

Applied Quantum Mechanics

Summary/Overview

created by Tizian Römer

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Contact via E-Mail: tiroemer@yahoo.de

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1 Approximations Methods

1.1 Matrix Formulation of Quantum Mechanics

Consider the time independent Schrödinger equation:

$$H|\psi\rangle = E|\psi\rangle.$$

Take any complete set of functions $|n\rangle$ and expand $|\psi\rangle = \sum_n a_n |n\rangle$ and multiply with $\langle m|$:

$$\sum_n a_n \langle m|H|n\rangle = E \sum_n a_n \langle m|n\rangle.$$

Using the definition $H_{mn} := \langle m|H|n\rangle$ and $S_{mn} := \langle m|n\rangle$ (note that $H_{mn} = H_{nm}^*$, $S_{mn} = S_{nm}^*$) simplifies this equation and makes it possible to write it at a matrix equation:

$$\sum_n a_n H_{mn} = E \sum_n a_n S_{mn} \Leftrightarrow \mathcal{H}\vec{a} = E\mathcal{S}\vec{a} \Leftrightarrow (\mathcal{H} - E\mathcal{S})\vec{a} = 0$$

$$\Leftrightarrow \begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & \dots \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & \dots \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = 0.$$

Here, \mathcal{H} is a matrix with elements H_{mn} , \mathcal{S} with S_{mn} and \vec{a} has the components a_n . To solve for E , set $\det(\mathcal{H} - E\mathcal{S}) = 0$.

Of course, often is $S_{mn} = \delta_{mn}$, which yields clearly an eigenvalue problem: $\det(\mathcal{H} - E\mathbb{I}) = 0$.

1.2 Variational Principle

Consider the problem:

$$H|n\rangle = E_n|n\rangle.$$

An arbitrary trial function $|\phi\rangle$ can be expanded $|\phi\rangle = \sum_n a_n |n\rangle$.

Next, evaluate the expectation value of the energy $\langle H \rangle$ for the trial function:

$$\langle H \rangle = \langle \phi|H|\phi\rangle = \sum_{n,m} a_n^* a_m \langle n|H|m\rangle = \sum_{n,m} a_n^* a_m E_m \langle n|m\rangle$$

$$= \sum_n |a_n|^2 E_n \geq \sum_n |a_n|^2 E_0 = E_0.$$

Hence, for any trial function the expectation value $\langle H \rangle$ is bigger than the true ground state energy E_0 . Caution: If $|n\rangle$ are not orthonormal, the energy is $\langle H \rangle = \langle \phi|H|\phi\rangle / \langle \phi|\phi\rangle$.

EXAMPLE 1: VARIATIONAL PARAMETER

To get a good guess on E_0 , it is possible to vary the trial function $\phi \rightarrow \phi_\lambda$ using a variational parameter. Assume the solution to the harmonic oscillator is unknown and the trial function is

$$\phi_\lambda = \begin{cases} \sqrt{2\lambda/\pi} \cos \lambda x & -\pi/2\lambda < x < \pi/2\lambda \\ 0 & \text{else} \end{cases}$$

Next, calculate $\langle H \rangle$:

$$E = \langle H \rangle = \int_{-\infty}^{\infty} dx \phi_\lambda^* \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2} x^2 \right) \phi_\lambda$$

$$= \frac{\hbar^2 \lambda^2}{2m} + \frac{m\omega^2 (\pi^2 - 6)}{24\lambda^2}$$

and find the λ_0 , which minimizes $\langle H \rangle$:

$$\frac{\partial E}{\partial \lambda} = \frac{\hbar^2 \lambda_0}{m} - \frac{m\omega^2 (\pi^2 - 6)}{12\lambda_0^3} \stackrel{!}{=} 0 \Leftrightarrow \lambda_0^4 = \frac{m^2 \omega^2 (\pi^2 - 6)}{12\hbar^2}.$$

Next, insert λ_0 into the original formula:

$$E = \pm \frac{\hbar^2}{2m} \sqrt{\frac{m^2 \omega^2 (\pi^2 - 6)}{12\hbar^2}} \pm \frac{m\omega^2 (\pi^2 - 6)}{24} \sqrt{\frac{12\hbar^2}{m^2 \omega^2 (\pi^2 - 6)}}$$

$$= \pm \frac{\hbar\omega}{2} \sqrt{\frac{\pi^2 - 6}{12}} \pm \frac{\hbar\omega}{2} \sqrt{\frac{\pi^2 - 6}{12}} = \pm \frac{\hbar\omega}{2} \left(2 \sqrt{\frac{\pi^2 - 6}{12}} \right).$$

The last bracket term equals ≈ 1.136 . Hence E is quite close to the actual value $\hbar\omega/2$.

EXAMPLE 2: LINEARKOMBINATION AS A TRIAL FUNCTION

Trial wave function of the form $\phi = \sum_{n=0}^N c_n \phi_n$. E. g. ϕ_n might be atomic solutions and one is looking for the molecule solution.

With this trial function, the energy is

$$E = \langle H \rangle = \frac{\langle \phi|H|\phi\rangle}{\langle \phi|\phi\rangle} = \frac{\sum_{n,m} c_n^* c_m \langle \phi_n|H|\phi_m\rangle}{\sum_{n,m} c_n^* c_m \langle \phi_n|\phi_m\rangle} = \frac{\sum_{n,m} c_n^* c_m H_{nm}}{\sum_{n,m} c_n^* c_m S_{nm}}$$

$$\Leftrightarrow \sum_{n,m} c_n^* c_m H_{nm} = E \sum_{n,m} c_n^* c_m S_{nm}.$$

Now, assume all c_n^* , c_m are independent and take c_n^* (or c_n or the real/imaginary parts) as variational parameters. To get the minimum energy, take d/dc_i^* on both sides of the equation and set $dE/dc_i^* = 0$:

$$\text{LHS: } \frac{d}{dc_i^*} \sum_{n,m} c_n^* c_m H_{nm} = \sum_{n,m} \delta_{in} c_m H_{nm} = \sum_m c_m H_{im} = \mathcal{H}\vec{c}.$$

$$\text{RHS: } \frac{d}{dc_i^*} E \sum_{n,m} c_n^* c_m S_{nm} = E \sum_{n,m} \delta_{in} c_m S_{nm} = E \sum_{n,m} c_m S_{im} = E\mathcal{S}\vec{c}.$$

This yields $(\mathcal{H} - E\mathcal{S})\vec{c} = 0$ which is just of the same form as the matrix in 1.1. Of course, if ϕ_n is complete ($N = \infty$), it is *exactly* the same as in 1.1 and there is no approximation whatsoever.

But ϕ_n does not have to be complete, which results in a truncated matrix and approximation.

1.3 Perturbation Theory

See the derivation in "Quantenmechanik I (Theo D)", chapter 9.

For the time-dependent perturbation theory see 3.1.

For a problem $H = H_0 + H'$, where the solutions of H_0 are known and H' is the perturbation, the approximate energies and eigenfunctions are

$$E_n \approx E_n^{(0)} + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}.$$

Here, $E_n^{(0)}$ and $\psi_n^{(0)}$ are the known solutions of H_0 .

Recall the matrix formulation from 1.1: Assume now, the complete set are the eigenfunctions of H_0 . Hence, the matrix becomes $\mathcal{H} - E\mathbb{I}$ (since now $S_{nm} = \delta_{nm}$) and the eigenvalues are given by $\det(\mathcal{H} - E\mathbb{I}) = 0$.

Now assume as an approximation that the off diagonal elements of \mathcal{H} are zero. Hence, the eigenvalues are the diagonal elements:

$$E_n = H_{nn} = \langle \psi_n^{(0)} | H_0 + H' | \psi_n^{(0)} \rangle = E_n^{(0)} + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle.$$

This is just the first order result of perturbation theory.

For the second order of the n -th energy, form all possible 2×2 matrices like

$$\begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \ddots \\ \dots & H_{nn} - E & \dots & H_{ni} & \dots \\ \dots & \vdots & \ddots & \vdots & \dots \\ \dots & H_{in} & \dots & H_{ii} - E & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \Rightarrow \mathcal{H}_{ni}^{(2)} := \begin{pmatrix} H_{nn} & H_{ni} \\ H_{in} & H_{ii} \end{pmatrix}.$$

The eigenvalues of $\mathcal{H}_{ni}^{(2)}$ are given by $\det(\mathcal{H}_{ni}^{(2)} - E\mathbb{I}) = 0$ which yields

$$E_{1,2} = \frac{H_{nn} + H_{ii}}{2} \pm \frac{H_{nn} - H_{ii}}{2} \sqrt{1 + \frac{4|H_{ni}|^2}{(H_{nn} - H_{ii})^2}}$$

$$\approx \frac{H_{nn} + H_{ii}}{2} \pm \frac{H_{nn} - H_{ii}}{2} \left(1 + \frac{2|H_{ni}|^2}{(H_{nn} - H_{ii})^2} \right)$$

$$= \frac{H_{nn} + H_{ii} \pm H_{nn} \mp H_{ii}}{2} \pm \frac{|H_{ni}|^2}{H_{nn} - H_{ii}} \pm H_{nn} + \frac{|H_{ni}|^2}{H_{nn} - H_{ii}}.$$

Here, H_{nn} is the 0th and 1st order. Now, assuming that the first order is much bigger than the second, it is

$$H_{nn} - H_{ii} = E_n^{(0)} + E_n^{(1)} - E_i^{(0)} - E_i^{(1)} \approx E_n^{(0)} - E_i^{(0)}$$

and this yields just the 2nd order perturbation term, if summed over i .

For a degenerate case just take the matrix view point and calculate the eigenvalues of

$$\begin{pmatrix} H_{nn} & H_{ni} \\ H_{in} & H_{ii} \end{pmatrix}$$

with $\psi_n^{(0)} \neq \psi_i^{(0)}$ but $E_n^{(0)} = E_i^{(0)}$. Since there are two eigenvalues, the degeneracy will be lifted.

