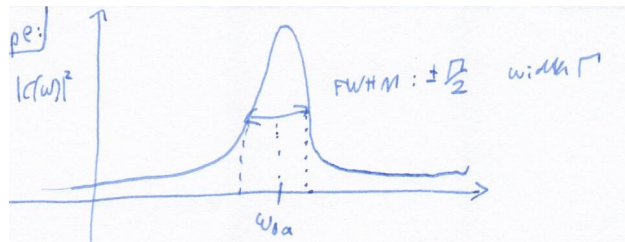
$$c(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{-i\omega t} dt, \tag{3.62}$$

and reach

$$c(\omega) = -\frac{E_0}{\sqrt{2\pi}} \left(\frac{1}{i(\omega_{ba} - \omega) - \Gamma/2} + \frac{1}{i(-\omega_{ba} - \omega) - \Gamma/2} \right). \tag{3.63}$$

The second term is typically much smaller and can hence be neglected. The overall frequency spectrum of spontaneously emitted light thus follows the

Natural line profile, also called Lorentzian frequency spectrum:

$$|c(\omega)|^2 = \frac{E_0^2}{2\pi} \frac{1}{(\omega_{ba} - \omega)^2 + (\Gamma/2)^2}. \tag{3.64}$$


top: Sketch of natural line profile Eq. (3.64). We also define the

Life-time of the upper state:

$$\tau = 1/\Gamma. \quad (3.65)$$

- Note, for quite highly excited states a large number of spontaneous decay channels k are often possible, each with rate Γ_k . In that case define the total decay rate as $\Gamma = \sum_k \Gamma_k$, then use Eq. (3.65).
- An intuitive picture for the origin of the frequency width is that the energy of a decaying state is uncertain by ΔE according to the energy time uncertainty relation $\Delta E \tau \sim \hbar$.

Measured line-profiles are frequently much broader and differently shaped than Eq. (3.64) due to the following effects:

- **Pressure broadening:** Also atomic collisions can cause a transition $b \rightarrow a$. If the collision rate exceeds the spontaneous decay rate, this can significantly shorten the life-time to $\rightarrow \tau_{\text{coll}}$. In this case the spectral line remains of Lorentzian shape, but with a width $\Gamma \sim 1/\tau_{\text{coll}}$. This effect becomes stronger with increasing gas pressure.
- **Doppler broadening:** Atoms of mass M move relative to the lab frame with some random velocity \mathbf{v} . The associated Doppler shift $\omega' = \omega - \mathbf{v} \cdot \mathbf{k}$ is then also randomly distributed. The distribution of velocities follows the Maxwell-Boltzmann form $\sim \exp[-M\mathbf{v}^2/(2k_B T)]$, which is a Gaussian in $|\mathbf{v}|$. The Doppler effect can thus broaden spectral lines from a gas and turn their shape into a Gaussian for high temperatures.

In the general case we have a mixture of Lorentzian and Gaussian shapes, called a Voigt profile.

3.4.3 Oscillator strength and sum rules

A useful concept to do with a spectral line due to a transition from a to k is their

Oscillator strength

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\langle \phi_b | \hat{r} | \phi_a \rangle|^2 \quad (3.66)$$

- These fulfill

Thomas-Reiche-Kuhn Sum rule

$$\sum_k f_{ka} = 1, \quad (3.67)$$

where the sum extends over all other states than a , including the continuum (see next section).

- The rule is useful to assess the importance of a certain transition. Knowing the matrix element for one transition we can infer f_{ka} . If this is close to one, we know from Eq. (3.67) that there are not going to be a lot of other important (strong) transitions.
- For proof see BJ book.

3.5 The photo-electric effect, photo ionization

Our treatment of atoms and atom light interaction so far only dealt with atomic bound states $|\phi_a\rangle$, $E_b < 0$. We can also find solutions of the Hydrogen TISE (1.30) with $E_b > 0$. These are called

Atomic continuum states, and fulfill

$$\left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \frac{Ze^2}{4\pi\epsilon_0 |\mathbf{r}|} \right) \Psi_b(\mathbf{k}_f, \mathbf{r}) = \underbrace{\frac{\hbar^2 \mathbf{k}_f^2}{2m}}_{=E_f > 0} \Psi_b(\mathbf{k}_f, \mathbf{r}). \quad (3.68)$$

- Continuum states $\Psi_b(\mathbf{k}_f, \mathbf{r})$ represent an electron that is not bound to the nucleus, so far away from the nucleus the solution behaves like a plane-wave $\sim \exp[i\mathbf{k}_f \cdot \mathbf{r}]$. Close to the nucleus, the plane-wave is modified since it feels the nuclear Coulomb potential.
- Ionisation by absorption of a photon can now be viewed as a transition between a bound and a continuum state.
- For $E_f \gg |E_a|$ we can even approximate $\Psi_b(\mathbf{k}_f, \mathbf{r}) \sim \exp[i\mathbf{k}_f \cdot \mathbf{r}]$ near the nucleus, and use our earlier result

$$\sigma = \frac{4\pi^2 \alpha \hbar^2}{m} \int d^3 \mathbf{k}_f \frac{1}{\omega_{ka}} |M_{ka}(\mathbf{k}_f, \omega_{fa})|^2 \delta(\omega - \omega_{ka}). \quad (3.69)$$

- This is just Eq. (3.21) and Eq. (3.19) for the absorption cross section with slight re-arrangements of constants, adding $\delta(\omega - \omega_{ka})$, which was implicitly assumed in Eq. (3.19) and integrating over all ejected electron momenta \mathbf{k}_f to get a total cross section.
- Note the matrix element

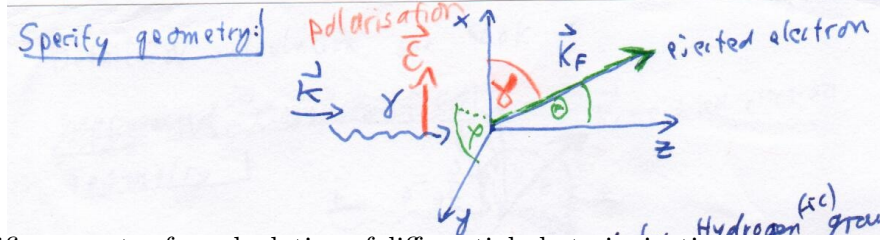
$$M_{ka} = \frac{1}{(2\pi)^{3/2}} \int d^3 \mathbf{r} \underbrace{\exp[-i\mathbf{k}_f \mathbf{r}]}_{\text{from } \Psi_b} \underbrace{\exp[i\mathbf{k} \mathbf{r}]}_{\text{from light}} \boldsymbol{\epsilon} \cdot \nabla \Psi_a(\mathbf{r}) \quad (3.70)$$

depends on \mathbf{k}_f , including its direction.

- We can re-write (3.69) using integration by parts to reach

$$M_{ka} = \frac{1}{(2\pi)^{3/2}} (-i\epsilon \cdot (\mathbf{k} - \mathbf{k}_f)) \int d^3\mathbf{r} \exp[-i(\mathbf{k} - \mathbf{k}_f)\mathbf{r}] \Psi_a(\mathbf{r}). \quad (3.71)$$

We now recognize that it is proportional to the 3D Fourier-Transform $\tilde{\Psi}_a(\mathbf{k} - \mathbf{k}_f)$ of $\Psi_a(\mathbf{r})$.



top: Specific geometry for calculation of differential photo-ionization cross-section. The x -axis is chosen along the light polarisation.

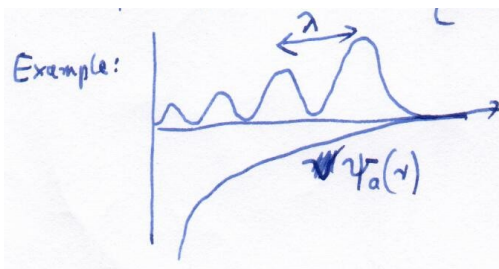
- Detailed calculation see BJ, using the geometry in the figure, one finds:

Differential cross-section for photo-ionization:

$$\frac{d\sigma}{d\Omega} = 32\alpha \frac{\hbar k_f^3}{m \omega} \frac{Z^5 a_0^3 \cos^2[\gamma]}{(Z^2 + \kappa^2 a_0^2)^4}, \quad (3.72)$$

where $\Omega = \{\theta, \varphi\}$ now corresponds to the ejection direction of the electron, $\kappa = |\boldsymbol{\kappa}|$, $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}_f$

- κ depends on θ .
- We see that electron ejection is most likely for $\gamma = 0, \pi$, where γ is the angle between the ejection direction and the incoming light linear polarisation axis. Hence the electron is ejected preferentially along the direction of E-field polarisation.



left: From Eq. (3.71) we can see that laser wavelength has to match size /oscillation scales of the wavefunction ^a. The fourier-transform of the example wavefunction shown on the left $\tilde{\Psi}_a(k)$, will have its main contributions at $k = 2\pi/\lambda$.

^aFor this argument assume $|\mathbf{k} - \mathbf{k}_f| \approx \mathcal{O}(|\mathbf{k}|)$, other cases are suppressed since $\gamma \approx 0, \pi/2$

- For this reason, X-rays are most likely to photo-ionize tightly bound electrons from the inner shells of heavy atom (their wavefunction has smallest “ λ ”, matching X-ray wavelengths).

Week 8

PHY 402 Atomic and Molecular Physics

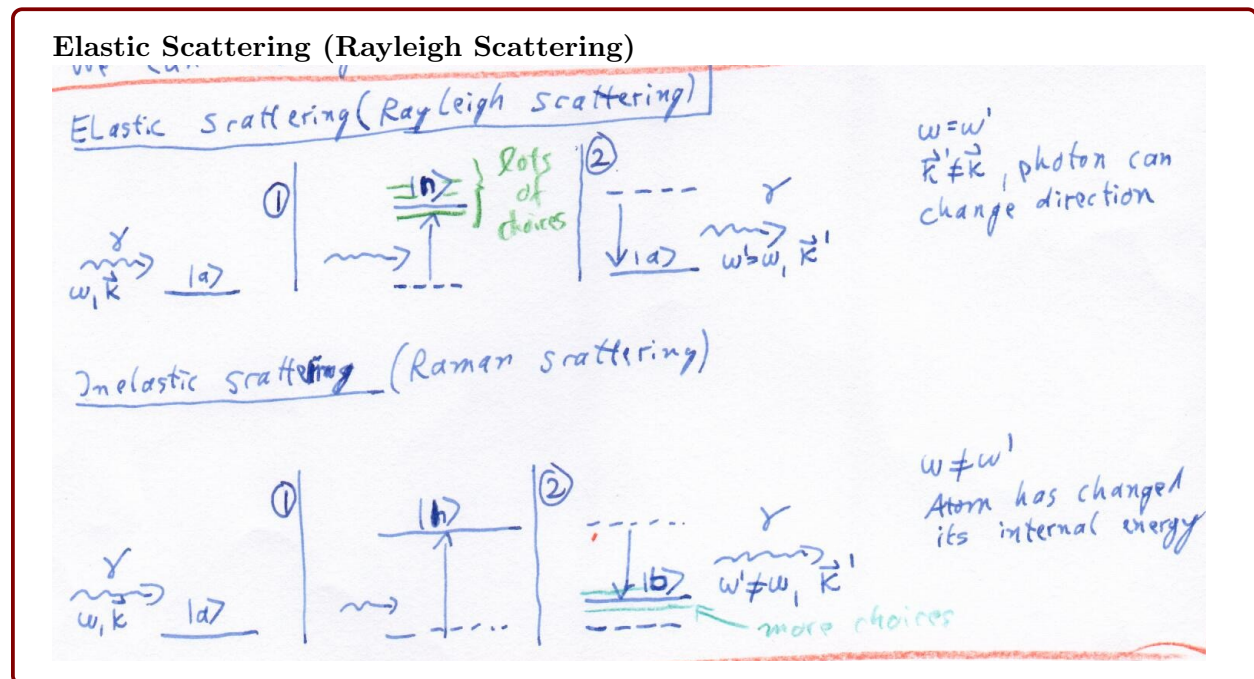
Instructor: Sebastian Wüster, IISER Bhopal, 2018

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3.6 Scattering of radiation by atoms

- So far we looked at processes where an atom makes a transition (b to a) and a photon is created, or the reverse using first order perturbation theory.
- Combining these in 2nd order perturbation theory yields the physics of light scattering.

We can distinguish two different possibilities:



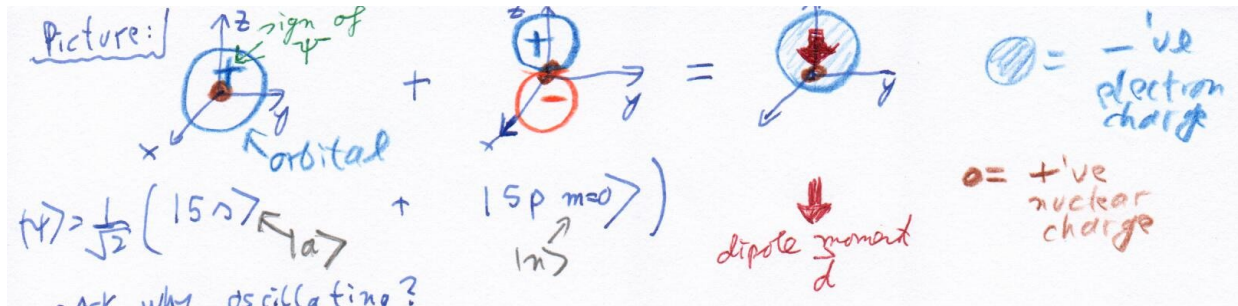
- Both processes can occur in a resonant or non-resonant version, depending on whether $\omega = \omega_{na}$ for two states a, n . They happen regardless of whether this is the case.

3.6.1 Rayleigh Scattering

The initial step (1), is a quantum mechanical amplitude for the atom to make the $|a\rangle \rightarrow |n\rangle$ transition. Afterwards/ during the process the atom will generically be in a superposition state

$$|\psi\rangle = c_a|a\rangle + c_n|n\rangle$$

Such a superposition state in general corresponds to an oscillating dipole. *Self-test: Why is the dipole oscillating?*



top: Sketch of oscillating charge distribution in atomic superposition states

- In turn, the oscillating dipole excited by the initial absorption of the incoming photon now emits radiation \rightarrow step 2, re-emission = scattering of the photon.
- This intuitive picture motivates a

Classical Treatment:

Electron as driven oscillator

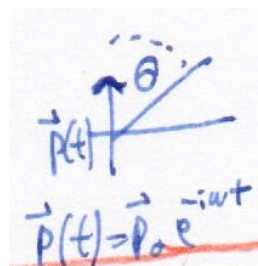
$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = -\frac{e}{m} E(t), \quad (3.73)$$

where $E(t) = E_0 \exp -i\omega t$ is the oscillating electric field of the incoming light, acting on the electron.

To retain connection with our quantum state picture above, we set $\omega_0 = \omega_{na}$ and $\gamma = \Gamma$ (decay rate, see Eq. (3.64)). The steady solution without initial transients is:

$$x(t) = \frac{-e/m}{\omega_0^2 - i\gamma\omega - \omega^2} E_0 e^{-i\omega t} \quad (3.74)$$

The resulting oscillating dipole moment of the electron is $p(t) = -e x(t)$. From electrodynamics, we know the power radiated by an oscillating dipole into a certain spherical angle $d\Omega$ is



left:

$$\frac{dP}{d\Omega} = \frac{c}{8\pi} k^4 |\mathbf{p}_0|^2 \sin^2 \theta, \quad (3.75)$$

when the dipole moment is $\mathbf{p}(t) = \mathbf{p}_0 \exp[-i\omega t]$, $\omega = ck$ and θ is the angle to the dipole axis, see sketch.

Combining Eq. (3.74) and Eq. (3.75) we reach the

Rayleigh Scattering formula

$$\frac{dP}{d\Omega} \sim \left(\frac{e}{m}\right)^2 \frac{\omega^4}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2} \sin^2 \theta \quad (3.76)$$

- For $\omega_0 \gg \omega$ this is $\sim \left(\frac{\omega}{\omega_0}\right)^4$
- This explains blue sky and red sunset via Rayleigh scattering off photons from atoms/-molecules in the atmosphere: optical wavelengths $\lambda \sim 400 - 800nm$ here $\omega_0 \gg \omega$ is true for N_2, O_2
Blue 450nm Red 650nm \implies Blue scattered 4.3 times more effectively
- Dipole direction \mathbf{p}_0 will be given by incoming polarisation vector $\epsilon \implies \theta$ is with respect to polarization of incoming light.

