17. Addition of angular momentum

17.1 Addition of angular momentum. Assume, that we have two independent subsystems with corresponding angular momenta $\hat{\vec{J}}_1$ and $\hat{\vec{J}}_2$. It is natural to ask which is the total angular momentum

$$\hat{\vec{J}} = \hat{\vec{J}}_1 + \hat{\vec{J}}_2 \ .$$

(Example: electron in atom. It has angular some momentum $\hat{\vec{L}}$ and spin $\hat{\vec{s}}$).

The problem is: the first system is characterized by quantum number j_1 and has states

$$\left| j_1 m_1 \right\rangle \ , \qquad m_1 = +j_1, \dots, -j_1 \ ,$$

the second one similarly by j_2 and states

$$\left| j_2 m_2 \right\rangle \ , \qquad m_2 = +j_2, \dots, -j_2 \ ,$$

which are the possible values of the total quantum number j and corresponding states $\left| jm \right\rangle$?

It is mathematically very complicated problem, therefore we give the result and later try to show, analysing some special cases, that the result is correct. The total quantum number has the corresponding values

$$j = j_1 + j_2, \, j_1 + j_2 - 1, \, \dots, \left| j_1 - j_2 \right| \ .$$

Mathematically the problem is, as follows. If the angular momenta of subsystems are $\hat{\vec{J}}_1$ and $\hat{\vec{J}}_2$, their components $\hat{J}_{1x}, \hat{J}_{1y}, \hat{J}_{1z}$ and $\hat{J}_{2x}, \hat{J}_{2y}, \hat{J}_{2z}$ satisfy the standard commutation relations

$$\left[\hat{J}_{1x}, \hat{J}_{1y} \right] = ih\hat{J}_{1z} \ , \quad \left[\hat{J}_{1y}, \hat{J}_{1z} \right] = ih\hat{J}_{1x} \ , \quad \left[\hat{J}_{1z}, \hat{J}_{1x} \right] = ih\hat{J}_{1y} \ ,$$

$$\left[\hat{J}_{2x}, \hat{J}_{2y} \right] = ih\hat{J}_{2z} \ , \quad \left[\hat{J}_{2y}, \hat{J}_{2z} \right] = ih\hat{J}_{2x} \ , \quad \left[\hat{J}_{2z}, \hat{J}_{2x} \right] = ih\hat{J}_{2y} \ .$$

Since subsystems are independent operators $\hat{J}_{1x}, \hat{J}_{1y}, \hat{J}_{1z}$ and $\hat{J}_{2x}, \hat{J}_{2y}, \hat{J}_{2z}$ mutually commute, i.e. for each $\hat{J}_{1i}$ and $\hat{J}_{2j}$ we have

$$\left[\hat{J}_{1i}, \hat{J}_{2j} \right] = 0$$

(i = x, y, z; j = x, y, z).

Now its is easy to verify, that projections of total angular momentum $\hat{\vec{J}}$

$$\hat{J}_x = \hat{J}_{1x} + \hat{J}_{2x} \ , \quad \hat{J}_y = \hat{J}_{1y} + \hat{J}_{2y} \ , \quad \hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$$

also satisfy

$$\left[\hat{J}_x,\hat{J}_y\right]=ih\hat{J}_z \ , \quad \left[\hat{J}_y,\hat{J}_z\right]=ih\hat{J}_x \ , \quad \left[\hat{J}_z,\hat{J}_x\right]=ih\hat{J}_y \ .$$

From here we can conclude that the total angular momentum quantum number must have the following values

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \ ,$$

as the quantum numbers j_1 and j_2.

As we already told j has values

$$j = j_1 + j_2, \ j_1 + j_2 - 1, \ \dots , \ \left| j_1 - j_2 \right| \ .$$

We give some simple considerations to convince that the above given expression may be valied. The states of whole system $\left| jm \right\rangle$ are some linear combinations of states

$$\left| j_1 m_1 \right\rangle \left| j_2 m_2 \right\rangle \ .$$

Total number of these states is $(2j_1 + 1)(2j_2 + 1)$. Let us assume that $j_1 \geq j_2$, then

$$j = j_1 + j_2, \ j_1 + j_2 - 1, \ \dots , \ j_1 - j_2 \ .$$

If we now calculate the total number of these states, we have a sum

$$\sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = (2j_1 + 1)(2j_2 + 1)$$

and gives the same result.

If we take

$$\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z} \ ,$$

we see that magnetic quantum numbers must be added: $m = m_1 + m_2$.