2 Atomic Physics

2.1 Normal Zeeman Effect

For an electron orbiting a proton with an angular momentum $L = mrv$, the dipole moment is

$$\mu_L = IA = \frac{q}{t}\pi r^2 = -\frac{ev}{2\pi r}\pi r^2 = -\frac{1}{2}evr,$$

where $I = q/t$ is the current and $A = \pi r^2$ the orbit area. This yields the correlation

$$\vec{\mu}_L = -\frac{e}{2m}\vec{L} = -g_L\frac{\mu_B}{\hbar}\vec{L}, \quad g_L = 1, \quad \mu_B = \frac{e\hbar}{2m}.$$

The energy of a hydrogen atom with magnetic moment $\vec{\mu}$ increases under the influence of a magnetic field $\vec{B} = B\vec{e}_z$ about

$$E_{\text{mag}} = -\vec{\mu}\vec{B} \Rightarrow H = H_{\text{atom}} + H_{\text{mag}} = H_{\text{atom}} + \frac{\mu_B B}{\hbar}L_z.$$

But since H_{atom} and L_z have the common eigenfunctions Y_{lm} , this is easily solvable:

$$H\psi = E\psi \Rightarrow E = E_n + \mu_B B m_l.$$

Here, $E_n = -13.6 \text{ eV}/n^2$ is the energy of the hydrogen atom.

Obviously, the degeneracy is lifted (removed) and each former level E_n is split into $2l + 1$ levels ($m_l = -l, \dots, l$).

The normal Zeeman effect is only observed under the neglect of spin, that is to say only at particles where the spin cancels out (e.g. the two electrons of the helium). Therefore, it is actually more a special than a normal case.

2.2 Hamiltonian of Spin-Orbit Coupling

Spin-orbit coupling considers the interaction between the electrons spin and the \vec{B} -field due to the current of the moving nucleus relative to the electron, which is in the magnitude of 1 T. Spin-orbit coupling gives an additional term in the Hamiltonian.

It can be calculated using the Biot-Savart law and $I d\vec{l} = \vec{j}dV$. Here, everything is from the viewpoint of the electron at the origin $\vec{0}$. \vec{v}_p and \vec{r}_p are velocity and position of the proton, $\vec{v} = -\vec{v}_p$ and $\vec{r} = -\vec{r}_p$ of the electron, where \vec{r} then is using the proton as the origin:

$$\begin{aligned} \vec{B}(\vec{0}) &= \frac{\mu_0 I}{4\pi} \oint d\vec{l}' \times \frac{\vec{0} - \vec{r}'}{|\vec{0} - \vec{r}'|^3} = -\frac{\mu_0}{4\pi} \int dV' \vec{j}(\vec{r}') \times \frac{\vec{r}'}{|\vec{r}'|^3} \\ &= -\frac{\mu_0}{4\pi} \int dV' e\delta(\vec{r}' - \vec{r}_p)\vec{v}_p \times \frac{\vec{r}'}{|\vec{r}'|^3} = -\frac{\mu_0 e \vec{v}_p \times \vec{r}_p}{4\pi |\vec{r}_p|^3} \\ &= -\frac{\mu_0 e \vec{v} \times \vec{r}}{4\pi |\vec{r}|^3} = \frac{\mu_0 e}{4\pi m r^3} \vec{L}. \end{aligned}$$

For the hydrogen atom, this is sufficient (except for a missing factor of 1/2, see below) but it can be generalized for any central potential: The electric field for the electron is

$$\begin{aligned} \vec{E} &= \frac{e}{4\pi\epsilon_0 r^3} \vec{r} \Rightarrow \vec{B} = -\epsilon_0 \mu_0 \vec{v} \times \vec{E} = -\frac{1}{c^2} \vec{v} \times \vec{E} = \frac{1}{ec^2} \vec{v} \times \vec{F} \\ &= -\frac{1}{ec^2 r} \frac{dV}{dr} \vec{v} \times \vec{r} = \frac{1}{emc^2 r} \frac{dV}{dr} \vec{L}, \end{aligned}$$

where it was used, that for central potentials it is $\vec{F} = -\nabla V = -(dV/dr)(\vec{r}/r)$. Now, similarly to 2.1, the magnetic dipole moment for the spin is

$$\vec{\mu}_s = -\frac{g_s e}{2m} \vec{s} = -\frac{e}{m} \vec{s}, \quad g_s = 2,$$

and the additional term in the Hamiltonian is

$$H' = -\vec{\mu}_s \vec{B} = \frac{e}{m} \vec{s} \vec{B} = \frac{1}{m^2 c^2 r} \frac{dV}{dr} \vec{s} \vec{L}.$$

However, since it is actual the electron which is accelerating and not the proton (as pretended in this simplified derivation), a factor of 1/2 is missing, which will not be derived here:

$$H' = \frac{1}{2m^2 c^2 r} \frac{dV}{dr} \vec{s} \vec{L}.$$

An alternative form can be given using $\vec{s} = \hbar \vec{\sigma}/2$:

$$\begin{aligned} \vec{B} &= \frac{1}{2ec^2} \vec{v} \times \vec{F} = -\frac{1}{2ec^2} \vec{v} \times \nabla V = \frac{1}{2mec^2} \nabla V \times \vec{p} \\ \Rightarrow H' &= -\vec{\mu}_s \vec{B} = \frac{1}{2m^2 c^2} \vec{s} (\nabla V \times \vec{p}) = \frac{\hbar}{4m^2 c^2} (\vec{\sigma} \times \nabla V) \vec{p}. \end{aligned}$$

2.3 Addition Rules of Angular Momentum

Adding two angular momenta $\vec{J} := \vec{J}_1 + \vec{J}_2$ with quantum numbers j_1, m_1, j_2, m_2 yields another angular momentum with possible eigenvalues

$$|\vec{J}| = \hbar \sqrt{j(j+1)}, \quad j = |j_1 - j_2|, \dots, |j_1 + j_2|;$$

$$J_z = \hbar m_j, \quad m_j = -j, \dots, j.$$

Note also:

$$\vec{J}^2 = \vec{J}_1^2 + \vec{J}_2^2 + 2\vec{J}_1 \vec{J}_2 \Leftrightarrow \vec{J}_1 \vec{J}_2 = \frac{1}{2}(\vec{J}^2 - \vec{J}_1^2 - \vec{J}_2^2).$$

A state can be described by (j_1, m_1, j_2, m_2) as well as by (j_1, j_2, j, m_j) . That is because, for fixed j_1, j_2 there are

$$(2j_1 + 1)(2j_2 + 1)$$

states, since $m_i = -j_i, \dots, j_i$. But if described by (j_1, j_2, j, m_j) the number of possible states for fixed j_1, j_2 is the same (w.l.o.g. assume $j_1 > j_2$):

$$\begin{aligned} \sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) &= \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = 2 \sum_{j=j_1-j_2}^{j_1+j_2} j + \sum_{j=j_1-j_2}^{j_1+j_2} 1 \\ &= 2((j_1 - j_2) + (j_1 - j_2 + 1) + \dots + (j_1 + j_2)) + (2j_2 + 1) \\ &= 2((2j_2 + 1)(j_1 - j_2) + \sum_{n=1}^{2j_2} n) + (2j_2 + 1) \\ &= 2((2j_2 + 1)(j_1 - j_2) + j_2(2j_2 + 1)) + (2j_2 + 1) \\ &= 2j_1(2j_2 + 1) + (2j_2 + 1) = (2j_1 + 1)(2j_2 + 1). \end{aligned}$$

2.4 Spin-Orbit Coupling for the Hydrogen Atom

Recall from 2.2 and use 2.3 to get

$$H = H_0 + H' = H_0 + \frac{1}{2m^2 c^2 r} \frac{dV}{dr} \vec{s} \vec{L} = H_0 + \frac{f(r)}{2} (\vec{J}^2 - \vec{L}^2 - \vec{s}^2).$$

Now, first order perturbation theory includes the term

$$\langle nlsjm_j | H' | nlsjm_j \rangle = \frac{\hbar^2}{2} \langle f \rangle \left(j(j+1) - l(l+1) - \underbrace{s(s+1)}_{=3/4} \right).$$

Now, examine an atom in the state $2p$, hence $n = 2, l = 1$, such that j can have two values:

$$\langle nlsjm_j | H' | nlsjm_j \rangle = \frac{\hbar^2}{2} \langle f \rangle \begin{cases} -2 & j = 1/2 \\ 1 & j = 3/2 \end{cases}.$$

For the hydrogen atom, the Coulomb potential yields

$$f(r) = -\frac{1}{2m^2 c^2 r} \frac{d}{dr} \frac{e^2}{4\pi\epsilon_0 r} = \frac{e^2}{8\pi\epsilon_0 m^2 c^2 r^3}.$$

The expectation value of r^{-3} can be given exactly (no derivation here, $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$, $a_0 = 4\pi\epsilon_0 \hbar^2 / me^2$):

$$\left\langle \frac{1}{r^3} \right\rangle = \int_0^\infty dr r^2 |R_{nl}(r)|^2 \frac{1}{r^3} = \frac{1}{a_0^3 n^3 l(l + \frac{1}{2})(l + 1)}.$$

Finally, the total first order perturbation correction is

$$\begin{aligned} \langle nlsjm_j | H' | nlsjm_j \rangle &= \frac{\hbar^2 e^2}{16\pi\epsilon_0 m^2 c^2} \frac{(j(j+1) - l(l+1) - \frac{3}{4})}{a_0^3 n^3 l(l + \frac{1}{2})(l + 1)} \\ &= \frac{E_n^{(0)2}}{mc^2} \frac{n(j(j+1) - l(l+1) - \frac{3}{4})}{l(l + \frac{1}{2})(l + 1)}, \end{aligned}$$

where $E_n^{(0)} = -e^2 / 8\pi\epsilon_0 a_0 n^2 = -13.6 \text{ eV}/n^2$. Note that $|E_n^{(0)}| / mc^2 = \alpha^2 / 2n^2$, where α is the fine structure constant.