Sketch of quantum treatment:

Second order time-dependent perturbation theory version of Eq. (1.57) (see QM textbook) is:

$$c_b^{(2)}(t) = -\frac{1}{\hbar^2} \sum_n \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{bn}t'} e^{\omega_{na}t''} \underbrace{H'_{bn}(t')H'_{na}(t'')}_{\text{see Eq. (3.11)}} \quad (3.77)$$

Note, time-ordering $0 < t'' < t' < t$

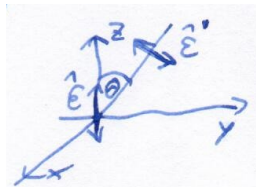
We can follow similar steps (but using QED) as for absorption cross-section (3.19) to find

Differential cross-section for photon scattering into (θ, ϕ)

$$\frac{d\sigma}{d\Omega} = r_0 \omega \omega' \left(\frac{m^2}{\hbar^2 e^4}\right) \left| \sum_n \frac{(\epsilon' \cdot \mathbf{D}_{bn})(\epsilon \cdot \mathbf{D}_{na})}{\omega_{na} - \omega} + \frac{(\epsilon \cdot \mathbf{D}_{bn})(\epsilon' \cdot \mathbf{D}_{na})}{\omega_{na} + \omega'} \right|^2 \quad (3.78)$$

- This describes both, Raman and Rayleigh scattering.
- Angular dependence of scattering is hidden in $\epsilon \cdot \mathbf{D}_{na}$.
- ϵ is the polarisation of the incoming photon, ϵ' of the outgoing one.

To check this with our earlier classical result on Rayleigh scattering, we assume that the only contributing intermediate state $|n\rangle$ is some p -state as in the picture above. We can set $\hat{\epsilon} \parallel \hat{k}$ along the z -axis as usual. Then one finds $\hat{D}_{na} \parallel \hat{k}$ for the reasons graphically shown in the picture. Let also $\omega = \omega'$ and assume $\omega_{na} \gg \omega$ as before.



left: We finally know $\epsilon' \cdot \mathbf{D}_{na} \sim \sin(\theta)$ from the diagram involving incoming and outgoing polarisation vectors.

With all these assumptions the cross-section (3.78) scales like

$$\frac{d\sigma}{d\Omega} \sim \left(\frac{\omega}{\omega_{na}}\right)^4 \sin^2 \theta \quad (3.79)$$

which reproduces the main features of the classical result.

We will take a closer look on Raman scattering later, in the context of molecules.

3.7 Interaction of many-electron atoms with radiation

All our discussion so far in chapter 3 generalizes from hydrogenic atoms to N -electron atoms if we replace the earlier matrix elements, e.g. M_{ba}^D instead by

Dipole Matrix element for many electrons

$$M_{ba}^D = \frac{m\omega_{ba}}{\hbar e} \epsilon \cdot \sum_{k=1}^N \langle \phi_b | (-e\mathbf{r}_k) | \phi_a \rangle \quad (3.80)$$

where \mathbf{r}_k is the coordinate of electron number k .

- To compare with Eq. (3.27).
- Since electrons are indistinguishable, we can instead also write

$$M_{ba}^D = \frac{Nm\omega_{ba}}{\hbar e} \epsilon \cdot \langle \phi_b | (-e\mathbf{r}_1) | \phi_a \rangle \quad (3.81)$$

It turns out that also the selection rules generalize quite straightforwardly:

Selection rules for many electron atoms:

$$\Delta J = 0, \pm 1 \quad (\text{No } J = 0 \rightarrow J' = 0), \quad \Delta M_J = 0, \pm 1 \quad (3.82)$$

where J now pertains to the total angular momentum of all electrons.

Week 9

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

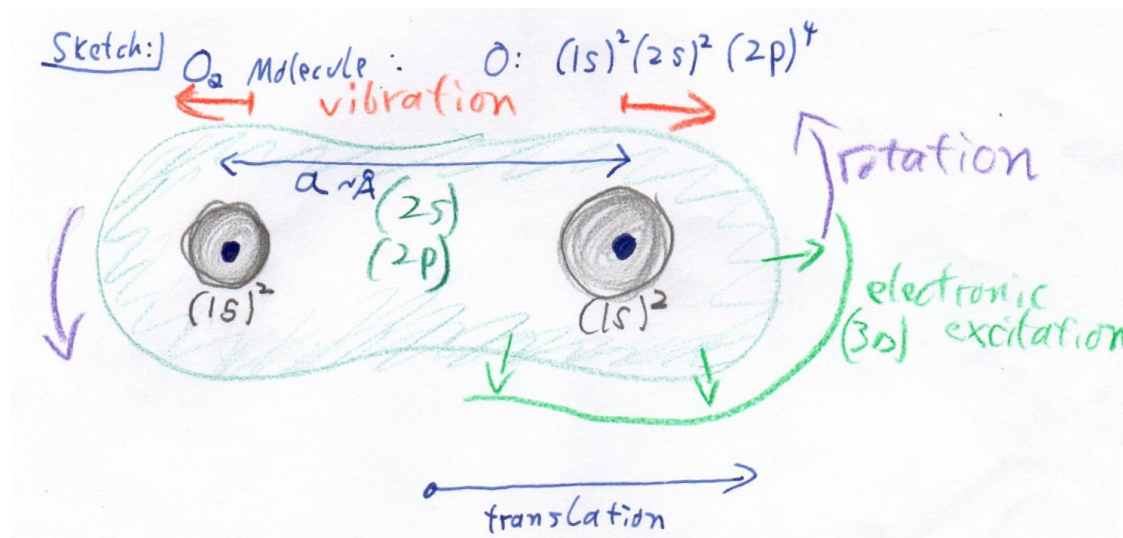
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4 Molecules

4.1 General Molecular Structure

- heavy atoms = one nucleus, many electrons
- molecule = at least two nuclei, many electrons

Complication: All e^- in an atom behave a bit "hydrogenic". No longer true in molecules.



From uncertainty relation, electronic energies $E_{elec} \sim \frac{\hbar^2}{ma_0^2} \sim eV$ as in atoms⁴. We shall see

$$\text{Vibrational energy} \quad E_{vib} \sim \left(\frac{m}{M}\right)^{\frac{1}{2}} E_{elec} \quad \text{Rotational energy} \quad E_{rot} \sim \left(\frac{m}{M}\right) E_{elec}$$

where, m = electron mass and M = nuclear mass (see Assignment 4, 2017).

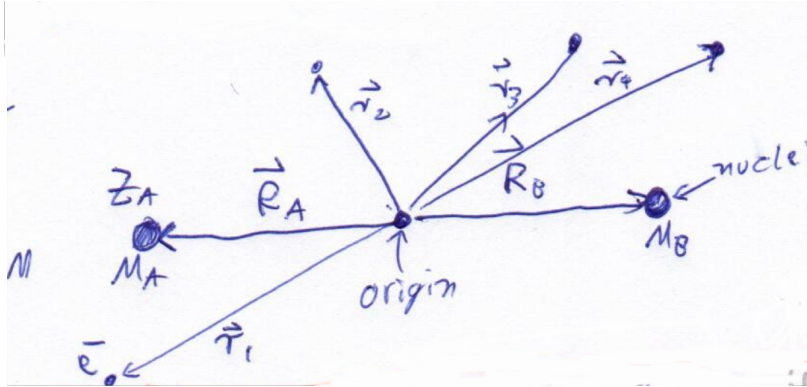
Since $\frac{m}{M} \ll 1$, we obtain the energy scale hierarchy $E_{elec} \gg E_{vib} \gg E_{rot}$. The fact that $\frac{m}{M} \ll 1$ also leads to the most essential approximation technique in molecular physics, see next section.

⁴Into $\Delta x \Delta p = \hbar$ insert $\Delta x \approx a_0$ (Bohr radius), then use $E_{elec} \approx \Delta p^2 / (2m)$

4.2 Born-Oppenheimer separation

We discuss di-atomic molecules to save notation, larger molecules can be treated the same. Consider N electrons

e.g., $N=4$



left: Sketch of co-ordinate system for generic di-atomic molecule. We choose the origin as the centre of mass of the nuclei A , B and employ the separation vector $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$.

Molecular Schrödinger equation:

$$[\hat{T}_n + \hat{T}_e + \hat{V}]\psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (4.1)$$

$$\text{Nuclear Kinetic energy } \hat{T}_n = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2,$$

$$\text{where } \mu = \frac{M_A M_B}{M_A + M_B}$$

$$\text{Electron Kinetic energy } \hat{T}_e = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 \right)$$

Potential Energy

$$\hat{V} = -\sum_{i=1}^N \frac{Z_A e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{R}_A|} - \sum_{i=1}^N \frac{Z_B e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{R}_B|} + \sum_{\substack{i,j=1 \\ i < j}}^N \frac{e^2}{(4\pi\epsilon_0)|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z_A Z_B e^2}{(4\pi\epsilon_0)|\mathbf{R}|}$$

- Nuclei are $\sim \mathcal{O}(10^5)$ heavier than electrons. They move much slower. Hence, let's first consider an equation for electrons only.

Electronic Wave Equation / Schrödinger equation for the electrons *only*:

$$\underbrace{[\hat{T}_e + \hat{V}(\mathbf{R})]}_{\hat{H}_{el}} \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (4.2)$$

- Here, \mathbf{R} is just viewed as a parameter in the Hamiltonian, since there are no derivatives with respect to it. Thus Eq. (4.2) is not a PDE in terms of \mathbf{R} .
- Since \hat{H}_{el} depends parametrically on \mathbf{R} , so do its eigenfunctions and energies.
- These electronic wave functions are a complete orthonormal basis for each choice of $R \Rightarrow$

can write total wavefunction as

$$\Psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_q F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (4.3)$$

The $F_q(\mathbf{R})$ are called the nuclear wave function. Read them as: " $|F_q(\mathbf{R})|^2 d^3\mathbf{R}$ " is the probability to find the nuclei at \mathbf{R} when electrons are in the state q . Now, insert (4.3) into (4.1). We find (using (4.2)):

$$\sum_q \left\{ \hat{T}_n[F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] + E_q(\mathbf{R}) F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) - E F_q(\mathbf{R}) \phi_q(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \right\} = 0. \quad (4.4)$$

In the first term (kinetic energy) $\nabla_{\mathbf{R}}^2$ acts on both $F_q(\mathbf{R})$ and $\Phi_q(\mathbf{R})$ so we need the product rule:

$$\hat{T}_n(F_q \Phi_q) = -\frac{\hbar^2}{2\mu} [(\nabla_{\mathbf{R}}^2 F_q) \phi_q + 2(\nabla_{\mathbf{R}} F_q \cdot \nabla_{\mathbf{R}} \phi_q) + F_q (\nabla_{\mathbf{R}}^2 \Phi_q)] \quad (4.5)$$

Finally we project (4.4) onto ϕ_s by performing the integration

$$\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \phi_s^*(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \dots$$

on both sides of Eq. (4.4) \Rightarrow

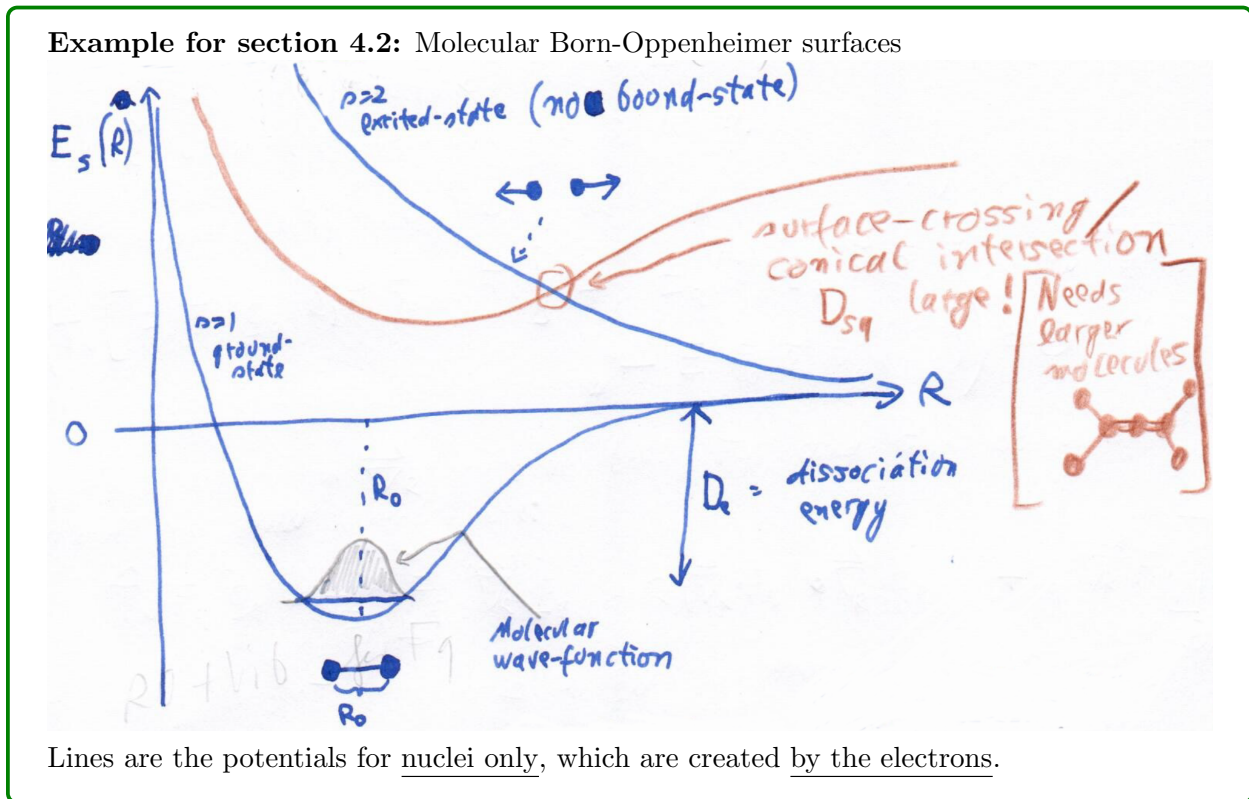
Molecular Schrödinger equation in Born-Oppenheimer separation

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + E_S(\mathbf{R}) \right] F_S(\mathbf{R}) + \sum_q D_{sq}(\mathbf{R}) F_q(\mathbf{R}) = E F_S(\mathbf{R}) \quad (4.6)$$

where we use the non-adiabatic coupling operator,

$$D_{sq}(\mathbf{R}) = -\frac{\hbar^2}{2\mu} (\langle \phi_s | \nabla_{\mathbf{R}}^2 | \phi_q \rangle + 2\langle \phi_s | \nabla_{\mathbf{R}} | \phi_q \rangle \cdot \nabla_{\mathbf{R}} \dots) \quad (4.7)$$

- Eq. (4.6) is an exact rewriting of Eq. (4.1). As such it is equally hard to solve.
- However, we can frequently neglect all D_{sq} . This is called the Born-Oppenheimer approximation. This allows a separate treatment of the electrons and the nuclei and often the use of a single index "q".
- $E_S(R)$ is called a Born-Oppenheimer (potential energy) surface.
- BO approximation is often good since electrons are much lighter than nuclei $m_e \ll \mu$. It fails however, whenever $E_{s_1}(\mathbf{R}) = E_{s_2}(\mathbf{R})$ regardless of masses, which does happen in quite a lot of molecules.



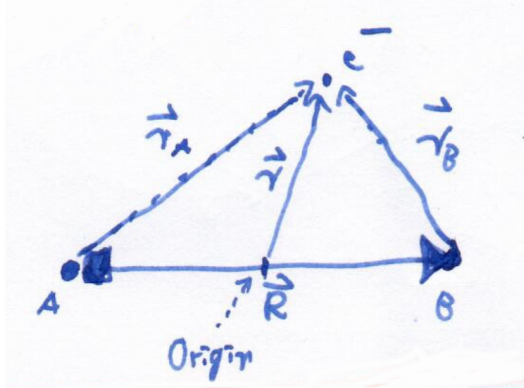
The next questions are now:

- Which nuclear energy surfaces $E_s(\mathbf{R})$ do we obtain from Eq. (4.2)?
 → Electronic structure of molecules, see section 4.3.
- What dynamics can nuclei undergo on the surfaces $E_s(\mathbf{R})$?
 → Molecular Rotations and vibrations, see section 4.6.