For the maximal projection $m = j_1 + j_2$ it corresponds only one combination of states

$$\left| j_1 j_1 \right\rangle \left| j_2 j_2 \right\rangle \ .$$

To the next projection $m = j_1 + j_2 - 1$ there are two possible combinations

$$\left| j_1 j_1 \right\rangle \left| j_2 j_2 - 1 \right\rangle , \quad \left| j_1 j_1 - 1 \right\rangle \left| j_2 j_2 \right\rangle \ ,$$

the next $m = j_1 + j_2 - 2$ has three combinations

$$\left| j_1 j_1 \right\rangle \left| j_2 j_2 - 2 \right\rangle , \quad \left| j_1 j_1 - 1 \right\rangle \left| j_2 j_2 - 1 \right\rangle , \quad \left| j_1 j_1 - 2 \right\rangle \left| j_2 j_2 \right\rangle ,$$

and so on up to $m = j_1 - j_2$ (if $j_1 \geq j_2$), which has $2j_2 + 1$ combinations. In the case of other diminishing projections the number of combinations remains the same, or starts to diminish. Now we see that we have $2(j_1 + j_2) + 1$ projections from $m = j_1 + j_2$ to $m = -(j_1 + j_2)$, corresponding to $j = j_1 + j_2$, $2(j_1 + j_2 - 1) + 1$ projections corresponding to $j = j_1 + j_2 - 1$, and so on up to $2(j_1 - j_2) + 1$ projections corresponding to $j = j_1 - j_2$.

Some simple examples.

Example 1. In atoms $\vec{L}$ is orbital angular momentum and $\vec{s}$ is elektron's spin. Total angular momentum

$$\vec{J} = \vec{L} + \vec{s} \ .$$

Orbital quantum number l has values $l = 0, 1, \ldots$, but spin quantum number $s = 1/2$, therefore the total angular momentum equals

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

Example 2. If $j_1 = 4$ and $j_2 = 2$, then $j = 6, 5, 4, 3, 2$.

17.2 Clebsh-Gordan coefficients. States $|jm\rangle$ are linear combinations of states with the same projection $|j_1 m_1\rangle |j_2 m_2\rangle$

$$|jm\rangle = \sum_{m_1 + m_2 = m} C^j_{m_1 m_2} |j_1 m_1\rangle |j_2 m_2\rangle \ ,$$

where the coefficients $C^j_{m_1 m_2}$ are called Clebsh-Gordani coefficients.

Derivation of Clebsh-Gordan coefficients is a quite complicated problem, therefore we give the results for two special cases, we need in following lectures. The next tables give Clebsh-Gordan coefficients for $j_2 = 1/2$ and $j_2 = 1$.

Table 1. $j_1 = l$ ja $j_2 = 1/2$, m_j is magnetic quantum number of j and σ_z is the same of spin (m_2)

j	$\sigma_z = 1/2$	$\sigma_z = -1/2$
$l + 1/2$	$\sqrt{\dfrac{1}{2} + \dfrac{m_j}{2l+1}}$	$\sqrt{\dfrac{1}{2} - \dfrac{m_j}{2l+1}}$
$l - 1/2$	$-\sqrt{\dfrac{1}{2} - \dfrac{m_j}{2l+1}}$	$\sqrt{\dfrac{1}{2} + \dfrac{m_j}{2l+1}}$

Table 2. $j_1 = l$ ja $j_2 = 1$ (l projections are denoted by l_z and $s = j_2$ projections by s_z).

j	$l_z = m-1$ $s_z = 1$	$l_z = m$ $s_z = 0$	$l_z = m+1$ $s_z = -1$
$j = l+1$	$\sqrt{\dfrac{(l+m)(l+m+1)}{(2l+1)(2l+2)}}$	$\sqrt{\dfrac{(l-m+1)(l+m+1)}{(2l+1)(l+1)}}$	$\sqrt{\dfrac{(l-m)(l-m+1}{(2l+1)(2l+2)}}$
$j = l$	$-\sqrt{\dfrac{(l+m)(l-m+1)}{2l(l+1)}}$	$\dfrac{m}{\sqrt{l(l+1)}}$	$\sqrt{\dfrac{(l-m)(l+m+1)}{2l(l+1)}}$
$j = l-1$	$\sqrt{\dfrac{(l-m)(l-m+1)}{2l(2l+1)}}$	$-\sqrt{\dfrac{(l-m)(l+m)}{l(2l+1)}}$	$\sqrt{\dfrac{(l+m+1)(l+m)}{2l(2l+1)}}$