2.5 Relativistic Correction

The relativistic kinetic energy is using $\sqrt{1+x} \approx 1 + x/2 - x^2/8$:

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 = mc^2 \left(\sqrt{1 + p^2/m^2c^2} - 1 \right) \\ \approx mc^2 \left(\frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} \right) = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}.$$

Therefore, the correction term will be $H' = -p^4/8m^3c^2$:

$$\langle nlm|H'|nlm\rangle = -\frac{1}{2mc^2} \left\langle nlm \left| \left(\frac{p^2}{2m} \right)^2 \right| nlm \right\rangle \\ = -\frac{1}{2mc^2} \left\langle nlm \left| (E_n^{(0)} - V)^2 \right| nlm \right\rangle \\ = -\frac{1}{2mc^2} \left(E_n^{(0)2} + \frac{2E_n^{(0)}e^2}{4\pi\epsilon_0} \left\langle nlm \left| \frac{1}{r} \right| nlm \right\rangle \right. \\ \left. + \frac{e^4}{16\pi^2\epsilon_0^2} \left\langle nlm \left| \frac{1}{r^2} \right| nlm \right\rangle \right).$$

Without proof, note that $\langle nlm|r^{-1}|nlm\rangle = 1/a_0n^2$ and $\langle nlm|r^{-2}|nlm\rangle = 1/a_0^2n^3(l+1/2)$. Recall again $E_n^{(0)} = -e^2/8\pi\epsilon_0a_0n^2 = -13.6\text{eV}/n^2$ to get:

$$\langle nlm|H'|nlm\rangle \\ = -\frac{1}{2mc^2} \left(E_n^{(0)2} + \frac{2E_n^{(0)}e^2}{4\pi\epsilon_0a_0n^2} + \frac{e^4}{16\pi^2\epsilon_0^2a_0^2n^3(l+1/2)} \right) \\ = -\frac{1}{2mc^2} \left(E_n^{(0)2} - 4E_n^{(0)2} + \frac{4nE_n^{(0)2}}{l+1/2} \right) \\ = -\frac{2E_n^{(0)2}}{mc^2} \left(\frac{n}{l+1/2} - \frac{3}{4} \right) = \frac{\alpha^2E_n^{(0)}}{n^2} \left(\frac{n}{l+1/2} - \frac{3}{4} \right).$$

The last step can be done by simple substitutions; α is the fine-structure constant.

2.6 Notation of Atomic States

An atomic state can be denoted as

$$^{2S+1}L_J,$$

where S is the total spin quantum number of all the electrons and J the total angular momentum of all the electron (spin+orbital). L represents the total orbital quantum number, but is denoted in letters not numbers:

$$L = 0 \rightarrow L = S,$$

$$L = 1 \rightarrow L = P,$$

$$L = 2 \rightarrow L = D, \text{ etc.}$$

For example, $^2P_{3/2}$ holds $S = 1/2, L = 1, J = 3/2$.

2.7 Anomalous Zeeman-Effect

The normal Zeeman effect neglects the spin and is therefore only observed, if the total spin is zero. The anomalous Zeeman effect takes the magnetic moment of the spin into account at the perturbation term, when applying an external \vec{B} -field $\vec{B} = B\vec{e}_z$:

$$H'_Z = -\vec{\mu}_L\vec{B} - \vec{\mu}_S\vec{B} = \frac{e}{2m}\vec{L}\vec{B} + \frac{e}{m}\vec{S}\vec{B} = \frac{eB}{2m}(L_z + 2S_z).$$

\vec{L} and \vec{S} are the total orbital and spin angular momentum respectively. Note, that $\vec{J} = \vec{L} + \vec{S} \neq \vec{L} + 2\vec{S}$.

The full Hamiltonian is now (H'_{SO} : spin-orbit-coupling, H'_Z : Zeeman-effect, ignoring the relativistic correction):

$$H = H_0 + H'_{SO} + H'_Z.$$

STRONG FIELD ZEEMAN-EFFECT (PASCHEN-BACK-EFFEKT):

Take the Hamiltonian $H = (H_0 + H'_Z) + H'_{SO}$ and treat H'_{SO} as a perturbation. Since $|nlm_l m_s\rangle$ is also an eigenstate of H'_Z :

$$(H_0 + H'_Z)|nlm_l m_s\rangle = (E_n^{(0)} + \mu_B B(m_l + 2m_s))|nlm_l m_s\rangle$$

($s = 1/2$ always). First order perturbation of H'_{SO} : Recall from 2.2 and 2.4 (However, it is treated differently here, since there is an external magnetic field):

$$\langle nlm_l m_s | f(r) \vec{S} \vec{L} | nlm_l m_s \rangle \\ = \langle f(r) \rangle \left(\underbrace{\langle S_x \rangle}_{=0} \langle L_x \rangle + \underbrace{\langle S_y \rangle}_{=0} \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle \right) = \hbar^2 \langle f(r) \rangle m_l m_s.$$

As seen in 2.4, $\langle f(r) \rangle$ is a number depending on n and l . The total energy is therefore ($\mu_B = \hbar e/2m$):

$$E_{nlm_l m_s} = E_n^{(0)} + \mu_B B(m_l + 2m_s) + \hbar^2 \langle f(r) \rangle m_l m_s.$$

For example for $l = 1$ there are 6 possible m_l - m_s -combinations:

m_l	m_s	$m_l + 2m_s$	$m_l m_s$
-1	-1/2	-2	1/2
-1	1/2	0	-1/2
0	-1/2	-1	0
0	1/2	1	0
1	-1/2	0	-1/2
1	1/2	2	1/2

Therefore, for $l = 1$ there are five different energies possible.

WEAK FIELD ZEEMAN EFFECT:

Take the Hamiltonian $H = (H_0 + H'_{SO}) + H'_Z$ and treat H'_Z as a perturbation. For the $H_0 + H'_{SO}$ -problem, the states were labeled by the quantum number $|nljm_j\rangle$, hence j, m_j is more important than m_l, m_s . Since $\vec{J} = \vec{L} + \vec{S}$ is more important, consider only the \vec{J} -component of \vec{L} and \vec{S} :

$$\vec{S}_j = \frac{\vec{S}\vec{J}}{|\vec{J}|} = \frac{\vec{J}^2 - \vec{L}^2 + \vec{S}^2}{2\vec{J}^2} \vec{J}, \quad \vec{L}_j = \frac{\vec{L}\vec{J}}{|\vec{J}|} = \frac{\vec{J}^2 + \vec{L}^2 - \vec{S}^2}{2\vec{J}^2} \vec{J}.$$

Here $\vec{L}^2 = \vec{J}^2 - 2\vec{J}\vec{S} + \vec{S}^2$ and equivalent expressions were used. Hence, it is approximately:

$$\vec{L} + 2\vec{S} \approx \vec{L}_j + 2\vec{S}_j = \frac{\vec{J}^2 + \vec{L}^2 - \vec{S}^2}{2\vec{J}^2} \vec{J} + 2 \frac{\vec{J}^2 - \vec{L}^2 + \vec{S}^2}{2\vec{J}^2} \vec{J} \\ = \frac{3\vec{J}^2 - \vec{L}^2 + \vec{S}^2}{2\vec{J}^2} \vec{J} = \left(1 + \frac{\vec{J}^2 - \vec{L}^2 + \vec{S}^2}{2\vec{J}^2} \right) \vec{J}.$$

$$\langle nlm_j | \vec{L} + 2\vec{S} | nlm_j \rangle \approx \left(1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right) \langle \vec{J} \rangle.$$

$g_{L,a}$ is called the Landé-factor. Finally, the energy correction is for $\vec{B} = B\vec{e}_z$ ($\mu_B = \hbar e/2m$):

$$\langle nlm_j | H'_Z | nlm_j \rangle = \frac{e}{2m} \langle (\vec{L} + 2\vec{S}) \vec{B} \rangle \approx \frac{g_{L,a} e B}{2m} \langle J_z \rangle = g_{L,a} \mu_B B m_j.$$

This result is the same as for the normal Zeeman-effect, except for $g_{L,a}$ and m_j replaces m_l .

2.8 Hyperfine-Structure

The hyperfine-structure is due to the interaction between the total angular momentum of the nucleus \vec{I} and of the electrons \vec{J} , due to the nuclear magnetic moment:

$$\vec{\mu}_I = \frac{g_I e}{2m_p} \vec{I}.$$

If $\vec{F} = \vec{I} + \vec{J}$ is the total angular momentum and \vec{B}_J the magnetic field caused by the electrons acting on the nucleus, the energy shift is

$$\begin{aligned} E_{\text{HFS}} &= -\vec{\mu}_I \vec{B}_J = \frac{g_I e B_J}{2m_p |\vec{J}|} \vec{I} \vec{J} = \frac{g_I \mu_N B_J}{\hbar} \frac{\vec{F}^2 - \vec{I}^2 - \vec{J}^2}{2|\vec{J}|} \\ &= g_I \mu_N B_J \frac{F(F+1) - I(I+1) - J(J+1)}{2\sqrt{J(J+1)}} \\ &= \frac{A}{2} (F(F+1) - I(I+1) - J(J+1)). \end{aligned}$$

Here, $\vec{B}_J = B_J \vec{J}/|\vec{J}|$ was assumed and the nuclear magneton $\mu_N = e\hbar/2m_p$ was used. Here, A is called the hyperfine-structure constant

$$A = \frac{g_I \mu_N B_J}{\sqrt{J(J+1)}}$$

HYDROGEN ATOM:

For the hydrogen atom, the nucleus is only the proton, hence it is $g_I = g_p \approx 5.586$. Furthermore, it is $I = J = 1/2$ and hence, due to the addition rules for angular momenta, $F = 0, 1$:

$$E_{\text{HFS}} = \frac{A}{2} (F(F+1) - 2 \cdot \frac{3}{4}) = \frac{A}{2} \left\{ \frac{3}{2} - \frac{3}{4} \right\} = \frac{A}{4} \left\{ 1 - \frac{3}{4} \right\}.$$

Hence, the energy gap is just A and can be given as

$$\Delta E = A = \frac{4g_p \hbar^4}{m_p m_e^2 c^2 a_0^4} \approx 5.88 \cdot 10^{-6} \text{ eV}.$$

2.9 The Helium Atom

The Hamiltonian of the Helium atom for a fixed nucleus is

$$H = \underbrace{\left(\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} \right)}_{=H_1} + \underbrace{\left(\frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_2} \right)}_{H_2} + \underbrace{\left(\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \right)}_{H'}$$

where H_1 and H_2 are almost the same as for hydrogen. Because of the interaction term, separation of variables like $\psi(\vec{r}_1, \vec{r}_2) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)$ doesn't work. But it does work for $H_1 + H_2$ alone, hence one can solve $H_1 + H_2$ exactly and treat H' as a perturbation.