4.3 Electronic Structure of Molecules

We begin with the simplest molecule which is H_2^+ (Hydrogen molecular ion).

Diagram



At A, B we have the two protons (nuclei), with separation vector $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$ as before.

H_2^+ Hamiltonian in atomic units: (to be used in the electronic SE (4.2))

$$\hat{H}_{el} = -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \quad \begin{aligned} \mathbf{r}_A &= \mathbf{r} + \frac{\mathbf{R}}{2} \\ \mathbf{r}_B &= \mathbf{r} - \frac{\mathbf{R}}{2} \end{aligned} \quad (4.8)$$

We can first try to find eigen-states using Linear Combination of Atomic Orbitals (LCAO). Consider $R \rightarrow \infty$. Physically an electron near one of the nuclei should be in a hydrogen state, unperturbed by the far away other proton. Using the Hydrogen states from ϕ_{nlm} from Eq. (1.35) we can write this e.g. as

$$\phi(\mathbf{R}; \mathbf{r}) = \phi_{nlm}(\mathbf{r}_A) \cdot \quad (4.9)$$

see Eq. (4.2) e.g. $nlm \rightarrow 100$

The wave function (4.9) represents the electron attached to nucleus A only, unperturbed by the presence of far-away B . \Rightarrow However, recall our discussion of symmetries in the Helium Hamiltonian, section 2.3: There the wave-function had to be symmetric or antisymmetric under swap of the two electrons, because the Hamiltonian was symmetric under this swap.

Now, (4.8) is symmetric under $\mathbf{R}_A \leftrightarrow \mathbf{R}_B \Rightarrow \mathbf{r}_A \leftrightarrow \mathbf{r}_B$. So reasonable ground state wave-functions have to again be symmetric or anti-symmetric under the swap $\mathbf{R}_A \leftrightarrow \mathbf{R}_B$.

gerade (even) wavefunction (molecular orbital)

$$\phi_g(\mathbf{R}; \mathbf{r}) = \frac{1}{\sqrt{2}} (\phi_{1s}(\mathbf{r}_A) + \phi_{1s}(\mathbf{r}_B)) \quad (4.10)$$

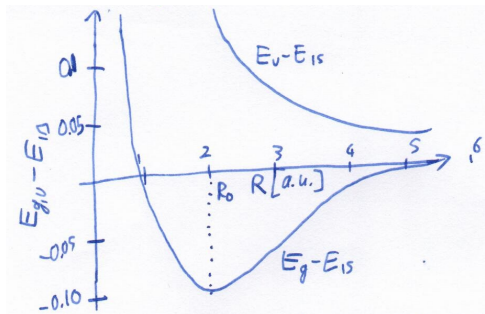
ungerade (odd) wavefunction

$$\phi_u(\mathbf{R}; \mathbf{r}) = \frac{1}{\sqrt{2}} (\phi_{1s}(\mathbf{r}_A) - \phi_{1s}(\mathbf{r}_B))$$

The reasoning above is strictly true for $R \rightarrow \infty$ only, but we can now use Eq. (4.10) as trial function for the variational principle (2.89). We can use that to get an upper bound on the ground-state energy of the molecule

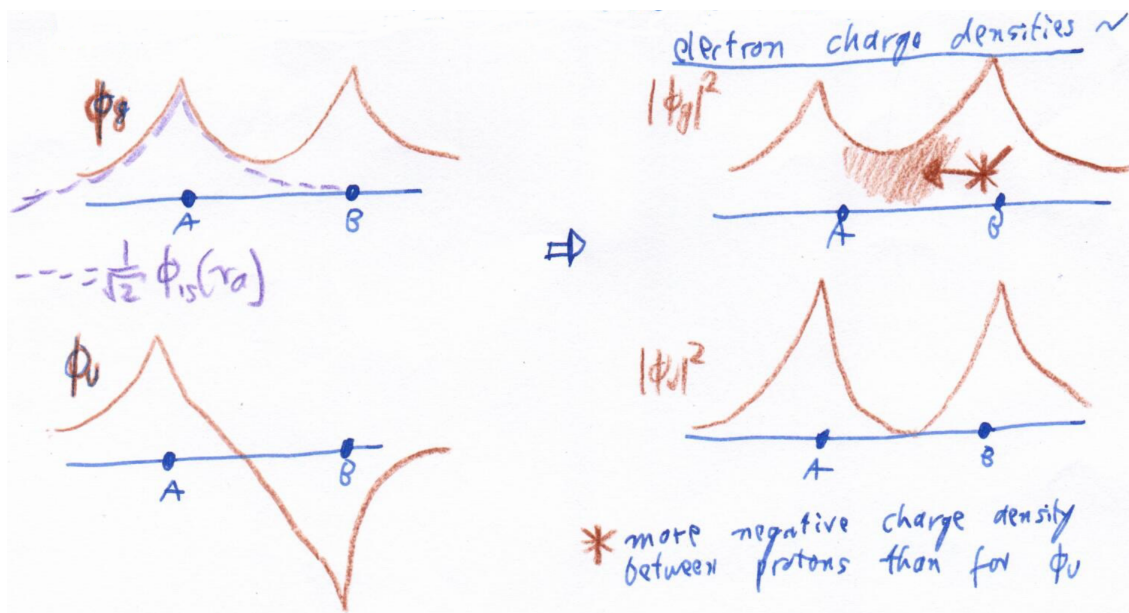
$$E_0 \leq E_{g,u}[R] \quad \text{where } E_{g,u}(R) = \frac{\langle \phi_{g,u} | \hat{H}_{se} | \phi_{g,u} \rangle}{\langle \phi_{g,u} | \phi_{g,u} \rangle} \quad (4.11)$$

Can evaluate the energy functional $E_{g,v(R)}$ (see text book), in particular now also taking into account the electron-electron repulsion in Eq. (4.8), which has been ignored in setting up the Ansatz (4.10). We get:



- ϕ_g is bonding
- ϕ_u is anti-bonding (repulsive)
- These are the lowest 2 molecular states, many more exist, based on $\phi_{2s}, \phi_{2p_1} \dots etc$

We can understand these two cases graphically, by drawing the states (their electron charge density):



It is apparent that in the bonding (gerade) state, electrons have an increased likelihood to be found exactly in between the nuclei. Their negative charge can then “glue” the two positive charges of the nuclei together.

Week 10

PHY 402 Atomic and Molecular Physics

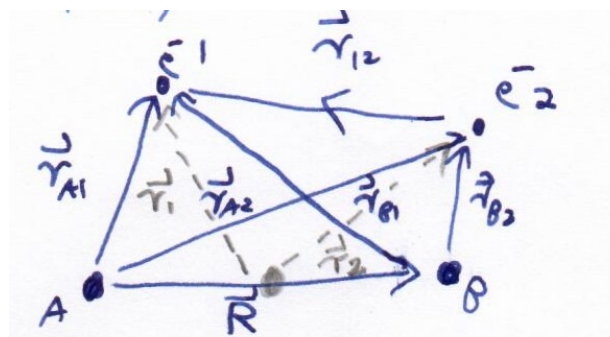
Instructor: Sebastian Wüster, IISER Bhopal, 2018

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4.3.1 Hund-Mulliken Molecular Orbital (MO) Method

The next simplest molecule is H_2 .

First let us define the co-ordinates now used:



We can then proceed by combining two molecular orbitals as in Eq. (4.10). As in Eq. (2.72), we again have spin wavefunctions:

$$|\chi_{S,m_S}\rangle = \begin{cases} \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) & S = 0, m_S = 0 \\ \hline |\uparrow\uparrow\rangle & m_S = 1 \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) & S = 1, m_S = 0 \\ |\downarrow\downarrow\rangle & m_S = -1 \end{cases}$$

We need to combine this with spatial wavefunctions as in (4.10) such that the total wavefunction is anti-symmetric under $1 \leftrightarrow 2$

We shall use shorthand the $\phi_g(1) = \phi_g(\mathbf{R}; \mathbf{r}_1)$

Two-electron states for H_2 (molecular electronic states) Out of the gerade and ungerade orbitals (4.10), we can form four combinations for two-electron states:

$${}^1\Sigma_g^+ \quad \Phi_A(\mathbf{r}_1, \mathbf{r}_2) = \phi_g(1) \phi_g(2) |\chi_{00}\rangle \quad (4.12)$$

$${}^1\Sigma_g^+ \quad \Phi_B(\mathbf{r}_1, \mathbf{r}_2) = \phi_u(1) \phi_u(2) |\chi_{00}\rangle \quad (4.13)$$

$${}^1\Sigma_u^+ \quad \Phi_C(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_g(1) \phi_u(2) + \phi_g(2) \phi_u(1)] |\chi_{00}\rangle \quad (4.14)$$

$${}^3\Sigma_u^+ \quad \Phi_D(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_g(1) \phi_u(2) - \phi_g(2) \phi_u(1)] |\chi_{1m_S}\rangle \quad \text{with } m_S = 0, \pm 1 \quad (4.15)$$

- Note: We are considering the lowest molecular electronic states only [(4.10) based on electronic ground states ϕ_{1s} of each separate atom].
- All states are totally antisymmetric under exchange of positions $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ and have fixed symmetry (g or u) under $\mathbf{R}_A \leftrightarrow \mathbf{R}_B$, which is shown as subscript in the green spectroscopic label on the left (the rest of the label is defined only in section 4.4).
- Based on the example in section 4.2, the electronic state Φ_A will have lowest energy
- We can again calculate $E(\mathbf{R})$ as in section 4.2 to get BO-surfaces

Let's look in more detail at Φ_A in (4.15) and insert the details of single electron orbitals from (4.10) We obtain

$$\Phi_A = \Phi_A^{cov} + \Phi_A^{ion}, \quad (4.16)$$

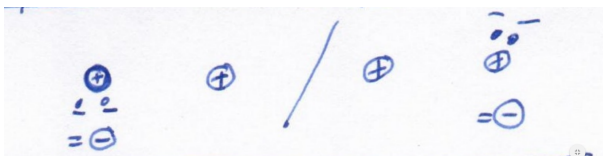
where the first part represents covalent bonding

$$\Phi_A^{cov} = \frac{1}{2} [\phi_{1s}(\mathbf{r}_{A1}) \phi_{1s}(\mathbf{r}_{B2}) + \phi_{1s}(\mathbf{r}_{B1}) \phi_{1s}(\mathbf{r}_{A2})] |\chi_{00}\rangle. \quad (4.17)$$

We see that this essentially involves the sharing of electrons. The second part,

$$\Phi_A^{ion} = \frac{1}{2} [\phi_{1s}(\mathbf{r}_{A1}) \phi_{1s}(\mathbf{r}_{A2}) + \phi_{1s}(\mathbf{r}_{B1}) \phi_{1s}(\mathbf{r}_{B2})] |\chi_{00}\rangle, \quad (4.18)$$

is responsible for ionic bonding to do with an unequal division of charge, see sketch below.



- As in our initial discussion of Helium, the lowest order wave functions discussed here neglect $e^- - e^-$ interactions.

They can be improved via variational principle, e.g. using the Ansatz

$$\Phi_{trial} = \Phi_A + \lambda\Phi_B \rightarrow \text{use variational principle to find best value of } \lambda \quad (4.19)$$

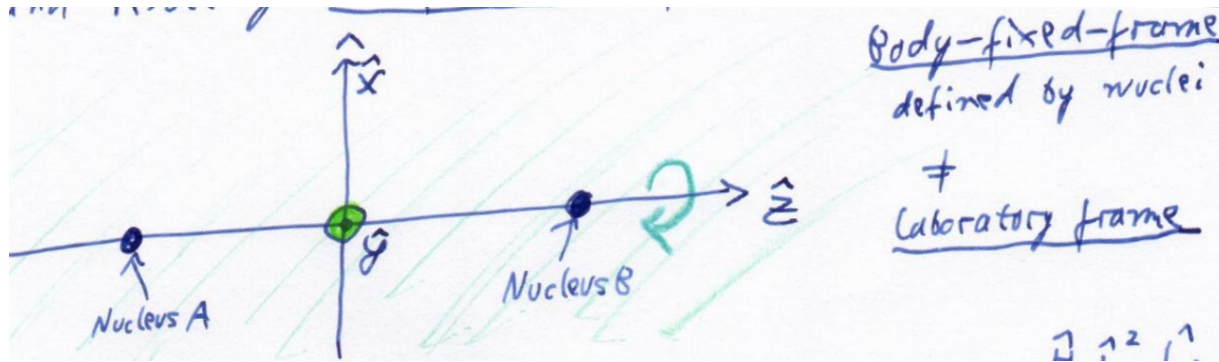
If this calculation is performed, the fraction of ionic binding in H_2 turns out as only 0.2 (compared to 0.5 in (4.16)).

- Instead of first assembling molecular orbitals (MOs) (4.10) out of atomic orbitals and then from MOs create molecular electronic states (4.15), we can also skip (4.10) and directly write a guess or variational Ansatz for molecular electronic states in terms of the original atomic orbitals.
 ↪ This is called Heitler - London / Valence Bond Method.
- Some even more sophisticated methods for the calculation of molecular electronic states are the Hartree-Fock and DFT methods that we already discussed for atoms in section 2.4.4.

4.4 Symmetries in homo-nuclear di-atomic molecules

We are anyway focussing on this type of molecule. Here we list all symmetries and resulting classifications of electronic states.

Diagram:



- – Earlier around an atomic nucleus we had a spherical symmetry and could classify states via the operators \hat{H} , \hat{L}^2 , \hat{L}_z
- Here, we can only use the cylindrical symmetry around the z axis, indicated by the green circular arrow above. We thus classify states via \hat{H} and \hat{L}_z only.
- Thus all electronic states of a di-atomic molecule satisfy $\hat{L}_z|\phi_s\rangle = \hbar M_L|\phi_s\rangle = \pm\hbar\Lambda|\phi_s\rangle$, where we define $|M_L| = 0, 1, 2, \dots$. According to this, molecular states are then given the code letters shown in green, and a single electron in a molecular orbital the ones in red

Code Letters: $\Lambda =$	0,	1,	2,	3
	Σ	Π	Δ	Φ
(= Greek Capital for	S	P	D	F...)
(For <u>single</u> e^- in MO	σ	π	δ	ϕ)

- The system is also symmetric under reflection off x, z plane, shown as green shade above: This swaps $M_L \rightarrow -M_L$ for fixed $\Lambda \Rightarrow$ each quantum number Λ is two-fold degenerate. This is called (Λ -doubling)
- For a molecular state with label Σ we thus write $\Sigma^+, (\Sigma^-)$ for symmetric (antisymmetric) states under the swap $y \rightarrow -y$.
- Finally the system is also symmetric under reflection through the origin shown as \bullet (point-reflection). For this symmetry the feature homo-nuclear is crucial. \Rightarrow The wavefunction will also be symmetric or anti-symmetric under this operation \Rightarrow This gives rise to the g(gerade), u(ungerade) labels, as before in section 4.3.

All this information is summarized in

Molecular State Label:

Examples of these labels were found in (4.15) before. (4.20)

Example for section 4.4: Li_2 Molecule:

- $\text{Li } Z=3 \Rightarrow$ We have total of 6 electrons to distribute

For atoms we were following:

- ▶ Construct atomic states similar to Hydrogen
- ▶ Understand Differences to Hydrogen
- ▶ Fill from low to high energy, respecting the Pauli principle.

For Molecules:

- ▶ Construct Molecular states based on atoms (4.15)
- ▶ Understand differences compared to atoms ($E_g < E_u$)
- ▶ Fill from low to high energy, respecting the Pauli principle

• We can write an electron configuration of molecules, similar to what we did for atoms

$$\text{Li}_2 : 1\Sigma_g^+ = (1s\sigma_g)^2 (1s\sigma_u)^2 (2s\sigma_g)^2 \quad (4.21)$$

4.5 More General overview of chemical bonds

- Mathematically all bonds arise the same manner: We solve Eq. (4.2) (the electronic Schrödinger equation) as a function of static nuclear nuclear co-ordinates \mathbf{R} . If some resulting Born-Oppenheimer surface $E_q(\mathbf{R})$ has a local minimum, there may be a bond, depending on its depth.
- However the physical interpretation for the reason of the bond may vary, depending on the underlying electronic quantum state $\phi_q(\mathbf{R}; \mathbf{r}_1, \dots, \mathbf{r}_n)$.