H_i can be solved like hydrogen with a charge $e \rightarrow \tilde{e} = \sqrt{2}e$.

Hence, the ground state energy of H_i is

$$E_i = -\frac{m_e \tilde{e}^4}{32\pi\epsilon_0^2 \hbar} = -4 \frac{m_e e^4}{32\pi\epsilon_0^2 \hbar} = -4 \cdot 13.6 \text{ eV}$$

and the ground state energy of $H_1 + H_2$ is $2E_i = -108.8 \text{ eV}$. The perturbation term yields for the ground state, using the ground state wavefunctions of the hydrogen atoms (with charge \tilde{e}):

$$\begin{aligned} \langle \psi_{GS}(\vec{r}_1, \vec{r}_2) | H' | \psi_{GS}(\vec{r}_1, \vec{r}_2) \rangle &= \frac{e^2}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \frac{|\phi(\vec{r}_1)|^2 |\phi(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ &= 5/2 \cdot 13.6 \text{ eV}. \end{aligned}$$

Hence, the total energy up to first order of perturbation is

$$-108.8 \text{ eV} + 5/2 \cdot 13.6 \text{ eV} = -74.8 \text{ eV},$$

which is not too far away from the true value of 79 eV.

2.10 Many Particle Systems

For two identical, indistinguishable particles 1 and 2 should $|\psi(1,2)|^2 = |\psi(2,1)|^2$ be true. In general, this yields $\psi(1,2) = e^{i\phi} \psi(2,1)$, but only $\psi(1,2) = \pm \psi(2,1)$ occurs in nature, where $+$ holds for bosons and $-$ for fermions.

BOSONS:

For two particles 1,2 in two different ψ_a, ψ_b , the total wavefunction must obey $\psi(1,2) = \psi(2,1)$ (symmetric):

$$\psi(1,2) = 1/\sqrt{2} (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)).$$

FERMIONS:

For two particles 1,2 in two different ψ_a, ψ_b , the total wavefunction must obey $\psi(1,2) = -\psi(2,1)$ (antisymmetric):

$$\psi(1,2) = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix}.$$

For more than two fermions, using the Slater determinants as a total wave function ensures antisymmetry:

$$\psi(1,2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix}.$$

Helium ground state: The spatial part of the total wavefunction is symmetric, but since electrons are concerned, it has to be antisymmetric, which is achieved by including the spin:

$$\psi(1,2) = \underbrace{\psi(1)\psi(2)}_{\psi_{\text{spatial}} \text{ (symmetric)}} \underbrace{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}_{\psi_{\text{spin}} \text{ (antisymmetric)}} / \sqrt{2}.$$

α is a spin-up state, β a spin-down state.

2.11 Atomic Units

By using atomic units, quantities are expressed as dimensionless factors of natural constants:

→ Mass	electron mass m_e	$9.109 \cdot 10^{-31} \text{ kg}$
→ Charge	proton charge e	$1.602 \cdot 10^{-19} \text{ C}$
→ Ang. Mom.	red. Planck's constant \hbar	$1.055 \cdot 10^{-34} \text{ Js}$
→ Length	Bohr radius a_0	$5.292 \cdot 10^{-11} \text{ m}$
→ Energy	Hartree energy E_h	$4.360 \cdot 10^{-18} \text{ J}$

The Bohr radius and Hartree energy are

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}, \quad E_h = \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2}.$$

For example the Hamiltonian of the hydrogen atom becomes:

$$\begin{aligned} H &= -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} = E_h \left(-\frac{4\pi\epsilon_0 a_0}{e^2} \frac{\hbar^2}{2m_e} \nabla^2 - \frac{a_0}{r} \right) \\ &= E_h \left(-\frac{4\pi\epsilon_0}{e^2 a_0} \frac{\hbar^2}{2m_e} (a_0 \nabla)^2 - \frac{a_0}{r} \right) = E_h \left(-\frac{1}{2} (a_0 \nabla)^2 - \frac{a_0}{r} \right). \end{aligned}$$

Now, if r is measured in a_0 and H in E_h (r, H now dimensionless)

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r}.$$

2.12 Hartree Approximation

As in 2.11, the Hamiltonian of the helium atom is

$$H = \left(-\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{2}{r_2} \right) + \frac{1}{r_{12}}, \quad r_{12} := |\vec{r}_1 - \vec{r}_2|.$$

The ground state wave function should be of the form

$$\psi(\vec{r}_1, \vec{r}_2) = \underbrace{\phi(\vec{r}_1)\phi(\vec{r}_2)}_{\text{spatial part}} \underbrace{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}_{\text{spin part}} / \sqrt{2}.$$

Now, $|\phi(\vec{r}_2)|^2 d^3r_2$ is the probability of finding electron 2 in the volume d^3r . Therefore, "in average", the influence of electron 2 on electron 1 is

$$V_{\text{eff}}(\vec{r}_1) := \int d^3r_2 \frac{|\phi(\vec{r}_2)|^2}{r_{12}}$$

and the problem can be reduced to two single particle problems:

$$H'_i \phi(\vec{r}_i) \approx E_i \phi(\vec{r}_i), \quad H'_i = \left(-\frac{1}{2} \nabla_i^2 - \frac{2}{r_i} \right) + V_{\text{eff}}(\vec{r}_i), \quad i = 1, 2.$$

But H'_i depends on ϕ ! The method is to iteratively guess the ϕ in H'_i and check, if the equation $H'_i \phi \approx E_i \phi$ gives the same ϕ .

3 Atomic Transitions

3.1 Time-Dependent Perturbation Theory

For the time-dependent Schrödinger equation $i\hbar \partial\Psi/\partial t = H\Psi$, the time development of ψ is given by

$$\Psi(x, t) = \sum_n a_n \underbrace{\phi_n(x)}_{=\psi_n(x,t)} e^{-iE_n t/\hbar}, \quad H\phi_n = E_n\phi_n.$$

Consider the problem $H = H_0 + H'(t)$, where H_0 is not time-dependent and $H(t)$ is the perturbation. The idea is, to insert the time dependence of $H'(t)$ completely into the coefficients:

$$\Psi(x, t) = \sum_n a_n(t)\psi_n(x, t).$$

Plugging this into the Schrödinger equation yields

$$i\hbar \frac{\partial\Psi}{\partial t} = i\hbar \sum_n \left(\frac{\partial a_n}{\partial t} \psi_n + a_n \frac{\partial\psi_n}{\partial t} \right) \stackrel{!}{=} \sum_n a_n (H_0 + H')\psi_n = (H_0 + H')\Psi.$$

Since it is known that $H_0\psi_n = i\hbar \partial\psi_n/\partial t$, certain terms cancel:

$$i\hbar \sum_n \frac{\partial a_n}{\partial t} \psi_n \stackrel{!}{=} \sum_n a_n H' \psi_n.$$

In Dirac notation, multiply both sides with $\langle\phi_m|$:

$$\begin{aligned} i\hbar \sum_n \frac{\partial a_n}{\partial t} \underbrace{\langle\phi_m|\psi_n\rangle}_{=e^{-iE_n t/\hbar}\delta_{mn}} &= i\hbar e^{-iE_m t/\hbar} \frac{\partial a_m}{\partial t} \\ &\stackrel{!}{=} \sum_n a_n e^{-iE_n t/\hbar} \langle\phi_m|H'|\phi_n\rangle = \sum_n a_n \langle\phi_m|H'|\psi_n\rangle \\ \Leftrightarrow i\hbar \frac{\partial a_m}{\partial t} &= \sum_n a_n e^{-i(E_n - E_m)t/\hbar} \langle\phi_m|H'|\phi_n\rangle. \end{aligned}$$

This equation is a system of differential equations with which $a_n(t)$ can be determined and so far there is no approximation. For a two level system and for $a_1(0) = 1, a_2(0) = 0$ with a *small perturbation* it is $a_1(t) \approx 1, a_2(t) \approx 0$ and the equation becomes:

$$\begin{aligned} i\hbar \frac{\partial a_2}{\partial t} &= a_1 e^{-i\Delta E t/\hbar} \langle\phi_2|H'|\phi_1\rangle + a_2 \langle\phi_2|H'|\phi_2\rangle \\ &\approx e^{-i\Delta E t/\hbar} \langle\phi_2|H'|\phi_1\rangle, \quad \Delta E := E_1 - E_2. \end{aligned}$$

It is not specified here, whether $E_1 > E_2$ or $E_1 < E_2$.

3.2 Stimulated Absorption/Emission

Consider $H = H_{\text{atom}} + H'$ with H' being a (classical) z -polarized light beam of frequency ω and intensity \mathcal{E}_0^2 :

$$H' = ez\mathcal{E}_0 \cos \omega t = ez\mathcal{E}_0 (e^{i\omega t} + e^{-i\omega t})/2.$$

Hence, the last equation of 3.1 becomes (recall $\Delta E := E_1 - E_2$):

$$\begin{aligned} i\hbar \frac{\partial a_2}{\partial t} &\approx e^{-i\Delta E t/\hbar} \langle\phi_2|H'|\phi_1\rangle \\ &= \frac{e\mathcal{E}_0}{2} \underbrace{\langle\phi_2|z|\phi_1\rangle}_{=z_{21}} (e^{i(\hbar\omega - \Delta E)t/\hbar} + e^{-i(\hbar\omega + \Delta E)t/\hbar}). \end{aligned}$$

To solve for a_2 one has to integrate:

$$\begin{aligned} a_2(t) &= \frac{e\mathcal{E}_0}{2i\hbar} z_{21} \int_0^t dt' (e^{i(\hbar\omega - \Delta E)t'/\hbar} + e^{-i(\hbar\omega + \Delta E)t'/\hbar}) \\ &= -\frac{e\mathcal{E}_0}{2} z_{21} \left(\frac{e^{i(\hbar\omega - \Delta E)t/\hbar} - 1}{\hbar\omega - \Delta E} + \frac{e^{-i(\hbar\omega + \Delta E)t/\hbar} - 1}{-\hbar\omega - \Delta E} \right). \end{aligned}$$

The probability for the system to be in state 2 is $|a_2(t)|^2$, which is tedious to calculate. But obviously, $|a_2(t)|^2$ is big for $\Delta E = \pm\hbar\omega$, which is the expected result.

Stimulated absorption occurs for $E_2 > E_1, \Delta E = E_1 - E_2 = -\hbar\omega$, stimulated emission occurs for $E_1 > E_2, \Delta E = E_1 - E_2 = \hbar\omega$ (or the other way around, if a_1 had been considered instead of a_2).

Consider absorption and assume $\Delta E \approx -\hbar\omega$:

$$\begin{aligned} |a_2(t)|^2 &\approx \frac{e^2 \mathcal{E}_0^2}{4} |z_{21}|^2 \left| \frac{e^{-i(\hbar\omega + \Delta E)t/\hbar} - 1}{-\hbar\omega - \Delta E} \right|^2 \\ &= \frac{e^2 \mathcal{E}_0^2}{4} |z_{21}|^2 \left| \frac{e^{-i(\hbar\omega + \Delta E)t/2\hbar} - e^{i(\hbar\omega + \Delta E)t/2\hbar}}{-\hbar\omega - \Delta E} e^{-i(\hbar\omega + \Delta E)t/2\hbar} \right|^2 \\ &= \frac{e^2 \mathcal{E}_0^2}{\hbar^2} |z_{21}|^2 \frac{\sin^2((\omega - \omega_{21})t/2)}{(\omega - \omega_{21})^2}, \quad \omega_{21} := -\Delta E/\hbar > 0 \\ &= \frac{e^2 \mathcal{E}_0^2}{\hbar^2} |z_{21}|^2 \frac{\sin^2 x t^2}{x^2} \frac{1}{4}, \quad x := (\omega - \omega_{21})t/2. \end{aligned}$$

3.3 Selection Rules

Recall the probability for a transition from 3.2:

$$|a_2(t)|^2 \approx e^2 \mathcal{E}_0^2 |z_{21}|^2 \frac{\sin^2((\hbar\omega + \Delta E)t/2\hbar)}{(\hbar\omega + \Delta E)^2}, \quad \Delta E := E_1 - E_2.$$

If $|z_{21}|^2 = 0$, the transition is forbidden.

Z-POLARISATION:

Consider the hydrogen atom with wave functions $\psi_{nlm} = Y_{lm}R_{nl}$. If the light beam is z -polarized, z_{21} is, using $z = r \cos \theta$:

$$z_{21} = \langle n'l'm'|z|nlm\rangle = \int dr r^3 R_{n'l'}^* R_{nl} \int d\Omega Y_{l'm'}^* Y_{lm} \cos \theta.$$

Since the angle φ in the spherical harmonics appears only as a phase factor $e^{im\varphi}$, it is:

$$z_{21} \sim \int_0^{2\pi} d\varphi e^{-im'\varphi} e^{im\varphi} = 2\pi \delta_{mm'}.$$

Hence, one selection rule is, that only $m = m'$ or in other words $\Delta m = 0$ transitions are allowed.

X-POLARIZATION:

If the light beam is x -polarized, z_{21} is, using $x = r \cos \varphi \sin \theta$:

$$\begin{aligned} z_{21} &= \langle n'l'm'|x|nlm\rangle \sim \int_0^{2\pi} d\varphi e^{-im'\varphi} e^{im\varphi} \cos \varphi \\ &= \frac{1}{2} \int_0^{2\pi} d\varphi e^{-im'\varphi} e^{im\varphi} (e^{i\varphi} + e^{-i\varphi}) \\ &= \frac{1}{2} \int_0^{2\pi} d\varphi (e^{-i(m-m'+1)\varphi} + e^{-i(m-m'-1)\varphi}). \end{aligned}$$

Hence, only transitions $m = m' \pm 1$ or $\Delta m = \pm 1$ are allowed. y -polarization yields the same result.

SUMMARY OF THE SELECTION RULES:

All the selection rules are

$$\Delta m = 0, \pm 1; \quad \Delta l = \pm 1.$$

The Δl -selection rule is also due to the integral $|z_{21}|^2$, but will be given here without proof.

3.4 Stimulation with Non-Monochromatic Light

If there is non-monochromatic light, meaning different values for ω , the intensity depends on ω and $\mathcal{E}_0^2(\omega)d\omega$ is the total intensity of the light beam in a section $d\omega$. Hence, the transition probability due to the frequency ω becomes (starting from 3.2):

$$\begin{aligned} |a_2(t)|^2 &= \int d\omega \frac{e^2 \mathcal{E}_0^2(\omega)}{\hbar^2} |z_{21}|^2 \frac{\sin^2 x t^2}{x^2} \frac{1}{4} \\ &= \frac{e^2 |z_{21}|^2 t}{\hbar^2} \int dx \mathcal{E}_0^2(x) \frac{\sin^2 x}{x^2}. \end{aligned}$$

For large t , $\sin^2 x/x^2 \approx \pi\delta(x)$ (the factor π is because integrating $\sin^2 x/x^2$ yields π instead of 1) and only the value $x' = 0 \Leftrightarrow \omega = \omega_{21}$ matters:

$$|a_2(t)|^2 \approx \frac{\pi e^2}{2\hbar^2} \mathcal{E}_0^2(\omega_{21}) |z_{21}|^2 t = \frac{\pi e^2}{\epsilon_0 \hbar^2} U(\omega_{21}) |z_{21}|^2 t.$$

In the last step, the solution was rewritten in terms of the energy density $U(\omega) = \epsilon_0 \mathcal{E}_0^2/2$. The transition rate λ is then given by:

$$\lambda = \frac{\pi e^2}{3\epsilon_0 \hbar^2} U(\omega_{21}) |r_{21}|^2.$$

Here, also the x - and y -polarization was taken into account.

3.5 Fermi's Golden Rule

Especially in many atom systems it is also possible to have many possible transitions energies $\hbar\omega_{12}$ described by a density of states function $g(\omega_{21})$. Similar to 3.4 those possibilities can be summed up with an integral. Start from 3.2 and recall $x := (\omega - \omega_{21})t/2$:

$$\begin{aligned} |a_2(t)|^2 &= \frac{e^2 \mathcal{E}_0^2}{\hbar^2} |z_{21}|^2 \frac{t^2}{4} \int d\omega_{21} g(\omega_{21}) \frac{\sin^2 x}{x^2} \\ &\approx \frac{\pi e^2 \mathcal{E}_0^2 t^2}{4\hbar^2} |z_{21}|^2 \int dx g(x) \delta(x) = \frac{\pi e^2 \mathcal{E}_0^2 t^2}{4\hbar^2} |z_{21}|^2 g(\omega). \end{aligned}$$

Note, that $g(x=0) = g(\omega_{21} = \omega)$.

3.6 Einstein Coefficients, Spontaneous Emission

EINSTEIN COEFFICIENTS:

To derive Planck's black body radiation formula

$$U(\omega, T)d\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} d\omega,$$

Einstein introduced his coefficients (probabilities)

→ A for spontaneous emission

→ UB_E for stimulated emission (the probability is $\sim U$)

→ UB_A for stimulated absorption (the probability is $\sim U$)

and in equilibrium $N_1 B_A U = N_2 B_E U + N_2 A$ should hold, where N_1 and N_2 are the number of particles in the lower and higher level respectively, for which is known that ($\hbar\omega = E_2 - E_1$):

$$\frac{N_2}{N_1} = e^{-\hbar\omega/kT} = \frac{B_A U}{B_E U + A} \Leftrightarrow U = \frac{A}{B_A e^{\hbar\omega/kT} - B_E}.$$

To equal Planck's result, it must be $B := B_A = B_E$, which would also be the result if emission is considered as was absorption in

3.2. This yields, from Planck's formula:

$$\frac{A}{B} = \frac{\hbar\omega^3}{\pi^2 c^3} \Leftrightarrow A = \frac{\hbar\omega^3}{\pi^2 c^3} B = \frac{e^2 \omega^3}{3\pi\epsilon_0 \hbar c^3} |r_{21}|^2.$$

Here, the transition probability $\lambda = UB$ was used from 3.4.

SPONTANEOUS EMISSION:

If N_2 atoms are excited, the change in time due to the spontaneous emission coefficient is

$$\frac{dN_2}{dt} = -AN_2 \Leftrightarrow N_2(t) = N_2(0)e^{-At} = N_2(0)e^{-t/\tau}$$

with $\tau = 1/A$. If the excited state can decay to many states, it is

$A = \sum_i A_i$, A_i being the emission probabilities for the different decays. Hence, the life time is given by

$$\tau = \frac{3\pi\epsilon_0 \hbar c^3}{e^2 \omega^3} \frac{1}{|r_{21}|^2}.$$

4 Molecular Physics

4.1 Principles of Ionic Bonding

To form an ionic bond between atoms A and B , they have to be ionized to A^+ and B^- . For the reaction $A \rightarrow A^+$ the ionization energy E_{ion} is necessary, for the reaction $B \rightarrow B^-$, the system gains the electron affinity E_{aff} . Usually is

$E_{\text{ion}} > 0$, $E_{\text{aff}} < 0$, $|E_{\text{ion}}| > |E_{\text{aff}}|$, $\Delta E := E_{\text{ion}} + E_{\text{aff}} > 0$. After the energy ΔE was invested to transfer the electron, energy can be regained by coulombic attraction and the total energy becomes, relative to single atoms A, B

$$E(R) = \Delta E - \frac{e^2}{4\pi\epsilon_0 R} + (\text{repulsion term for very small } R),$$

where R is the distance between A^+ and B^- . There is a critical radius R_c , such that $E(R) < 0$ for $R < R_c$ and the bonding pays off. Including the repulsion term, there is also an equilibrium separation r_0 for which $E(R)$ is minimized.