Chemical bonds:

Covalent:

left: Nuclei share electrons: → larger negative charge density in the spatial area between the nuclei. As in the sketch this is typically important when $R < r_a + r_b$, where R is the inter-nuclear distance and $r_{a/b}$ would be the size of the individual unbound atoms. In that case the electron clouds of individual atoms strongly overlap.

Ionic:



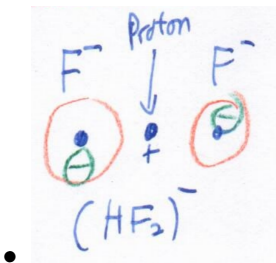
left: Nuclei transfer electrons from one to another → this causes excess positive charge \oplus on one of them, and excess negative charge \ominus on the other. Overall we obtain the usual Coulomb attraction with $V \sim 1/R$. This becomes more important at slightly larger separations than for covalent bonding, when $R \geq r_a + r_b$.

Van-der Waals:

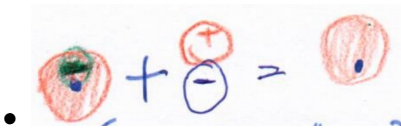


left: Essentially individual atoms can polarise each other, the resulting dipole moments (their fluctuations) then attract, which gives rise to a potential $V \sim 1/R^6$. This will be dominant at even larger distances $R \gg r_a + r_b$, but can also lead to binding.

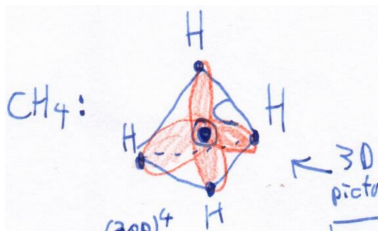
Some more peculiar bond types:



- **left:** Hydrogen bonding [\approx charge reverse of a covalent bond], e.g. DNA strands bind like this



- **left:** s-p hybrid molecular orbital = $|s\rangle + |p\rangle$. As first sketched in section 3.6.1, in such a superposition the electron on one atom is shifted into a specific direction. Many such orbitals can be nicely formed in Carbon: $(1s)^2 (2s)^2 (2p)^2 \rightarrow (1s)^2 (2sp)^4$.



- **left:** Carbon can thus shift its four valence electron into four specific directions, for example in Methane

Week 11

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

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4.6 Molecular ro-vibronic states

We now know how to calculate/ construct the molecular electronic energies/Born- Oppenheimer (BO) surfaces $E_q(\mathbf{R})$ from Eq. (4.2). Insertion into (4.6) then gives us the motional eigen states of the nuclei.

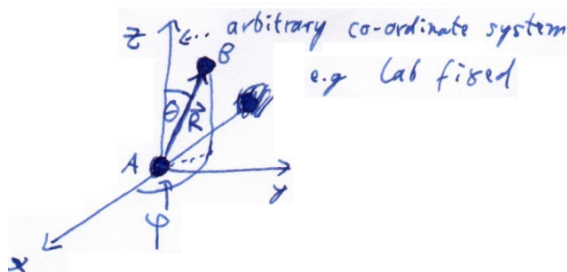
In BO-approximation (where we take only a single surface s in (4.6)) we have:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}} + E_s(\mathbf{R}) \right] F_s(\mathbf{R}) = E F_s(\mathbf{R}). \quad (4.22)$$

For a di-atomic molecule electronic energies can only depend on the distance between nuclei $|\mathbf{R}|$, not on the orientation of the inter-nuclear axis (direction of \mathbf{R}), hence $E_s(\mathbf{R}) = E_s(|\mathbf{R}|) \rightarrow$ mathematically (4.22) is a spherically symmetric Schrödinger equation (like e.g., Hydrogen).

Thus as for Hydrogen we can write the solution as a product of an angular part and a radial part (compare Eq. (1.35)), where the angles are defined in the sketch below.

$$F_s(\mathbf{R}) = \frac{\mathcal{F}_{\nu K}^s}{R} \mathcal{H}_{K m_K}(\theta, \varphi). \quad (4.23)$$




We know due to spherical symmetry that the angular part is given by spherical harmonics:

$$\mathcal{H}_{K m_K}(\theta, \varphi) = \overbrace{Y_{K m_K}(\theta, \varphi)}^{\text{Spherical harmonics}}.$$

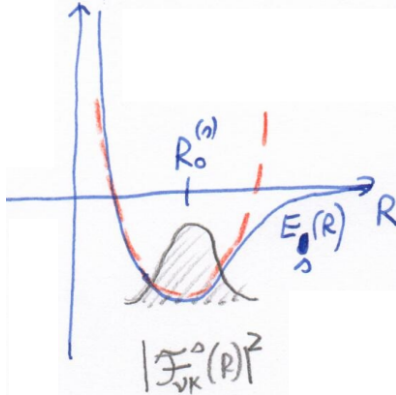
Now we insert ((4.23)) into ((4.22)) and use the 3D Laplacian, following all the same steps as for Hydrogen. We obtain again a Radial Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} - \underbrace{\frac{K(K+1)}{R^2}}_* \right) + (E_s(R) - \underbrace{E_{s,\nu,K}}_{=E \text{ earlier}}) \right] \mathcal{F}_{\nu K}^s(R) = 0. \quad (4.24)$$

- The electronic energies $E_s(R)$ take the role of the “potential energy” for the nuclei.

- If $K > 0$, the molecule is rotating about the center-point . * represents the centrifugal force due to this.
- The detailed shape of $E_s(R)$ is calculated as discussed in section 4.3.

Let us consider the rough potential energy shape found in section 4.3:



The binding BO-surfaces usually have one well-defined local minimum.

We can Taylor expand $E_s(R)$ around this minimum $R_0^{(s)}$, the expansion gives the red dashed line.

$$E_s(R) = E_s(R_0^{(s)}) + \frac{1}{2}k_s(R - R_0^{(s)})^2$$

where,

$$k_s = \left. \frac{d^2 E_s(R)}{dR^2} \right|_{R=R_0^{(s)}}.$$

(From now, write $R_0^{(s)} = R_0$.)

- Since usually it turns out that also $|\mathcal{F}_{\nu K}^s(R)|^2$ is non-zero only close to this minimum, we can write $+\frac{\hbar^2}{2\mu} \frac{K(K+1)}{R^2} \rightarrow \frac{\hbar^2}{2\mu} \frac{K(K+1)}{R_0^2}$ in Eq. (4.24).

We call this quantity the

Rotational energy

$$E_{\text{rot}} = \frac{\hbar^2}{2\mu R_0^2} K(K+1) = \frac{\hbar^2}{2I} K(K+1), \quad (4.25)$$

where $I = \mu R_0^2$ is the moment of inertia.

We can now rewrite Eq. (4.24) as harmonic oscillator TISE

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}k_s(R - R_0)^2 - E_\nu \right] \mathcal{F}_\nu^s(R) = 0, \quad (4.26)$$

where, we used the definitions

Total energy The total energy of the molecular state $E_{s,\nu,k}$ can be decomposed into several contribution:

$$E_{s,\nu,K} = \overbrace{E_s(R_0)}^{\text{electronic energy}} + \overbrace{E_\nu}^{\text{vibrational energy}} + \overbrace{E_{\text{rot},K}}^{\text{rotational energy}}. \quad (4.27)$$

Here s : electronic state label

ν : vibrational quantum number


K : rotational quantum number

R_0 : equilibrium position.

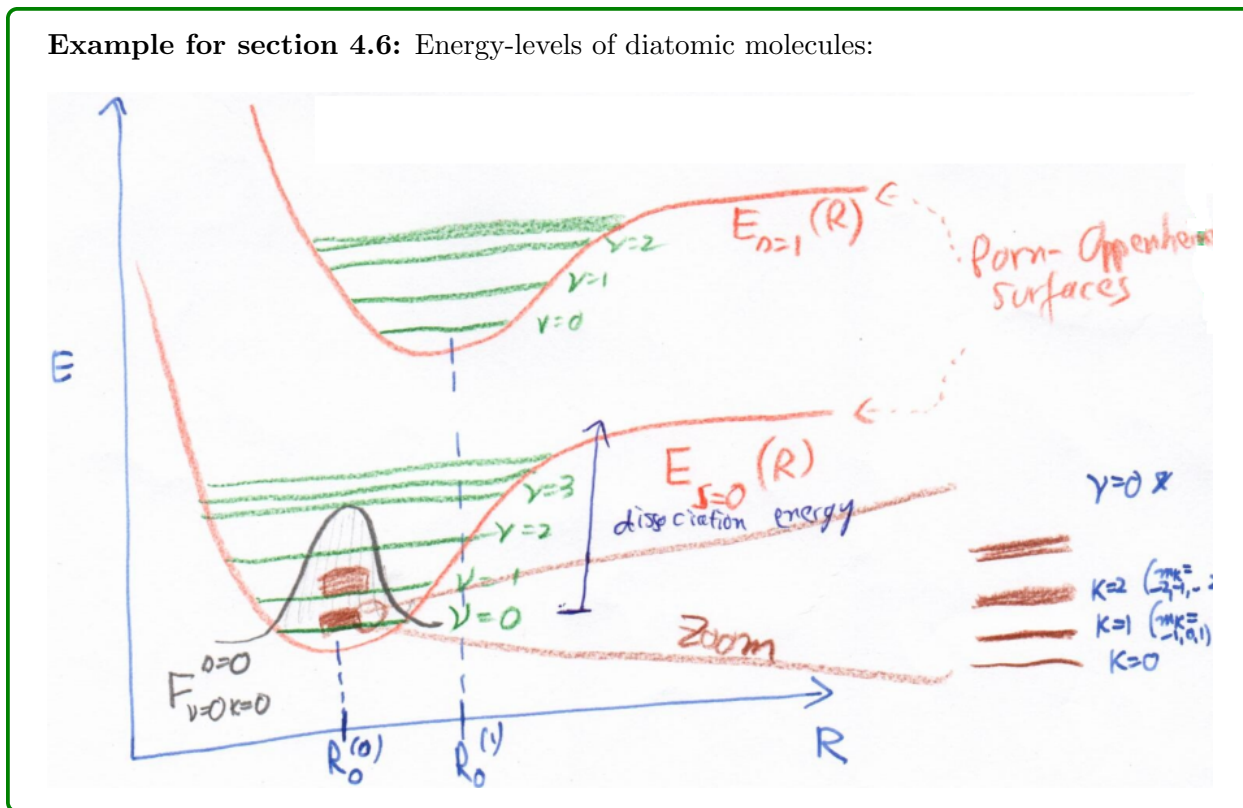
Vibrational energy as usual

$$E_\nu = \hbar\omega_0 \left(\nu + \frac{1}{2} \right) \quad \nu = 0, 1, 2, \dots \quad (4.28)$$

where, $\omega_0 = \sqrt{k_s/\mu}$.

- There can be deviations from Eq. (4.28) due to an anharmonicity of $E_s(R)$ at larger vibrational quantum numbers ν , see sketch above.
- $\frac{\mathcal{F}_\nu^s(R)}{R} \mathcal{H}_{K m_K}(\theta, \varphi)$ is called a ro-vibronic state.
- Di-atomic molecules can also rotate around the inter nuclear axis : This is represented within the electronic wavefunction $\Phi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots)$ as non-zero Λ (see section 4.4).
- Rotations usually weakly couple to vibrations: Fast rotation increases centrifugal potential $\sim K(K+1)/R^2$ and can thus cause vibrations. This effect drops out if we can replace $R \rightarrow R_0$ in Eq. (4.24). If we include it, we have to keep the centrifugal term in Eq. (4.26) and thus also the vibrational part of the wave functions continues to depend on the rotational quantum number K : $\mathcal{F}_\nu^s(R) \rightarrow \mathcal{F}_{\nu K}^s(R)$.

Example for section 4.6: Energy-levels of diatomic molecules:



Now we know all the quantum numbers that should be allocated for molecular states (mainly focussing on di-atomic molecules for simplicity). Just as with atoms, it is frequently convenient to group all quantum numbers into one collective index label $a = \{s, \nu, K, m_K\}$. This thus includes the electronic state label s (see section 4.3), the vibrational quantum number ν , the rotational quantum number K and the z-component of rotational angular momentum (in the lab frame) m_K . Written as a wave function, the label a represents

Complete molecular state: e.g., $\Psi_a = \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \underbrace{\frac{\mathcal{F}_\nu^s(R)}{R} \mathcal{H}_{K m_K}(\theta, \varphi)}_{=F_s(\mathbf{R})}$.

4.7 Molecular spectra

- Now we can describe all molecular states, we again ask how transitions between such states can occur through interactions with electromagnetic radiation, and thus which shape molecular spectra will take.
- For the same arguments as used in section 3 for the case of atoms, transitions between different molecular states ($a = \{s, \nu, K, m_K\}$) are governed by the

Molecular dipole-moment operator:

$$\hat{\mathbf{D}} = e \left(\sum_i Z_i \mathbf{R}_i - \sum_j \mathbf{r}_j \right) \quad (4.29)$$

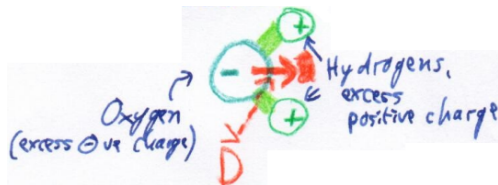
where, \mathbf{R}_i : positions of nuclei
 \mathbf{r}_j : positions of electrons.

Unlike the case for atoms, where always $\langle \phi_n | (-e\mathbf{r}) | \phi_n \rangle = 0$, molecules can have a

permanent electric dipole-moment

$$\mathbf{D}_{aa} = \langle \psi_a | \hat{\mathbf{D}} | \psi_a \rangle \neq 0. \quad (4.30)$$

Example: Water molecule, H_2O :



Dipole-moment of water:

$$|\mathbf{D}| = 1.85 D \quad (D = \text{Debye})$$

1 Debye $\approx 0.2 e\text{\AA}$

It will also be useful to consider the dipole-moment in electronic state s for a specific fixed nuclear configuration⁵ \mathbf{R} :

$$\hat{\mathbf{D}}_s(\mathbf{R}) = \langle \Phi_s | \hat{\mathbf{D}} | \Phi_s \rangle = \underbrace{\int d^{3N} \mathbf{r}_i \Phi_s^*(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots) \hat{\mathbf{D}} \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots)}_{\text{still depends on } \mathbf{R}}. \quad (4.31)$$

For the same reasons as in atoms, transitions between molecular states due to absorption or emission of elm-radiation (which give rise to spectra) are governed by transition matrix elements:


$$\mathbf{D}_{ba}(\mathbf{R}) = \langle \psi_b | \hat{\mathbf{D}} | \psi_a \rangle. \quad (4.32)$$

However, a major difference to atoms, is that for molecules we can differentiate a large number of different types of internal transitions.

4.7.1 Rotational transitions

Consider a transition without change of electronic or vibrational state, i.e. from a state with label $a = \{s, \nu, K, m_K\}$ to a state with label $b = \{s, \nu, K', m'_K\}$. Assume $\nu = 0$, i.e., vibrational ground state.

⁵In contrast, Eq. (4.30) contains an average over all possible nuclear configurations.

For simplicity assume di-atomic molecule, but not necessarily a homonuclear one, e.g. CO  (this has a permanent dipole moment of $0.122D$). Also move to a ket notation for the total state

$$\begin{aligned} \psi(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \frac{\mathcal{F}_\nu^s(R)}{R} \mathcal{H}_{K m_K}(\theta, \varphi) \\ &\downarrow \\ |\psi_a\rangle &= |s\nu K m_K\rangle = \underbrace{|s\rangle}_{\text{electrons}} \otimes \underbrace{|\nu K m_K\rangle}_{\text{nuclei}}. \end{aligned}$$

We now see

$$\begin{aligned} \mathbf{D}_{ba} &= \langle \psi_b | \hat{\mathbf{D}} | \psi_a \rangle = \langle \nu K' m'_K | \underbrace{\langle s | \hat{\mathbf{D}} | s \rangle}_{= \mathbf{D}_s(\mathbf{R})} | \nu K m_K \rangle \\ &\quad \text{using Eq. (4.31)} \\ &= \int d\Omega \mathcal{H}_{K' m'_K}^*(\theta, \varphi) \underbrace{\left(\int_0^\infty dR |\mathcal{F}_{\nu=0}^s(R)|^2 \mathbf{D}_s(R) \right)}_{\approx \mathbf{D}_s(\mathbf{R}_0) \text{ dipole moment at equilibrium configuration}} \mathcal{H}_{K m_K}(\theta, \varphi). \end{aligned} \quad (4.33)$$

The approximation in the last line is actually exact if the vibrational wave-packet $|\mathcal{F}_{\nu=0}^s(R)|^2 = \delta(R - R_0)$. If, instead, the vibrational wave-packet is just a very narrow Gaussian, it still is a very good approximation.