4.2 Covalent Bonds: Born-Oppenheimer Approximation

Consider covalent bonding between two atoms. Since the nucleic mass (and thereby the time scale) is much larger than the electron mass, it is reasonable to treat the motion of the nuclei and electrons separately; that is to say assume the nuclei to be fixed in a distance R . The motion of the nuclei can be split into relative and center of mass coordinates (the electron influence on the latter is neglected). Considering only the relative motion \vec{R} of the nuclei, the Hamiltonian becomes

$$H = -\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0} \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \sum_i \left(-\frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \frac{Z_B}{|\vec{r}_i - \vec{R}_B|} \right) \right) = -\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + H_{\text{el}},$$

where H_{el} is the electronic Hamiltonian only for which R is only an parameter and no operator. Thereby, the separation approach

$$\psi(\{\vec{r}_i\}, \vec{R}) \approx \psi_{\text{nuc}}(\vec{R}) \psi_{\text{el}}(\{\vec{r}_i\})$$

is used, which is not exactly true, since \vec{R} and $\{\vec{r}_i\}$ are coupled. The eigenvalues of H_{el} will depend on R , hence $E_{\text{el}}(R)$, which is expected to be a function with a minimum at some equilibrium bonding distance R_0 . By a Taylor expansion at $R = R_0$ (R_0 is a minimum, hence no 1st order term)

$$E_{\text{el}}(R) \approx E_{\text{el}}(R_0) + \frac{1}{2} \frac{d^2 E_{\text{el}}}{dR^2} \Big|_{R_0} (R - R_0)^2$$

the distance oscillation of the two nuclei will be approximately harmonic. Moreover, there will also be a rotational motion with the energy

$$\frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2\mu R_0^2}.$$

For more details on the motion of the nuclei see 4.5.

4.3 The Molecular Ion of Hydrogen

Consider the simplest case: H_2^+ . The electronic Hamiltonian is

$$H_{\text{el}} = -\frac{1}{2} \nabla^2 - \frac{1}{|\vec{r} - \vec{R}_A|} - \frac{1}{|\vec{r} - \vec{R}_B|} + \frac{1}{R} = -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R},$$

which actually is exactly solvable. Here, however, it will be approximately solved by the method "linear combination of atomic orbitals" or "LCAO", which labels the ansatz

$$\psi_{\text{el}} = \sum_{i=1}^{\infty} (c_{Ai} \phi_{Ai} + c_{Bi} \phi_{Bi}),$$

where ϕ_{Ai} and ϕ_{Bi} are the atomic orbitals of the two atoms A, B and the index i sums up the single atomic states (hence, the quantum numbers n, l, m). As shown in 1.2, this yields an matrix equation $(\mathcal{H} - ES)\vec{c} = 0$.

ENERGIES:

For the roughest approximation, consider only the ground states of the two atoms. Therefore, $\mathcal{H} \in \mathbb{C}^{2 \times 2}$ and

$$(\mathcal{H} - ES)\vec{c} = \begin{pmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0,$$

where $H_{XY} = \langle \phi_X | H | \phi_Y \rangle$ and $S_{XY} = \langle \phi_X | \phi_Y \rangle$ ($S_{XX} = 1$). Consider:

$$H_{AA} = \underbrace{\langle \phi_A | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) | \phi_A \rangle}_{=E_0} + \underbrace{\langle \phi_A | \left(-\frac{1}{r_B} + \frac{1}{R} \right) | \phi_A \rangle}_{=J(R)},$$

where $E_0 = -13.6$ eV. Out of symmetry, it is $H_{BB} = H_{AA}$. And it is

$$H_{BA} = \underbrace{\langle \phi_B | \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) | \phi_A \rangle}_{=E_0 S_{BA}} + \underbrace{\langle \phi_B | \left(-\frac{1}{r_B} + \frac{1}{R} \right) | \phi_A \rangle}_{=K(R)} = H_{AB}^*,$$

such that the matrix becomes ($S := S_{BA} = S_{AB}$):

$$(\mathcal{H} - ES)\vec{c} = \begin{pmatrix} E_0 + J - E & E_0 S + K - ES \\ E_0 S + K - ES & E_0 + J - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0.$$

Non-trivial solution require $\det(\mathcal{H} - ES) = 0$ which yields:

$$E_0 + J - E = \pm (E_0 S + K - ES) \Leftrightarrow E_{\pm} = E_0 + \frac{J \pm K}{1 \pm S}$$

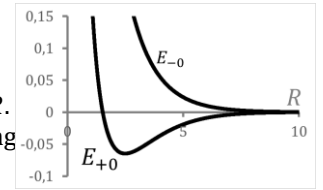
The integrals S, J, K turn out to be

$$S(R) = e^{-R} (1 + R + R^2/3),$$

$$J(R) = e^{-2R} (1 + 1/R),$$

$$K(R) = -e^{-R} (1 + R) + S(R)/R.$$

The plot shows, that E_+ is the bonding and E_- the anti-bonding state



($E_{\pm 0} := E_{\pm} - E_0$).

COEFFICIENTS AND WAVEFUNCTIONS:

Out of symmetry, it should be $c_A = \pm c_B$. Normalization yields

$$\langle \psi_{\text{el}} | \psi_{\text{el}} \rangle = \int d^3r (c_A^* \phi_A^* + c_B^* \phi_B^*) (c_A \phi_A + c_B \phi_B) = c_A^* c_A + c_A^* c_B S + c_A c_B^* S + c_B c_B^* = 2|c_A|^2 \pm 2|c_A|^2 S \stackrel{!}{=} 1 \Leftrightarrow c_A = \frac{1}{\sqrt{2(1 \pm S)}} \text{ for } c_A = \pm c_B.$$

Therefore, the bonding state ψ_+ and the anti-bonding state ψ_- is:

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (\phi_A \pm \phi_B).$$

4.4 Qualitative Remarks on Bonding by LCAO

BOND ORDER:

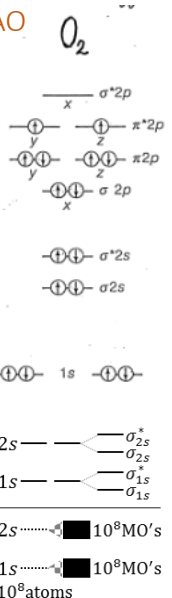
Anti-bonding states do not contribute to bonding, since their energy is higher than the energy of separated atoms. However, some of the 16 electrons of the molecule O_2 also occupy anti-bonding states. It is just that *more* bonding states are occupied. The bond order is

$$((e^- \text{ bonding}) - (e^- \text{ anti bonding}))/2.$$

In the right diagram, anti-bonding states are denoted by a star (*). Its bond order is 4, to which only 2p states contribute (1s, 2s: bond order 0).

ENERGY BANDS:

For two atoms, each atomic orbital splits into two molecular orbitals (MO's). For 10^8 atoms, they split into 10^8 molecular orbitals. Hence, for huge molecules (metals), there are energy bands and band gaps.



4.5 The Vibrational-Rotational Spectrum

Recall from 4.2

$$H = -\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + H_{\text{el}}, \quad \psi(\{\vec{r}_i\}, \vec{R}) \approx \psi_{\text{nuc}}(\vec{R}) \psi_{\text{el}}(\{\vec{r}_i\}).$$

Using 4.3, it is

$$H\psi(\{\vec{r}_i\}, \vec{R}) = \psi_{\text{el}}(\{\vec{r}_i\}) \left(-\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + E_{\text{el}}(R) \right) \psi_{\text{nuc}}(\vec{R}),$$

therefore, the remaining nuclear problem with the total energy E is

$$\left(-\frac{\hbar^2}{2m} \nabla_{\vec{R}}^2 + E_{\text{el}}(R) \right) \psi_{\text{nuc}}(\vec{R}) = E \psi_{\text{nuc}}(\vec{R}).$$

Considering the relative motion only means $m \rightarrow \mu$ (reduced mass). Since E_{el} is spherical symmetrical, the solution is

$$\begin{aligned} \psi_{\text{nuc}}(\vec{R}) &= \mathcal{R}(R) Y_{lm}(\theta, \varphi). \text{ This yields} \\ -\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left(R^2 \frac{d}{dR} \mathcal{R}(R) \right) + \left(\frac{l(l+1)\hbar^2}{2\mu R^2} + E_{\text{el}}(R) \right) \mathcal{R}(R) \\ &= -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \chi(R) + \left(\frac{l(l+1)\hbar^2}{2\mu R^2} + E_{\text{el}}(R) \right) \chi(R) = E \chi(R), \end{aligned}$$

where $\chi(r) := R \cdot \mathcal{R}(R)$. The rotational and vibrational motion is couple, since the rotational term depends on R like $\sim R^{-2}$. Since it is always $R \approx R_0$, where R_0 is the equilibrium separation (minimum of $E_{\text{el}}(R)$), one can approximately decouple the two motions by taking $l(l+1)\hbar^2/2\mu R^2 \approx l(l+1)\hbar^2/2\mu R_0^2$.

Furthermore, one can expand the energy around its minimum:

$$E_{\text{el}}(R) \approx E_{\text{el}}(R_0) + \underbrace{\frac{1}{2} \frac{d^2 E_{\text{el}}}{dR^2}}_{=k} \Big|_{R_0} (R - R_0)^2.$$

Hence, the Schrödinger equation can be written as

$$\begin{aligned} \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{k}{2} (R - R_0)^2 \right) \chi(R) \\ = \left(E - \frac{l(l+1)\hbar^2}{2\mu R_0^2} - E_{\text{el}}(R_0) \right) \chi(R), \end{aligned}$$

which is just a harmonic oscillator and the total result is

$$E = E_{\text{el}}(R_0) + \hbar\omega \left(n + \frac{1}{2} \right) + \frac{l(l+1)\hbar^2}{2\mu R_0^2} \equiv E_{nl}, \quad \omega := \sqrt{k/\mu}.$$

The energies depend on two quantum numbers n, l . Note that for small l (e.g. $l < 6$) it is

$$E_{(n+1),l} - E_{nl} > E_{n,(l+1)} - E_{nl}.$$

Moreover, similar to 3.3, there are the selection rules

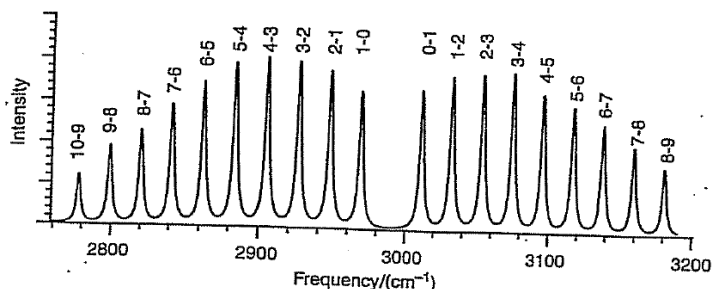
$$\Delta n = \pm 1, \quad \Delta l = \pm 1.$$

The allowed transitions thus have the following energies:

$$E_{n+1,l+1} - E_{nl} = \hbar\omega + \frac{\hbar^2}{2\mu R_0^2} (2l+3)$$

$$\begin{aligned} E_{n\pm 1, l\pm 1} - E_{nl} \\ = \hbar\omega \underbrace{(n \pm 1 - n)}_{=\pm 1} + \frac{\hbar^2}{2\mu R_0^2} \underbrace{((l \pm 1)(l \pm 1 + 1) - l(l+1))}_{=\pm 2l \pm 1 + 1} \end{aligned}$$

Those transitions yield the vibrational-rotational spectrum as shown below (here, it is always that n changes $0 \rightarrow 1$ and the numbers written on the peak is the transition of l):



From the data of such kind of spectrum, the equilibrium separation R_0 and the coupling constant k can be determined.

4.6 Mulliken Theory vs. Heitler-London

The LCAO approximation of molecular bonding from 4.3 was developed by R. Mulliken. For the H_2 molecule (two electrons), the form of the total spatial electronic wavefunction is

$$\begin{aligned} \psi &= \psi_{\text{trial}}(1) \psi_{\text{trial}}(2) = (\phi_A(1) + \phi_B(1))(\phi_A(2) + \phi_B(2)) \\ &= \underbrace{\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)}_{=\psi_{\text{VB}}} + \underbrace{\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)}_{\psi_{\text{ion}}} \end{aligned}$$

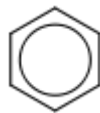
Here, only one single atomic state is considered, namely ψ_A and ψ_B of atom A and B respectively and 1 and 2 mark the two electrons. Obviously, ψ can be divided into a valence bond part ψ_{VB} and a ionic bond part ψ_{ion} . The approach of Heitler-London used only ψ_{VB} . However, the most accurate results can be achieved by varying the parameters c_1 and c_2 in

$$\psi = c_1 \psi_{\text{VB}} + c_2 \psi_{\text{ion}}.$$

4.7 The Hückel Molecular Orbital Theory for Benzene

ONE DELOCALIZED ORBITAL:

Consider only the third valence electron of each carbon atom and take a LCAO trial wave function



$$\sum_{n=1}^6 c_n \phi_n.$$

Using the matrix in 1.2, the definitions/approximations

$$a := H_{ii}, \quad b := \beta := H_{ij} < 0, \quad S_{ij} = \delta_{ij}$$

(where $\langle ij \rangle$ indicates that this holds only for nearest neighbours) yields the equation:

$$(\mathcal{H} - ES)\vec{c} = \begin{pmatrix} a & b & & & & \\ b & a & b & & & \\ & b & a & b & & \\ & & b & a & b & \\ & & & b & a & b \\ b & & & & b & a \end{pmatrix} \vec{c} = 0, \quad a := \alpha - E.$$

Using $\tilde{a} := a^2$, non-trivial solutions have to obey

$$\det(\mathcal{H} - ES) = \tilde{a}^3 - 6\tilde{a}^2 b^2 + 9\tilde{a} b^4 - 4b^6 \stackrel{!}{=} 0$$

which has only the two solutions $\tilde{a}_1 = b^2$ and $\tilde{a}_2 = 4b^2$, because \tilde{a}_1 has multiplicity two:

$$\partial/\partial \tilde{a} \det(\mathcal{H} - ES)|_{\tilde{a}_1} = 3b^4 - 12b^4 + 9b^4 = 0.$$

Hence, \tilde{a}_1 has four eigenstates (two for each $a_{1,2}$) and \tilde{a}_2 has two (one for each $a_{3,4}$), where

$$a_{1,2} = \pm\sqrt{\tilde{a}_1} = \pm b = \pm\beta \stackrel{!}{=} \alpha - E_{1,2} \Leftrightarrow E_{1,2} = \alpha \pm \beta,$$

$$a_{3,4} = \pm\sqrt{\tilde{a}_2} = \pm 2b = \pm 2\beta \stackrel{!}{=} \alpha - E_{3,4} \Leftrightarrow E_{3,4} = \alpha \pm 2\beta.$$

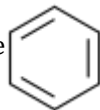
The ground state energy for the six electrons is therefore (recall, that $\beta < 0$):

$$E = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

THREE DOUBLE BONDS:

Before Hückel established the delocalized orbital, it was thought that benzene has three double bonds. Hence, the matrix is (using, as before, $a := \alpha - E, b := \beta$)

$$\mathcal{M} = \begin{pmatrix} a & b & & & & \\ b & a & & & & \\ & & a & b & & \\ & & b & a & & \\ & & & & a & b \\ b & & & & b & a \end{pmatrix}$$



In the same way as before, this yields

$$\det \mathcal{M} = \tilde{a}^3 - 3\tilde{a}^2 b^2 + 3\tilde{a} b^4 - b^6 \stackrel{!}{=} 0,$$

where the only solution $\tilde{a}_0 = b^2$ has multiplicity three.

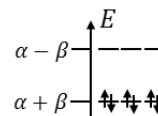
Therefore, $a_{1,2}$ has three eigenstates each, where

$$a_{1,2} = \pm\sqrt{\tilde{a}_0} = \pm b = \pm\beta = \alpha - E_{1,2} \Leftrightarrow E_{1,2} = \alpha \pm \beta.$$

Hence, the ground state energy is

$$E = 6(\alpha + \beta) = 6\alpha + 6\beta.$$

Since $\beta < 0$, this energy is higher than for the delocalized orbitals.



4.8 Hybridization

SP-HYPRIDIZATION:

Consider one electron in the s -state ($l = 0$) and a second in a p -state ($l = 1$). Then, the wavefunction can be written as the following Slater determinand:

$$\psi(1,2) = \begin{vmatrix} \psi_s(1) & \psi_p(1) \\ \psi_s(2) & \psi_p(2) \end{vmatrix}.$$

Introducing hybridized orbitals

$$\psi_A := (\psi_s - \psi_p)/\sqrt{2}, \quad \psi_B := (\psi_s + \psi_p)/\sqrt{2}$$

and writing them as a slater determinand yields

$$\begin{vmatrix} \psi_A(1) & \psi_B(1) \\ \psi_A(2) & \psi_B(2) \end{vmatrix}$$

which is, if expanded, just equal to $\psi(1,2)$. So the situation has not changed, only the description.

SP²-HYPRIDIZATION:

Consider C_2H_4 . Each carbon has four valence electrons (all at $n = 2$), which are in states $|200\rangle, |210\rangle, |2,1,-1\rangle, |211\rangle$. Now, describe them as

$$\psi_s := |200\rangle, \quad \psi_{p_z} := |210\rangle,$$

$$\psi_{p_x} := (|2,1,-1\rangle - |211\rangle)/\sqrt{2}, \quad \psi_{p_y} := (|2,1,-1\rangle + |211\rangle)/\sqrt{2},$$

hence as s, p_x, p_y, p_z orbitals, where the p -orbitals have all the same shape but along different axes. One electron of each carbon atom is in a pure p -orbital (lets say p_y), an forms a π -bond (half of the double bond). Now, consider the following hybrid orbitals ξ_i of the s, p_x and p_z states:

$$\xi_1 = a\psi_s + b_1\psi_{p_z} + c_1\psi_{p_x}$$

$$\xi_2 = a\psi_s + b_2\psi_{p_z} + c_2\psi_{p_x}$$

$$\xi_3 = a\psi_s + b_3\psi_{p_z} + c_3\psi_{p_x}$$

where it is assumed that all hybrid orbitals have the same fraction of the ψ_s state (hence $a = 1/\sqrt{3}$) and that ξ_i are orthonormal. Next, choose to place the z -direction along ξ_1 such that $c_1 = 0$. Normalization then yields $b_1 = \sqrt{2/3}$ and thus

$$\xi_1 = \sqrt{1/3}\psi_s + \sqrt{2/3}\psi_{p_z}.$$

Requiring ξ_2 being orthogonal to ξ_1 yields

$$\xi_1\xi_2 = a^2 + b_1b_2 = \frac{1}{3} + \frac{2}{3}b_2 \stackrel{!}{=} 1 \Rightarrow b_2 = -\frac{1}{\sqrt{6}}$$

normalization yields $c_2 = 1/\sqrt{2}$ and thus

$$\xi_2 = \sqrt{1/3}\psi_s - \sqrt{1/6}\psi_{p_z} + \sqrt{1/2}\psi_{p_x}.$$

Similarly ξ_3 turns out to be

$$\xi_3 = \sqrt{1/3}\psi_s - \sqrt{1/6}\psi_{p_z} - \sqrt{1/2}\psi_{p_x}.$$

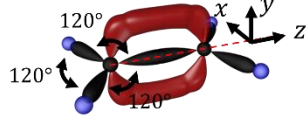
The maximum of ξ_2 w.r.t. to θ is obtained by (note $\partial_\theta\psi_s = 0$)

$$\begin{aligned} \frac{\partial \xi_2}{\partial \theta} &= \frac{\partial}{\partial \theta} \left(-\sqrt{1/6}\psi_{p_z} + \sqrt{1/2}\psi_{p_x} \right) \\ &= R_{21}(r) \frac{\partial}{\partial \theta} \left(-\sqrt{1/6}Y_{10} + 1/2(Y_{1,-1} - Y_{11}) \right) \\ &= \sqrt{3/4\pi} R_{21}(r) \frac{\partial}{\partial \theta} \left(-\sqrt{1/6}\cos\theta + 1/\sqrt{2}\sin\theta\cos\varphi \right) = 0 \end{aligned}$$

Considering the x - z -plane only means $\varphi = 0$ and hence

$$\tan\theta = -\sqrt{3} \Leftrightarrow \theta = 120^\circ.$$

Similarly, the angle of ξ_3 is $\theta = -120^\circ$.