Now we directly see the

Rule for purely rotational transitions: \Rightarrow only molecules with permanent dipole moment at \mathbf{R}_0 can have purely rotational transition.

The remaining integration in Eq. (4.33) over $d\Omega$ gives (as for Hydrogen atom)

Rotational selection rules:

$$\text{(for } \Lambda = 0 \text{ states)} \quad \Delta K = K' - K = \pm 1 \quad \Delta m_K = m'_K - m_K = 0, \pm 1. \quad (4.34)$$

- Photo absorption implies angular momentum change by ± 1 through angular momentum conservation.

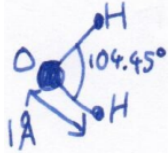
From Eq. (4.25), we find that photon energies matching a rotational transition are

$$\Delta E = E_{\text{rot}}(K+1) - E_{\text{rot}}(K) = \underbrace{\frac{\hbar^2}{\mu R_0^2}}_{\text{di-atomic case}} (K+1) = \underbrace{\frac{\hbar^2}{I}}_{\text{more generally valid}} (K+1). \quad (4.35)$$

Example: Microwave-Oven:

These operate typically at a frequency $\sim \nu_M = 2.4\text{GHz} \rightarrow \lambda = 12\text{cm}$

Consider a water-molecule: As seen in the preceding example, it has $|\mathbf{D}_{aa}| \neq 0$ and can thus undergo purely rotational transitions.



$$I \approx 2 \times 10^{-47} \text{kg m}^2 \text{ and } \Delta E = \underbrace{\frac{\hbar^2}{2I}}_{E_0} (K+1) \stackrel{!}{=} h\nu. \text{ This}$$

$$\text{gives } \nu = \frac{E_0}{h} = 420\text{GHz} \text{ or } \lambda = \frac{hc}{E_0} = 0.7 \text{ mm.}$$

Since rotations are the lowest energy excitations, the micro-wave frequency ν_M is closest to some rotational resonances and the oven hence excites rotations.

Q: Why is the oven not designed to operate precisely on the rotation resonance?

4.7.2 Ro-vibrational transitions

Next consider the slightly more general transition

$$a = \{s, \underline{\nu}, K, m_K\} \rightarrow b = \{s, \underline{\nu}', K', m'_K\}, \quad \nu \neq \nu', \quad (4.36)$$

where in addition to the rotational state also the vibrational state is allowed to change.

As before we can write

$$\mathbf{D}_{ba} = \langle \psi_b | \mathbf{D} | \psi_a \rangle = \langle \nu' K' m'_K | \mathbf{D}_s(\mathbf{R}) | \nu K m_K \rangle.$$

Let us expand the dipole-moment around the equilibrium position

$$\mathbf{D}_s(\mathbf{R}) \approx \mathbf{D}_s(\mathbf{R}_0) + \underline{\underline{\nabla D_s(\mathbf{R}_0)}} \cdot (\mathbf{R} - \mathbf{R}_0) + \dots, \quad (4.37)$$

where $\underline{\underline{\nabla D_s(\mathbf{R})}}$ denotes the Jacobian matrix of the vector field $\mathbf{D}_s(\mathbf{R})$, defined via $[\underline{\underline{\nabla D_s(\mathbf{R}_0)}}]_{ij} = \partial D_{s,i} / \partial R_j |_{\mathbf{R}=\mathbf{R}_0}$.

Insertion into Eq. (4.33) (however with allowing $\nu' \neq \nu$ in the ket) gives

$$\mathbf{D}_{ba} = \int d\Omega \mathcal{H}_{K'm'_K}^*(\theta, \varphi) \left(\int_0^\infty dR \mathcal{F}_{\nu'}^{s*}(R) \left[\underbrace{\mathbf{D}_s(R_0)}_{= \delta_{\nu'\nu} \text{ since } \mathcal{F}_{\nu'}, \mathcal{F}_\nu \text{ are orthonormal}} + \underbrace{\underline{\underline{\nabla D_s(\mathbf{R}_0)}} \cdot (\mathbf{R} - \mathbf{R}_0)}_{\text{If } \mathbf{D}_s \text{ constant, (independent of } \mathbf{R} \text{) this and all h.o.t. vanish.}} \right] \mathcal{F}_\nu^s(R) \right) \mathcal{H}_{K m_K}(\theta, \varphi). \quad (4.38)$$

From the two statements below (4.38) we can infer the

Rule for rotational-vibrational transitions: \Rightarrow only molecules where the dipole-moment changes as a function of \mathbf{R} (= as “a function of vibrations”) can have purely ro-vibrational transitions (without electronic state change, which means: $s = s'$).

If $\frac{\partial}{\partial R} \mathbf{D}_s(R)$ is non-zero, integration over R and angles gives

Ro-vibrational selection rules (valid for harmonic vibrations only)

$$\text{(For } \Lambda = 0 \text{ states)} \quad \Delta\nu = \nu' - \nu = \pm 1 \quad \Delta K = \pm 1 \quad \Delta m_K = 0, \pm 1. \quad (4.39)$$

- To see the rule $\Delta\nu = \pm 1$, use oscillator states for $\mathcal{F}_\nu(R)$ and the recursion relation

$$2x H_\nu(x) = 2\nu H_{\nu-1}(x) + H_{\nu+1}(x) \quad \text{for Hermite polynomials } H_\nu(x). \quad (4.40)$$

- We still need a change of rotational state $\Delta K = \pm 1$ for angular momentum conservation (vibration does not directly affect angular momentum).
- Deviations from the rules (4.39) happen due to
 - higher than linear terms of $(R - R_0)$ in Eq. (4.38).
 - anharmonicity (deviations from an oscillator potential) of $E_s(R)$, see comment below Eq. (4.28).

These deviations then weakly allow $\Delta\nu = \pm 2$, $\Delta\nu = 3$, etc.

All up, photon energies matching ro-vibrational transitions are:

$$\Delta E = \underbrace{\hbar\omega_0}_{\text{see Eq. (4.28)}} + \begin{cases} +\frac{\hbar^2}{I}(K+1) & \Delta K = +1 \quad \text{R-branch} \\ -\frac{\hbar^2}{I}K & \Delta K = -1 \quad \text{P-branch} \end{cases}$$

Example: Greenhouse effect:

Earth likes to shed excess energy through IR radiation around $\lambda \simeq 4 - 100 \mu\text{m}$.

Atmosphere is mostly O_2 , N_2 . For N_2 : $\lambda = c/\nu_0 = 6 \mu\text{m}$, O_2 : $\lambda = c/\nu_0 = 3 \mu\text{m}$. (dangerously close)

These would scatter IR radiation and thus retain heat, but cannot, since $\mathbf{D}_{ss}(\mathbf{R}) = 0$ for a homonuclear molecule due to symmetry, regardless of nuclear separation \mathbf{R} .

However: CO_2 or CH_4 can have $\nabla D_s(\mathbf{R}_0) \neq 0$ (even though also for them $D_s(\mathbf{R}_0) = 0$).

\implies these are green house gases that scatter IR radiation.



(No net dipole in equilibrium, but becomes non-zero under vibration.)

Week 12

PHY 402 Atomic and Molecular Physics

Instructor: Sebastian Wüster, IISER Bhopal, 2018

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4.7.3 Molecular electronic transitions

Finally, we move to the completely general transition

$$a = (s, \nu, K, m_K) \rightarrow b = (s', \nu', K', m'_K), \quad (4.41)$$

involving different electronic states with $s \neq s'$.

The matrix element is

$$D_{ba} = \langle \psi_b | \hat{\mathbf{D}} | \psi_a \rangle = \langle \nu' K' m'_K | \underbrace{\langle s' | \mathbf{D} | s \rangle}_{\equiv \hat{D}_{s's}(\mathbf{R})} | \nu' K' m'_K \rangle \quad (4.42)$$

Where we have used the

electronic transition matrix element for nuclear position \mathbf{R}

$$\hat{D}_{s's}(\mathbf{R}) = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots \Phi_{s'}^*(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots) \left(e \left(\sum_i Z_i \mathbf{R}_i - \sum_j \mathbf{r}_j \right) \right) \Phi_s(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, \dots) \quad (4.43)$$

Note that this is still an operator in the space of nuclear wave functions. As with permanent dipole moments before, we can expand the transition dipole moment around the nuclear equilibrium position

$$\hat{D}_{s's}(\mathbf{R}) = \hat{D}_{s's}(\mathbf{R}_0) + \left. \underline{\underline{\nabla D_{s's}}} \right|_{\mathbf{R}_0} (\mathbf{R} - \mathbf{R}_0) \quad (4.44)$$

For simplicity let us now take the first term only (even though this is often not quite accurate enough). We then define

Franck-Condon factors and molecular transition dipole matrix elements

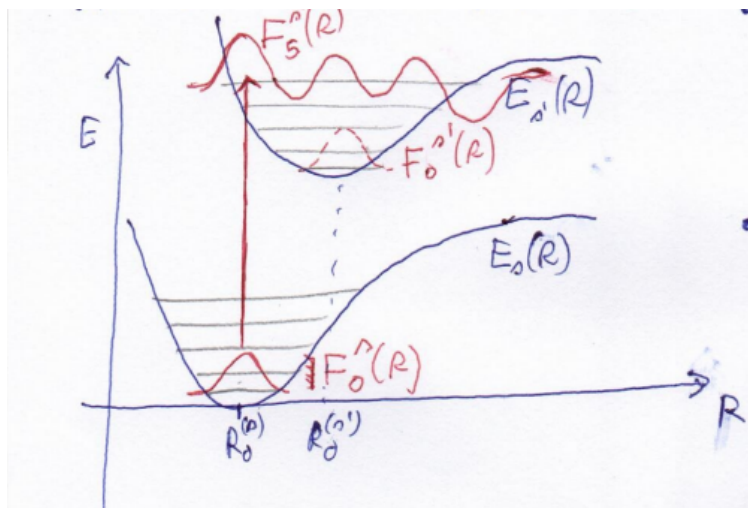
$$D_{ba} = \underbrace{\left(\int_0^\infty F_{\nu'}^{*s'}(R) F_\nu^s(R) dR \right)}_{= FC F_{\nu'\nu}^{s's}} \underbrace{\left(\int \mathcal{H}_{K'm_{K'}}^*(\theta, \phi) \underbrace{\hat{D}_{s's}(\mathbf{R}_0)}_{\text{electronic matrix-element}} \mathcal{H}_{K m_K}(\theta, \phi) d\Omega \right)}_{\text{angular factor, angular momentum}} \quad (4.45)$$

Franck-Condon factor
angular factor, angular momentum

- We only could take out the Franck-Condon factor as a pre-factor because we had approximated $\hat{D}_{s's}(\mathbf{R})$ in Eq. (4.43) as a constant in R .
- Electronic transitions are typically accompanied by vibrational and rotational transitions.
- Rotations obey the usual selection rules, discussed in section 4.7.1 and section 4.7.2, due to the second term.
- Vibrations are governed by the Franck-Condon factor. Note the FCF is non-zero since $s \neq s'$, and hence $F_{\nu'}^{s'}$ and F_ν^s are not (necessarily) orthogonal even if $\nu' \neq \nu$.
- $\hat{D}_{s's}(\mathbf{R}_0)$ gives rise to additional electronic selection rules in terms of $g/u, \Lambda, +/-$ etc. [see books]

Excitation of vibrations due to electronic excitation:

These are described by the Franck-Condon factor, and best understood graphically:



left: Sketch illustrating FCF

- BO surfaces s, s' are in general shifted, with different equilibrium position $R_0^{(s)}$ and $R_0^{(s')}$.
 - FCF measure overlap between initial and final vibrational states.
- electronic excitation is instantaneous \implies The nuclear wave-function $F(\mathbf{R})$ remains unchanged during the transition (the nuclei are static) but later they can slowly start to vibrate.

- The FCF can be thought of as re-expressing the (unchanged) initial vibrational state ν for electronic state s in the new vibrational basis for electronic state s' .
- For electronic transitions we now no longer have $\Delta\nu = 1$. Instead the most likely $\Delta\nu$ is the one that has the largest overlap between the initial and final vibrational wave functions. In the “Sketch illustrating FCF”, for an initial $\nu = 0$, the most likely final state would be $\nu' = 5$, because that places the large outer lobe of the $\nu' = 5$ oscillator state on the upper surface into the same space like the ground state on the lower surface.
- This combination of electronic and vibrational state change is called vibronic transition.

Electronic Spectra:

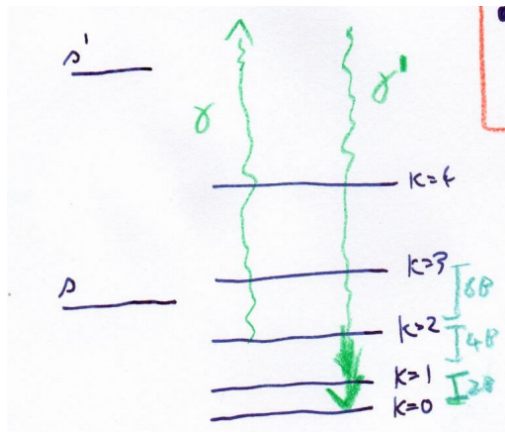
- Since $E_{s'} - E_s \sim \mathcal{O}(eV)$ as in atoms, photon energies for molecular electronic transitions are in the visible/UV part of the electromagnetic spectrum.
- Photon frequencies are $\nu = \frac{(E_{s'} + E_{\nu'} + E_{K'}) - (E_s + E_\nu + E_K)}{h}$, from Eq. (4.27). hence
- $\nu = \underbrace{\nu_{s's}}_{\text{large}} + \underbrace{\nu_{\nu'\nu} + \nu_{K'K}}_{\text{small}}$ with e.g. $\nu_{s's} = \frac{E_{s'} - E_s}{h}$ etc.
- Spectrum has appearance of bands and band systems (many bands) for each electronic transition, see next example.

4.7.4 Raman Scattering / Raman spectra

Our discussion of light scattering by atoms in section 3.6 largely applies to molecules as well. Due to the large number and close energy spacing of rotational and vibrational energy levels in molecules, it is much more common to have an in-elastic scattering process than in atoms:

$$\begin{array}{c} \text{~~~~~}\gamma\text{~~~~~} \\ \text{~~~~~}\blacktriangleright \\ \omega, \mathbf{k} \end{array}, |a\rangle \rightarrow |b\rangle, \begin{array}{c} \text{~~~~~}\gamma'\text{~~~~~} \\ \text{~~~~~}\blacktriangleright \\ \omega' \neq \omega, \mathbf{k}' \end{array} \quad (4.46)$$

Molecules also naturally are already in rotationally excited states at room temperature, so that the final state can frequently even have a lower energy than the initial one.



left: Sketch illustrating a Raman transition, governed by

Raman-selection rule

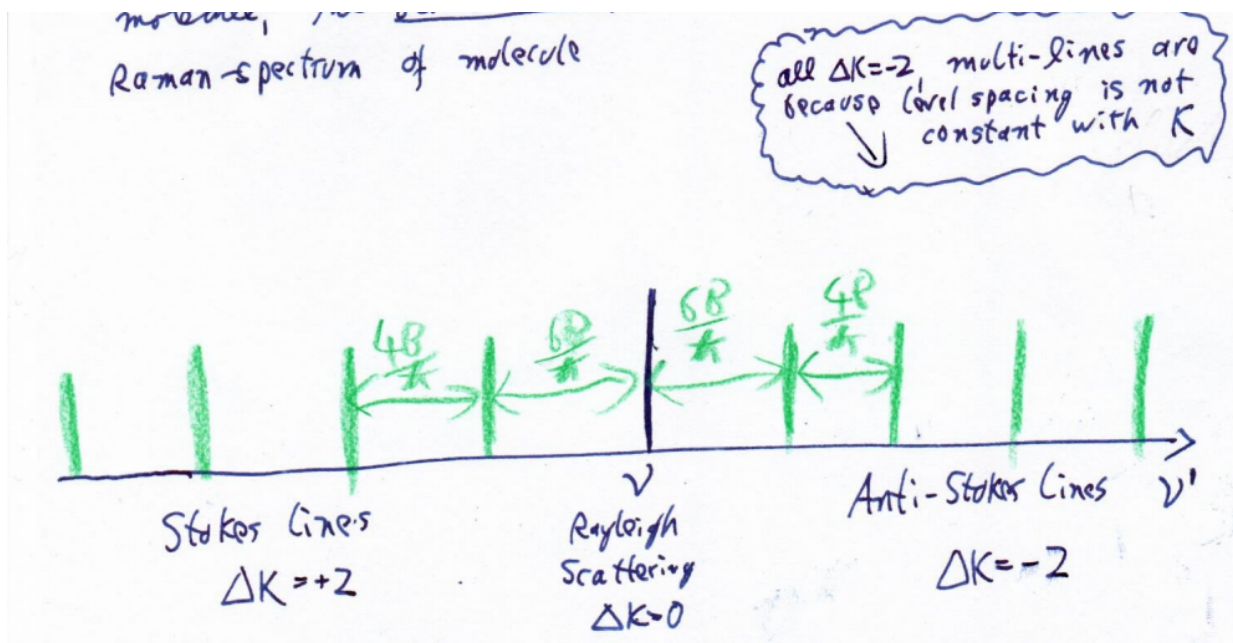
$$\Delta K = \pm 2, 0. \quad (4.47)$$

Since we have two subsequent transitions and the rule $\Delta K = \pm 1$ for each of those, see Eq. (4.34).

$$E_{rot} = \underbrace{\frac{\hbar^2}{2I}}_{=B} K(K+1) \quad (4.48)$$

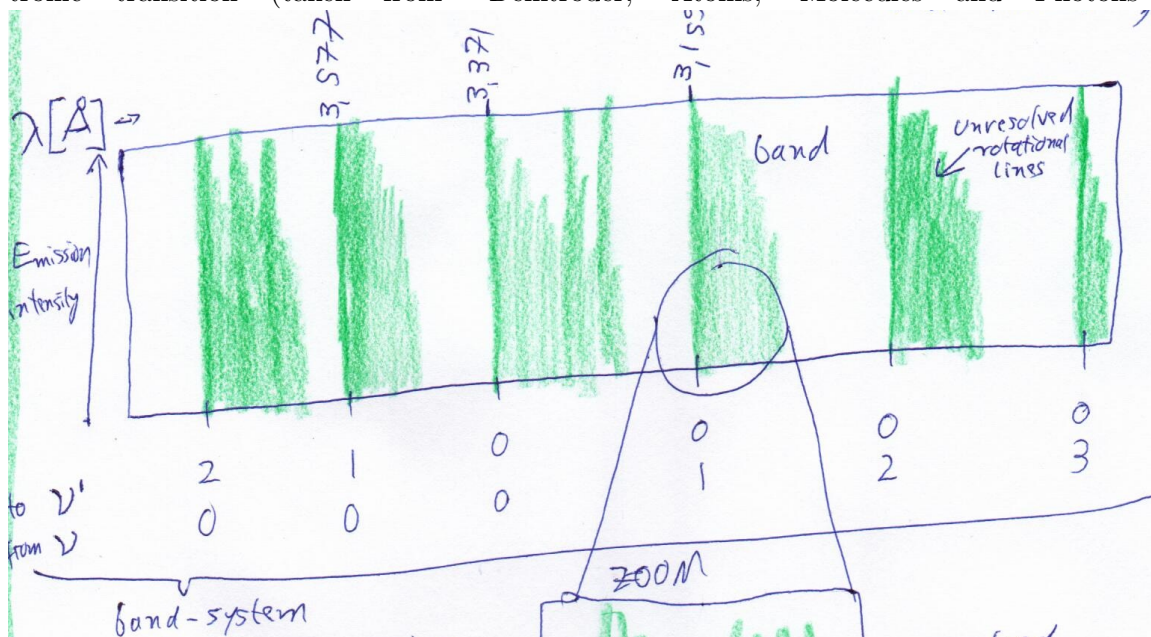
$\Delta K = -2$ in the example, hence $\Delta E = 6B$.

Let us assume we scatter light at frequency ν off a molecule, the scattered light has the following spectrum:

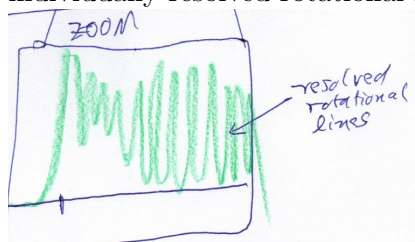


Clarification of inset: All lines besides the central one correspond to a fixed change of angular momentum by $|\Delta K| = 2$. We can calculate $E_{rot}(K+2) - E_{rot}(K) = B[4K+6]$. For $K \in \mathbb{N}_0$ this gives the lines shown (with sign of frequency shift depending on whether the initial or final atomic state is higher in energy). The many lines thus only exist as long as we have multiple choices for K of the initial state (non-zero temperature).

Molecular Raman spectrum: of N_2 near the $3\Pi_u \rightarrow 3\Pi_g$ electronic transition (taken from “Demtröder, Atoms, Molecules and Photons”).



We can zoom into the band system shown above, to see the details of a single band with individually resolved rotational lines, seen below

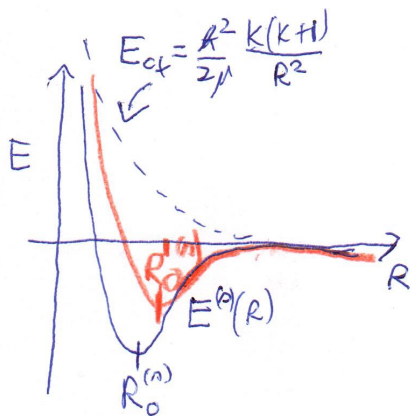


left:

- asymmetric band spacing up vs. down $\Delta\nu$, due to the not necessarily equal $\hbar\omega_0$ on s and s' .
- rotational lines are not equally spaced, as expected from Eq. (4.35), since I does actually depend on K .

4.7.5 Coupling between rotations and vibrations

See book “Demtröder, Atoms, Molecules and Photons” for (too many) more details.



left: Sketch for rotation-vibration coupling:

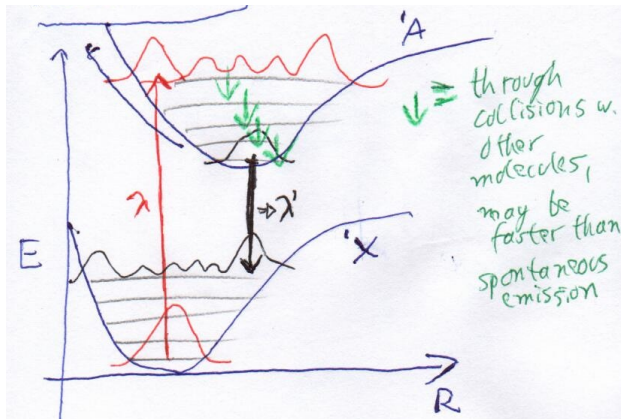
- For large rotations K , we need to fully include the centrifugal potential $E_{cf} = \hbar^2 K(K+1)/(2\mu R^2)$ in Eq. (4.24).
 - This causes an effective outwards shift of the basic BO surface (blue) towards larger separations (red), with then a larger equilibrium separation $R_0'^{(s)} > R_0^{(s)}$.
 - This is called centrifugal distortion.
-
- The discussion so far in week 12 and week 11 allowed a completely independent treatment of electronic energies, vibrations and rotations. This crucially hinges on the replacement $R \rightarrow R_0$ above Eq. (4.25) and the harmonic approximation used for Eq. (4.26).
 - In reality an increase of angular momentum (rotation) causes a shift of the equilibrium position $R_0^{(s)} \rightarrow R_0'^{(s)}$, see figure. This is due to the centrifugal force pulling the nuclei apart. This has the following effects:
 - (i) For large K rotational energies deviate from Eq. (4.25) since the moment of inertia changes due to the stretch.
 - (ii) A sudden increase in rotation K may in turn excite vibrations, since the equilibrium position is shifted.
 - (iii) A sudden increase in vibration ν towards the anharmonic part may in turn change the rotation state, since the mean separation of nuclei and hence moment of inertia is changed.

4.7.6 Fluorescence and Phosphorescence

We can use the Franck-Condon principle illustrated earlier to also understand the phenomena:

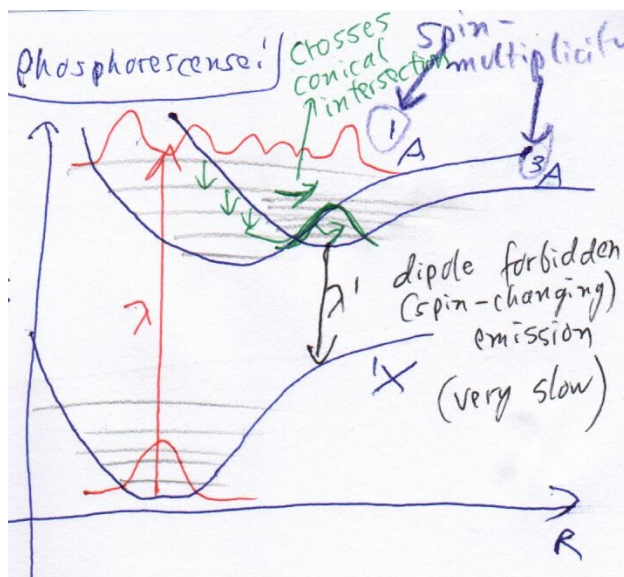
Fluorescence: Molecule absorbs at λ but emits at $\lambda' > \lambda$ (e.g. UV to visible, shirt glows when exposed to UV).

Phosphorescence: Same as fluorescence, but strongly delayed so that molecule (material) continues to emit/glow a long time (seconds) after excitation light source is removed.



left: Fluorescence:

- Franck-Condon principle results in excitation to higher vibrational state, e.g. $\nu = 0 \rightarrow \nu' = 5$.
- Molecules then relaxes to lower vibrational states (cools down) through collisions with other molecules (green arrows).
- Franck-Condon principle final requires de-excitation at a position with a much reduced electronic energy gap as shown by the black arrow and hence much larger wave length. (In the example shown $\nu' = 0 \rightarrow \nu = 5$)



left: Phosphorescence:

- If after excitation the molecule makes a radiationless transition (e.g. via non-adiabatic couplings in Eq. (4.6)) to another spin state, the de-excitation can end up being dipole forbidden (since elm radiation does not change the spin).
- This can lead to very long lifetime in the excited state and hence much delayed spontaneous emission of the photon.

Week 13

PHY 402 Atomic and Molecular Physics

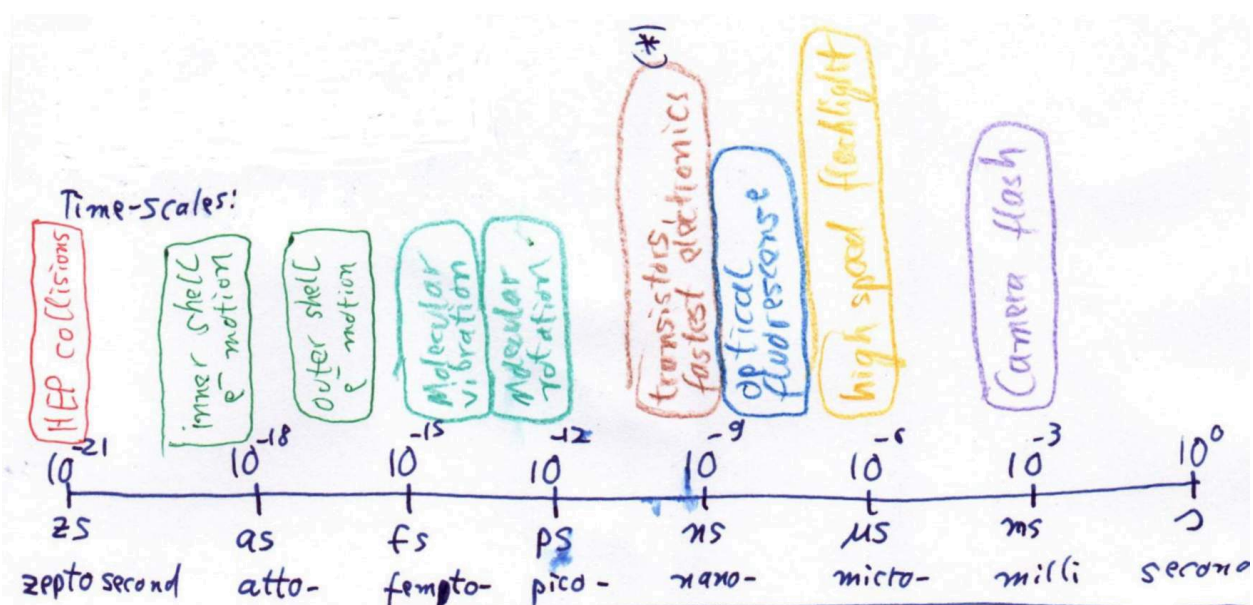
Instructor: Sebastian Wüster, IISER Bhopal, 2018

These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.

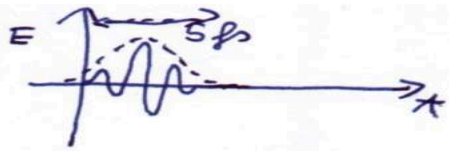
5 Frontiers of Modern AMO physics

We can only cover a small section biased by my own interests.

5.1 Ultrafast

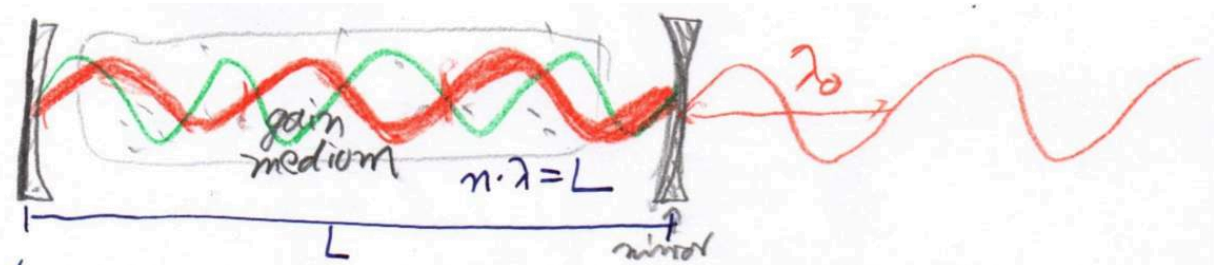


- To resolve e.g., vibrational molecular motion need \sim fs light pulses
- consider visible, e.g. 500nm $\implies \nu = 6 \times 10^{14}$ Hz and a pulse duration of $\Delta T = 1$ fs. In that case $\Delta T \nu \sim 0.6$, thus an optical pulse of a few fs duration has only a few oscillation cycles:
- Such short pulses are challenging to generate, we cannot simply switch on and off the laser that fast, since the required electronic processes are much slower, see (*) in time-scale figure above. One solution is portrayed in the following.



5.1.1 Frequency combs/ Femtosecond lasers

Laser resonators have multiple "eigenmodes" numbered with n , such that the light fulfils the boundary conditions at each end-mirror, thus $\lambda_n = 2L/n$.

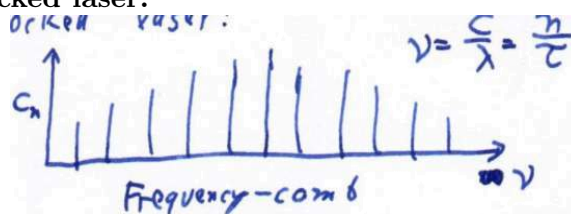


- For a normal laser, we rather want "single-mode" operation, where only a single λ_n is relevant.
- If we use a multi-mode, also called mode-locked, laser, the light field has the following Fourier spectrum

Frequency spectrum of mode locked laser:

$$\tilde{E}(\omega) = \sum_{\substack{n \\ N\text{-modes}}} c_n \delta(\omega - \omega_n)$$

τ = round-trip time [$\sim 2L/c$]



resulting time-domain picture ($c_n = \text{constant}$, $N = 1, 2, 3, 30, \dots$)

$$I(t) \sim \langle |E(t)|^2 \rangle$$



- Interpretation: Short pulse is bouncing back and forth in resonator and partially released out each time it hits the right-hand side (exit) mirror. As a result, outside the resonator we see a fs pulse train (large red line).

- This crucially results on the mode locking, i.e. all $c_n = 1$. If instead each c_n was a different random number, and we average over that, we get the small red line.