4.9 The Underlying Idea of Hybridization

Consider a general molecule AB_2 which bonds like $B - A - B$. Let the valence electron of each of the B atoms be in a s -state and the two valence electrons of A in a s and p state. LCAO yields the matrix from 1.2. Let the matrix elements $\langle n|H|m\rangle$ be renamed as

$$\mathcal{H} = \begin{pmatrix} E_s & \approx 0 & V_1 & V_1 \\ \approx 0 & E_p \approx E_s & V_2 & -V_2 \\ V_1 & V_2 & E_{B,s} & \approx 0 \\ V_1 & -V_2 & \approx 0 & E_{B,s} \end{pmatrix}, \quad \text{where} \quad \begin{array}{l} |1\rangle = |A, s\rangle \\ |2\rangle = |A, p\rangle \\ |3\rangle = |B_1, s\rangle \\ |4\rangle = |B_2, s\rangle \end{array}$$

Here, $E_s, E_p, E_{B,s}$ are the atomic energies of the $|A, s\rangle, |A, p\rangle, |B, s\rangle$ states. V_i are just defined by e.g. $V_1 := \langle 1|H|3\rangle$. Moreover, $\langle 3|H|4\rangle \approx 0$, because the two B atoms are far away from each other and don't influence each other. $\langle 1|H|2\rangle \approx 0$, because $|1\rangle, |2\rangle$ are orthogonal and $H \approx H_A$ close to atom A . A change of basis does not alter the eigenvalues. Hence, use the hybridization

$$|\pm\rangle := (|1\rangle \pm |2\rangle)/\sqrt{2}.$$

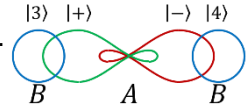
In this new basis $\{|+\rangle, |-\rangle, |3\rangle, |4\rangle\}$ the matrix becomes

$$\begin{pmatrix} \epsilon & 0 & V_1 + V_2 & V_1 - V_2 \\ 0 & \epsilon & V_1 - V_2 & V_1 + V_2 \\ V_1 + V_2 & V_1 - V_2 & E_{B,s} & 0 \\ V_1 - V_2 & V_1 + V_2 & 0 & E_{B,s} \end{pmatrix}, \quad \text{where } \epsilon := \langle \pm|H|\pm\rangle.$$

If it is assumed that $V_1 \approx V_2$, the matrix becomes ($V := 2V_1$)

$$\begin{pmatrix} \epsilon & 0 & V & 0 \\ 0 & \epsilon & 0 & V \\ V & 0 & E_{B,s} & 0 \\ 0 & V & 0 & E_{B,s} \end{pmatrix} \cong \left\{ \begin{pmatrix} \epsilon & V \\ V & E_{B,s} \end{pmatrix}, \begin{pmatrix} \epsilon & V \\ V & E_{B,s} \end{pmatrix} \right\}$$

which is separable into two 2×2 -matrices. The physical picture is that $|+\rangle$ interferes only with $|3\rangle$ and $|-\rangle$ only with $|4\rangle$.



5 Nuclear Physics

5.1 Weizsäcker Semiempirical Formula

THE ARGUMENTS USED IN DERIVATING THE FORMULAR:

To get a formula for the binding energy E_B of a nucleus, the roughest approximation assumes that, since the interaction is very short ranged, each nucleon interacts with about the same number of other nucleons and hence the binding energy is proportional to the number of nucleons A and hence

$$E_B = a_1 A.$$

However, the nucleons on the surface have less neighbours to interact with. For the number of nucleons and the nucleic radius R is $A \sim R^3$ and hence the surface area is $\sim R^2 \sim A^{2/3}$. Thus,

$$E_B = a_1 A - a_2 A^{2/3}.$$

The Coulomb interaction $\sim Z^2/R \sim Z^2/A^{1/3}$ destabilizes the nucleus (Z being the proton number) and hence

$$E_B = a_1 A - a_2 A^{2/3} - a_3 Z^2/A^{1/3}.$$

This formula is also called "liquid drop model" (more accurately it should be $Z^2 \rightarrow Z(Z-1)$). A further correction, called *asymmetric energy*, comes from the fact that nuclei with similar numbers of neutrons and protons are more stable (see derivation next subsection, note $N - Z = A - 2Z$):

$$E_B = a_1 A - a_2 A^{2/3} - a_3 Z^2/A^{1/3} - a_4 \frac{(A - 2Z)^2}{A}.$$

Another further correction comes from the fact, that even numbers of neutrons and protons are preferred over odd numbers:

$$E_B = a_1 A - a_2 A^{2/3} - a_3 \frac{Z^2}{A^{1/3}} - a_4 \frac{(A - 2Z)^2}{A} + a_5 \frac{(-1)^Z (1 + (-1)^A)}{A^{1/2}}.$$

Fitting to experimental data of nucleic binding energies yields

$$a_1 = 15.75 \text{ MeV}, \quad a_2 = 17.8 \text{ MeV}, \quad a_3 = 0.711 \text{ MeV}, \\ a_4 = 23.7 \text{ MeV}, \quad a_5 = 0.005 \text{ MeV}.$$

Obviously, the last term with a_5 is the first to be neglected.

DERIVATION OF THE ASYMMETRIC ENERGY TERM:

Although there are not so many nucleons in the nucleons, they can be considered as a Fermi gas at $T \approx 0$ (since room temperature energy $kT_{\text{room}} = 40^{-1} \text{ eV} \ll \text{MeV}$). From section 9.3 of *Statistical Mechanics (PHYS4031)*, the energy of a fermi has at $T = 0$ is for dimension $d = 3$ and exponent of the dispersion relation $E \sim k^q, q = 2$:

$$E = \frac{d}{d+q} N E_F = \frac{d}{d+q} N \left(\frac{dN}{q \tilde{\gamma} V} \right)^{q/d} \sim N \left(\frac{N}{V} \right)^{2/3} \sim N \left(\frac{N}{A} \right)^{2/3},$$

where, as above, $A \sim V$ was used. Since protons and neutrons are different particles, their Fermi gases have to be considered seperatly; once for $N = Z$ and for $N = \mathcal{N} := A - Z$. Hence, the total energy is, assuming that the proton and neutron mass are equal, and therefore the prefactors are equal:

$$E \sim \left(\mathcal{N} \left(\frac{\mathcal{N}}{A} \right)^{2/3} + Z \left(\frac{Z}{A} \right)^{2/3} \right) = \frac{1}{A^{2/3}} (\mathcal{N}^{5/3} + Z^{5/3})$$

Using $d := \mathcal{N} - Z$ to measure the difference in numbers, it is

$$d + A = \mathcal{N} - Z + \mathcal{N} + Z = 2\mathcal{N} \Leftrightarrow \mathcal{N} = (A + d)/2, \\ d - A = \mathcal{N} - Z - \mathcal{N} - Z = -2Z \Leftrightarrow Z = (A - d)/2$$

and writing E in terms of A and d yields

$$E \sim \frac{1}{A^{2/3}} ((A + d)^{5/3} + (A - d)^{5/3})$$

$$= A((1 + d/A)^{5/3} + (1 - d/A)^{5/3}) \approx 2A + \frac{10}{9} \frac{d^2}{A},$$

where in the last step, the terms $1 \pm d/A$ were Taylor expanded among $d/A \approx 0$ up to the second order. Hence, $E \sim (\mathcal{N} - Z)^2/A$.

5.2 Isobar Isotopes

Isobar Isotopes are Isotopes with the same nuclei number A .

MOST STABLE Z:

Taking the Weizsäcker binding energy from 5.1

$E(A, Z) \approx a_1 A - a_2 A^{2/3} - a_3 Z^2/A^{1/3} - a_4 (A - 2Z)^2/A$, the mass of a nucleus can be given as (using atomic units $c = 1$):

$$M(A, Z) = Z m_p + (A - Z) m_n - E(A, Z),$$

where m_p and m_n is the proton and neutron mass respectively.

For constant A , the most stable nucleus Z_0 can be found by

$$\left. \frac{\partial M}{\partial Z} \right|_{Z_0} = 0 \Leftrightarrow Z_0 = \frac{A m_n - m_p + 4a_4}{2 a_3 A^{2/3} + 4a_4}.$$

ENERGY DIFFERENCE FOR DIFFERENT Z:

For a constant A , the mass (or energy) difference $M(A, Z) - M(A, Z_0)$ goes like $\sim (Z - Z_0)^2$, as shown below. Multiplying out all the squares, it is

$$M(A, Z) - M(A, Z_0) \\ = \underbrace{(m_p - m_n + 4a_4)}_{c_1} (Z - Z_0) + \underbrace{\left(\frac{a_3}{A^{1/3}} + \frac{4a_4}{A} \right)}_{c_2} (Z^2 - Z_0^2) \\ \stackrel{!}{=} c_3 (Z - Z_0)^2 = c_3 (Z^2 - 2Z_0 Z + Z_0^2)$$

Obviously, that $Z_0 = -c_1/2c_2$. Now, comparing the coefficients of Z on both sides of the equation, it is

$$Z^2 \rightarrow c_2 = c_3$$

$$Z^1 \rightarrow c_1 = -2Z_0 c_3$$

$$Z^0 \rightarrow -c_1 Z_0 - c_2 Z_0^2 = c_3 Z_0^2$$

Using the Z^2 -equation, both the Z^1 and Z^0 equations are equivalent to $Z_0 = -c_1/2c_2$ which was already found to be true. Hence, it is

$$M(A, Z) - M(A, Z_0) = \left(\frac{a_3}{A^{1/3}} + \frac{4a_4}{A} \right) (Z - Z_0)^2.$$

β^\pm -DECAY:

β^\pm -decay keeps the isotope on its isobar. The mass (or energy) difference for β^\pm -decay is, using the Weizsäcker formula (skipping many steps):

$$\Delta M_{\beta^\pm} = M(A, Z \mp 1) - M(A, Z)$$

$$= \mp m_p \pm m_n \pm 4a_4 + \left(\frac{a_3}{A^{1/3}} + \frac{4a_4}{A} \right) (1 \mp 2Z).$$