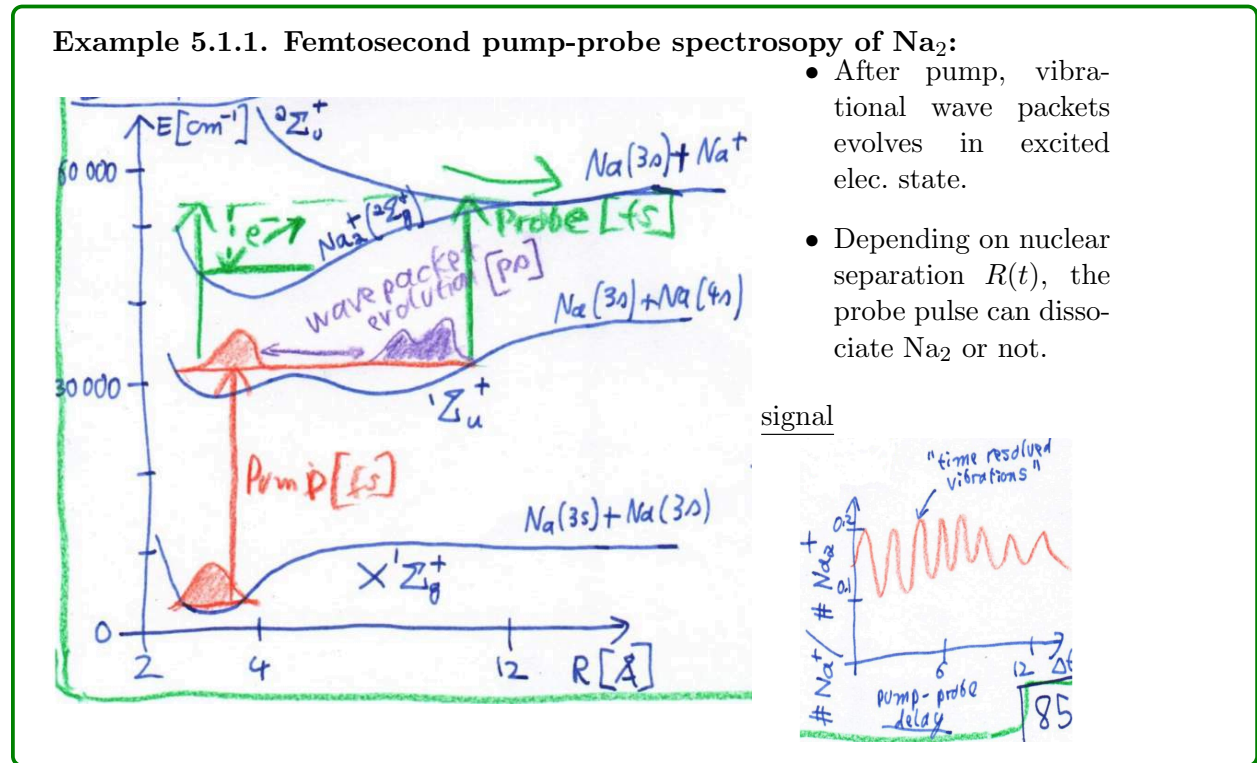
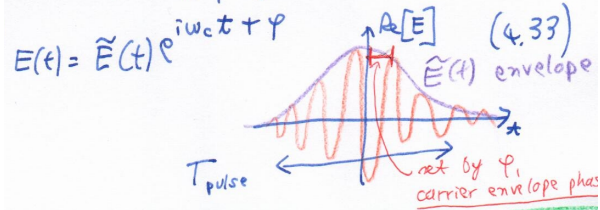
Pulse-waveform:

A single fs pulse is described by the waveform

$$E(t) = \tilde{E}(t)e^{i\omega_c t + \varphi} \quad (5.1)$$

where ω_c is the carrier frequency and $\tilde{E}(t)$ an envelope that changes only on slower time-scales than

$T = 2\pi/\omega_c$. φ is called carrier-envelope phase.



5.1.2 Strong fields, tunnel ionization

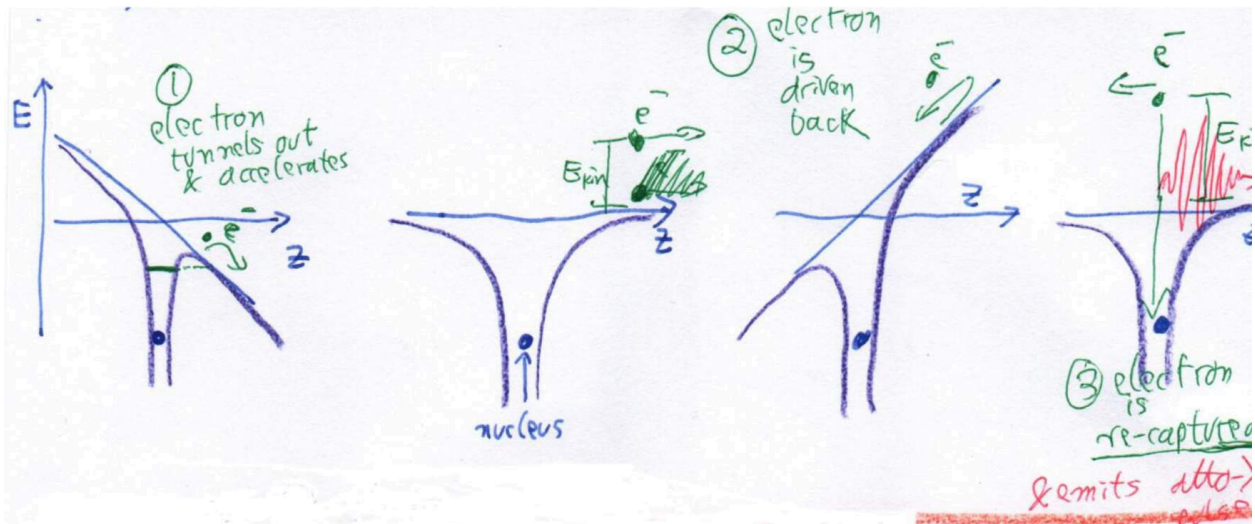
- Another consequence of the laser focussing all its energy into very short pulse: Very high intensities.
- In terms of Eq. (3.7), $\hat{H}'(t)$ may no longer be perturbative, $\mathbf{E}(t)$ may become comparable to Coulomb-field of nucleus!

Example:

- Electric field strength in hydrogen at a distance $r = a_0$ from the nucleus is $E(a_0) = \frac{Ze^2 m_e}{(4\pi\epsilon_0)^2 \hbar^2}$.
- Creating an equal field with a laser requires an intensity $I = \epsilon_0 |E(a_0)|^2 c$.
- Assume a continuously running laser that is tightly focussed to $r_{\text{foc}} = 1\mu\text{m}$. This then requires a power $P = I \times \pi r_{\text{foc}}^2 \sim 2 \text{ GigaWatt}$. (This is a large nuclear power plant).
- However using pulsed operation as in a fs laser, with pulse length T_{pulse} and pulse period τ , we only need $P' = P \frac{T_{\text{pulse}}}{\tau} \sim \text{few } 100W$

- These extreme conditions can be used to study interesting electron dynamics, and also to generate even shorter laser pulses than those in section 5.1.1.

Three-step model of HHG (high-harmonic generation)



Through steps (1) \Leftrightarrow (2), electron gains an energy corresponding to

Ponderomotive energy

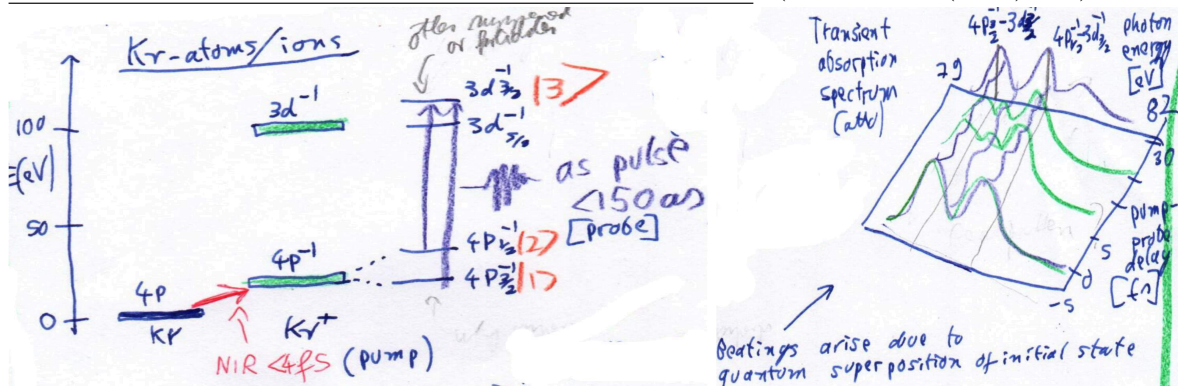
$$U_p = \frac{e^2 E_a^2}{4m\omega_0^2} \quad (\text{cycle averaged kinetic energy in field } \sim E_a \cos(\omega_0 t)) \quad (5.2)$$

Duration of emitted pulse \sim time-scale of electron motion.

- Classical electron orbit $z = 1$ (outer shell) $t_{\text{orb}} \simeq 150as$
 $z = 20$ (inner shell) $t_{\text{orb}} = 7as$

⇒ Can in this way (HHG) generate attosecond laser pulses.

Example: 5.1.2: Real-time valence electron motion: (Nature 466 (2010) 739)



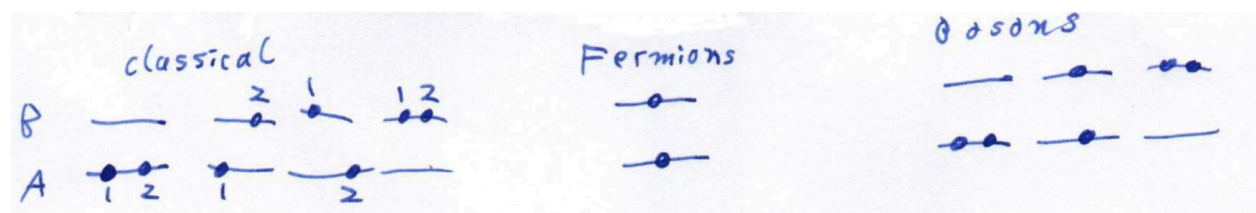
$$\begin{aligned}
 |\Psi(0)\rangle &\sim |1\rangle + |2\rangle \\
 |\Psi(t)\rangle &\sim e^{-iE_1 \frac{t}{\hbar}} |1\rangle + e^{-iE_2 \frac{t}{\hbar}} |2\rangle \\
 \left| \langle 3 | \hat{d} | \Psi(t) \rangle \right|^2 &= \left| \langle 3 | \hat{d} | 1 \rangle e^{-iE_1 \frac{t}{\hbar}} + \langle 3 | \hat{d} | 2 \rangle \exp^{-iE_2 \frac{t}{\hbar}} \right|^2 \\
 &= \langle 3 | \hat{d} | 1 \rangle^* \langle 3 | \hat{d} | 2 \rangle e^{i(E_1 - E_2) \frac{t}{\hbar}} + \text{c.c.} + \left| \langle 3 | \hat{d} | 1 \rangle \right|^2 + \left| \langle 3 | \hat{d} | 2 \rangle \right|^2
 \end{aligned}$$

5.2 Ultra Cold

We have discussed in section 3.2.3 how thermal motion of atoms Doppler broadens spectral lines. Since manipulations (excitation, trapping) are more controlled for narrow lines, it is appealing to cool atomic gases as much as possible.

5.2.1 Bose-Einstein Condensation

For indistinguishable quantum particles (see section 1.2.6) we need to change the way we count the total number of accessible many-body states. Consider two particles (1,2) distributed over two states (A,B):



This gives rise to quantum-statistics:

Bose-Einstein (-)/ Fermi-Dirac (+) distribution function

$$n_i = \frac{1}{e^{(E_i - \mu)/k_B T} \pm 1} \text{ for mean number } n_i \text{ of particles in a state with energy } E_i. \quad (5.3)$$

- μ is the chemical potential (fixes $N = \sum_i n_i$)
- In comparison the classical (Boltzmann) distribution does not have the ± 1 .
- BE- distribution diverges for groundstate ($E_u - \mu) = 0 \Rightarrow$ treat separately
- Find below a certain temperate, need macroscopic occupation of groundstate:

BEC transition temperature

$$k_B T_c \simeq (\hbar\omega) N^{1/3} \quad (5.4)$$

- N particles
- 3D harmonic trap $V(\mathbf{x}) = \frac{1}{2}m\omega^2|\mathbf{x}|^2$

e.g. $N = 10000$

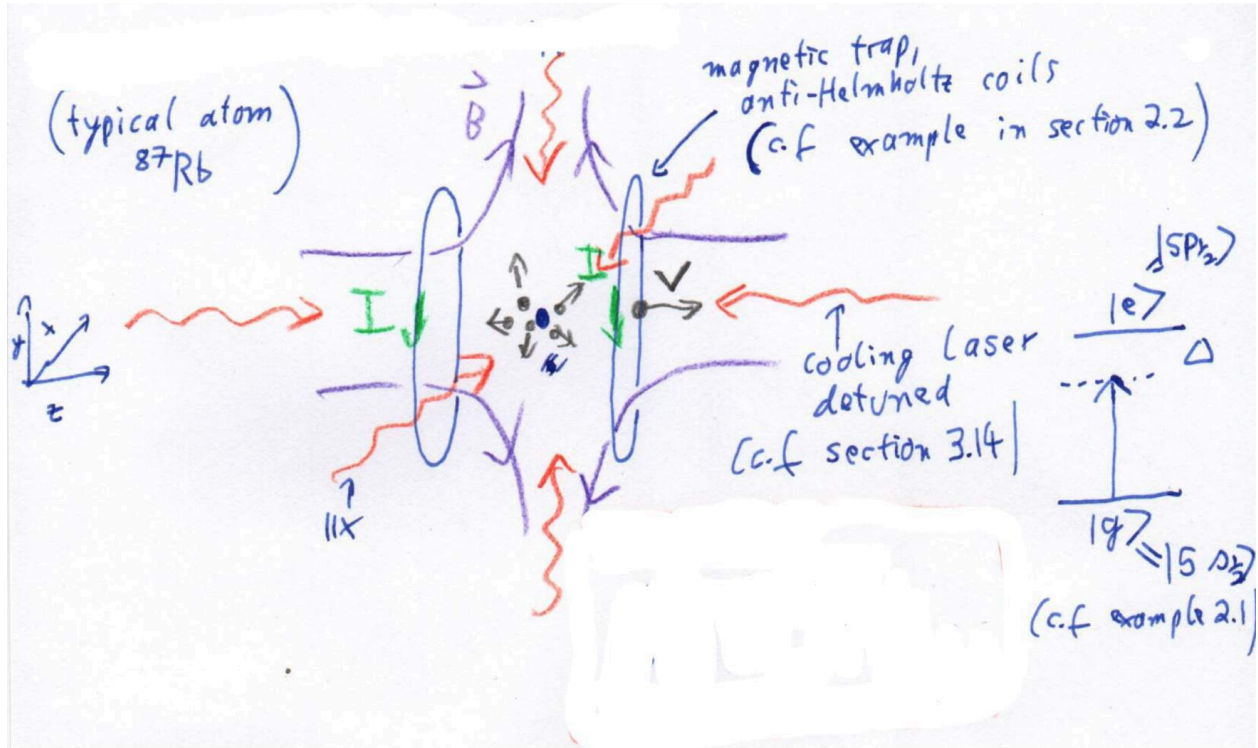
$$\omega = (2\pi)100Hz \quad T_c = 97nK$$

Groundstate/Condensate fraction

$$\frac{N_0(T)}{N} = \left[1 - \left(\frac{T}{T_c} \right)^3 \right] \quad (5.5)$$

5.2.2 Laser cooling and trapping

Typical ultra-cold atom apparatus



Doppler Shift

$$\omega' = \omega - \mathbf{v} \cdot \mathbf{k}$$

shifts only the fastest atoms into resonance. Photon absorption is most likely from against the motion direction, re-emission into a random direction. The atom thus experiences net cooling through photon recoil (momentum kicks).

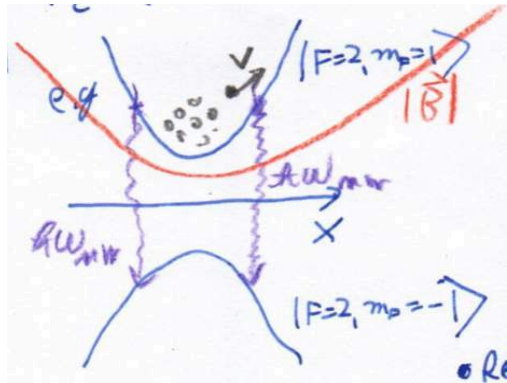
- Can combine magnetic field shifts on $|g\rangle, |e\rangle$ to get spatially dependent optical force \Rightarrow MOT (magneto-optical-trap)
- Laser-cooling can reach $\simeq 100\mu K$ (Doppler limit)
- Improved laser cooling (Sisyphus cooling)

Recoil Limit

$$k_B T = \frac{(\hbar k_{\text{las}})^2}{2M} \simeq 0.1 - 1\mu K \quad (5.6)$$

- To finally reach condensation temperature T_c :

Evaporative cooling:



- Magnetic trap:

$$E = \pm g_L \mu_B m_F |\mathbf{B}|, \quad (5.7)$$

see Eq. (2.63).

- Trapped atoms are in
- Drive microwave transition at frequency ω_{mw} to anti-trapped $m_F = -1$ state. This will be only resonant (likely) at large $|\mathbf{x}|$, see diagram ($x = 0$ is in the centre).
- Hence only the most energetic atoms can make a microwave transition to the anti-trapped state and are lost.
- This scheme loses the large majority of all atoms.
- However through collisions, the remaining ones rethermalize at a much lower temperature $T \simeq nK$.

5.2.3 Condensate mean-field

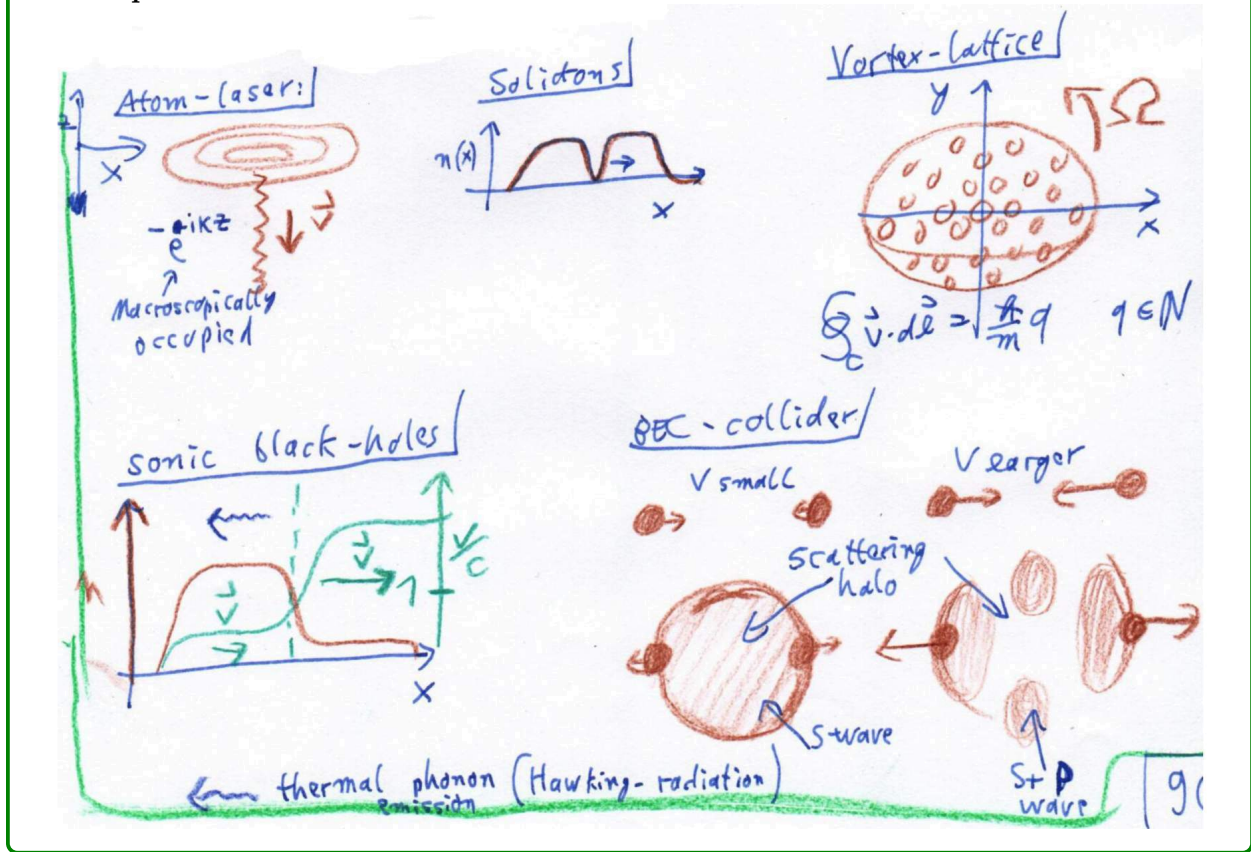
- Prior to condensation, we have to deal with a many-body wavefunction $\Psi(\mathbf{R}_1, \dots, \mathbf{R}_N)$ for N atoms. This is intractable for $N \simeq 10000$
- After condensation, can describe this using a condensate wave-function/order-parameter/mean-field $\phi(\mathbf{R})$ which obeys

Gross-Pitaevskii equation

$$i\hbar \dot{\phi}(\mathbf{R}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) + U_0 |\phi(\mathbf{R})|^2 \right] \phi(\mathbf{R}) \quad (5.8)$$

- where $V(\mathbf{x})$ is the trapping potential
- $U_0 = \frac{4\pi\hbar^2 a_s}{m}$ describes atomic collisions
- a_s = s-wave scattering length (see QM book, partial-wave treatment of scattering)
- $n(\mathbf{R}) = |\phi(\mathbf{R})|^2$ is the atom-density, $N = \int d^3\mathbf{R} |\phi(\mathbf{R})|^2$ the atom number.

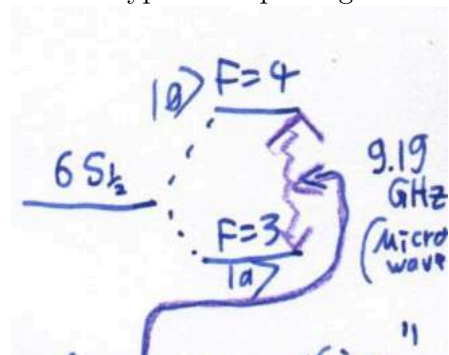
Example: BEC Phenomena:



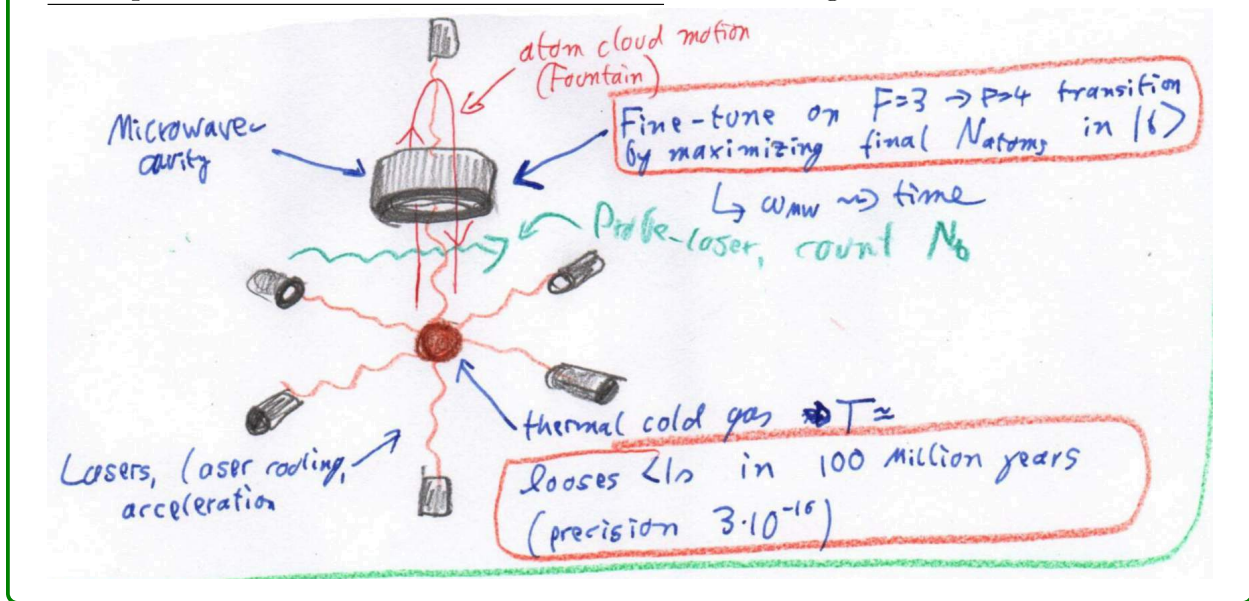
5.3 Atomic clocks

Consider a ^{133}Cs atom with nuclear spin $I = \frac{7}{2}$. The current definition of SI-unit "second" is as the "Duration of 9 192 631 770 periods of electromagnetic radiation resonant on the $F = 3$ to $F = 4$ hyperfine transition in the ground-state of that atom, see right.

Hyper-fine splitting



Example: NIST-F1 Cesium fountain clock: www.nist.gov



5.4 Quantum-simulation

As we have seen when studying multi-electron atoms or molecules: Many-body quantum mechanics is extremely challenging.

Many-body Hilbert space dimension For N particles that can be in M states each, the dimension of the many-body Hilbert space is

$$d \sim M^N \quad (5.9)$$

- As N , M increase, this becomes quickly too large to solve anything on classical computers

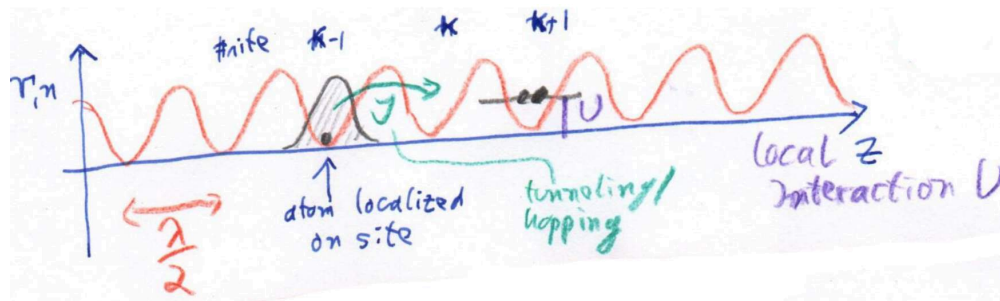
Idea by R. Feynman:

"Find another quantum-system with mathematically equivalent Hamiltonian where all parameters are under experimental control"

↔ (experimental) analogue quantum simulator

5.4.1 Bose-Hubbard model

Consider Bose-gas in optical lattice (= standing light wave), see e.g. Nature **415** 39 (2002).

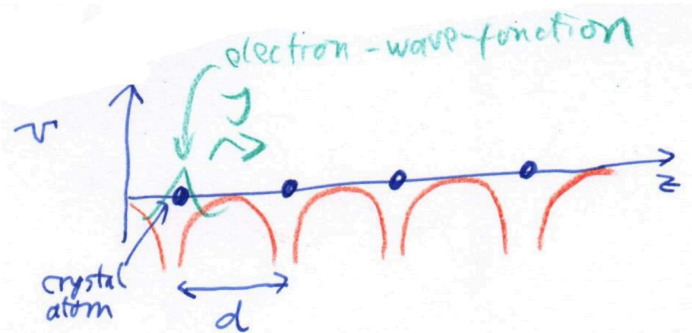


Many-body hamiltonian/Bose-Hubbard model

$$\hat{H} = -J \sum_k (\hat{a}_{k+1}^\dagger \hat{a}_k + \hat{a}_{k-1}^\dagger \hat{a}_k) + \frac{U}{2} \sum_k \hat{n}_k (\hat{n}_k - 1) \quad (5.10)$$

- $\hat{a}_k, (\hat{a}_k^\dagger)$ destroys (creates) a Boson at site k .
- $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ is the number operator on site k
- this setting provides.....

Quantum simulator for Hubbard model in condensed matter physics:

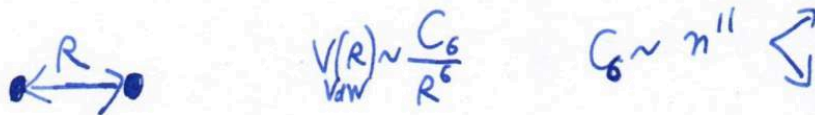


- electrons in a metal crystal (key difference: electrons are fermionic)
- here d, J, U cannot be changed in a given material.

- In cold atoms, J, λ, U can all be tuned.

5.4.2 Strongly interacting Rydberg systems

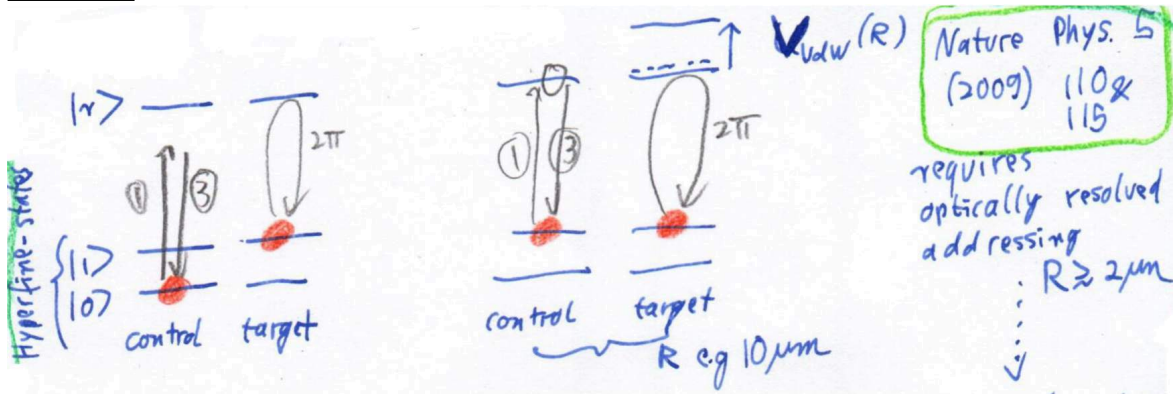
Consider Rydberg atoms, i.e. atoms in electronic states $|nlm\rangle$ with $n \gg 20$, see section 2.1.5. Two Rydberg atoms interact via Van-der-Waals interactions, see section 4.5.



In the ground state typical interaction ranges are $\sim 20a_0 \sim 0.01\mu m$

For Rydberg states their range is $\sim 10\mu m$

Example: Rydberg C-NOT Gate



Sequence:

In the following $|ab\rangle$ denotes a two atom state where $a \in \{0, 1\}$ is the state of the control atom and b of the target atom. We list the resulting transition sequence for all four possible initial quantum states.

(i) Rabi- π pulse on $|1\rangle \leftrightarrow |r\rangle$ transition for control only

$ 00\rangle$	$ 01\rangle$	$ 10\rangle$	$ 11\rangle$
↓			
$ 00\rangle$	$ 01\rangle$	$ r0\rangle$	$ r1\rangle$

(ii) Rabi- 2π pulse on $|1\rangle \leftrightarrow |r\rangle$ transition for target only

↓	↓	↓	↓
$ 00\rangle$	$- 01\rangle$	$ r0\rangle$	$ r1\rangle$
	<small>(see Eq. (3.51))</small>		

(iii) Rabi- π pulse on $|1\rangle \leftrightarrow |r\rangle$ transition for control only

↓	↓	↓	↓
$ 00\rangle$	$- 01\rangle$	$ 10\rangle$	$ 11\rangle$

Truth Table:	$ 00\rangle$	\rightarrow	$ 00\rangle$	
	$ 01\rangle$	\rightarrow	$- 01\rangle$	Controlled Z-gate \leftrightarrow can get C-NOT from here
	$ 10\rangle$	\rightarrow	$ 10\rangle$	
	$ 11\rangle$	\rightarrow	$ 11\rangle$	

Other Examples:

Nature Phys. 12 (2016) 1095

long-range spin chains

10µm

energy transport

10µm

Phys. Rev. Lett 114 (2015) 113002

Huge-range surfaces

molecular

Phys. Rev. Lett 106 (2011) 153002

The End

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