Example 3. $l = 0$ and $s = 1/2$. Now $j = 1/2$. Denoting the states by $|jm\rangle$, we get

$$|1/2\,1/2\rangle = Y_{00}Y_{1/2\,1/2} \ ,$$

$$|1/2\,-1/2\rangle = Y_{00}Y_{1/2\,-1/2} \ .$$

In two-component form (see next paragraph)

$$|1/2\,1/2\rangle = \begin{pmatrix} Y_{00} \\ 0 \end{pmatrix}, \quad |1/2\,-1/2\rangle = \begin{pmatrix} 0 \\ Y_{00} \end{pmatrix} .$$

Example 4. $j_1 = j_2 = s = 1/2$. Now $j = 1, 0$ and from table 1 we get:

$$|11\rangle = Y_{1/2\,1/2}Y_{1/2\,1/2} \ , \quad |10\rangle = \frac{1}{\sqrt{2}}(Y_{1/2\,1/2}Y_{1/2\,-1/2} + Y_{1/2\,-1/2}Y_{1/2\,1/2}), \quad |1-1\rangle = Y_{1/2\,-1/2}Y_{1/2\,-1/2} \ ,$$

$$|00\rangle = \frac{1}{\sqrt{2}}(Y_{1/2\,1/2}Y_{1/2\,-1/2} - Y_{1/2\,-1/2}Y_{1/2\,1/2}) \ .$$

Example 5. $l = 1$ ja $s = 1/2$. Now $j = 3/2, 1/2$. Using Table 1, we get

$$|3/2\,3/2\rangle = Y_{11}Y_{1/2\,1/2} \ ,$$

$$|3/2\,1/2\rangle = \sqrt{\frac{2}{3}}\,Y_{10}Y_{1/2\,1/2} + \frac{1}{\sqrt{3}}Y_{11}Y_{1/2\,-1/2} \ ,$$

$$|3/2\,-1/2\rangle = \frac{1}{\sqrt{3}}Y_{1-1}Y_{1/2\,1/2} + \sqrt{\frac{2}{3}}Y_{10}Y_{1/2\,-1/2} \ ,$$

$$|3/2\,-3/2\rangle = Y_{1-1}Y_{1/2\,-1/2} \ ,$$

$$|1/2\,1/2\rangle = -\frac{1}{\sqrt{3}}Y_{10}Y_{1/2\,1/2} + \sqrt{\frac{2}{3}}\,Y_{11}Y_{1/2\,-1/2} \ ,$$

$$|1/2\,-1/2\rangle = \sqrt{\frac{2}{3}}\,Y_{1-1}Y_{1/2\,1/2} - \frac{1}{\sqrt{3}}Y_{10}Y_{1/2\,-1/2}\ .$$

Next is the same, but we for $l=1$ use spherical functions Y_{1m} and for $s=1/2$ a two component matrix. Now the general form is (spherical spinors)

$$Y_{jm_j} = \begin{pmatrix} \alpha\,Y_{1m_j-1/2} \\ \beta\,Y_{1m_j+1/2} \end{pmatrix},$$

where α and β are Clebsh-Gordan coefficients. We get the representation

$$Y_{3/2\,1/2} = \begin{pmatrix} Y_{11} \\ 0 \end{pmatrix}, \quad Y_{3/2\,1/2} = \begin{pmatrix} \sqrt{\frac{2}{3}}\,Y_{10} \\ \frac{1}{\sqrt{3}}\,Y_{11} \end{pmatrix}, \quad Y_{3/2\,-1/2} = \begin{pmatrix} \frac{1}{\sqrt{3}}\,Y_{1-1} \\ \sqrt{\frac{2}{3}}\,Y_{10} \end{pmatrix}, \quad Y_{3/2\,-3/2} = \begin{pmatrix} 0 \\ Y_{1-1} \end{pmatrix},$$

$$Y_{1/2\,1/2} = \begin{pmatrix} -\frac{1}{\sqrt{3}}\,Y_{10} \\ \sqrt{\frac{2}{3}}\,Y_{11} \end{pmatrix}, \quad Y_{1/2\,-1/2} = \begin{pmatrix} \sqrt{\frac{2}{3}}\,Y_{1-1} \\ -\frac{1}{\sqrt{3}}\,Y_{10} \end{pmatrix}.$$

Example 6. Here we give one useful expression for $Y_{1m}Y_{lm'}$ we need further. Now one must use the inverse transformation of that given in Table 2. Shorthand of these expressions is

$$Y_{10}\,Y_{lm} = \alpha_z Y_{l+1\,m} + \beta_z\,Y_{l-1\,m}\ ,$$

$$Y_{1\mp1}\,Y_{lm} = \alpha_{\mp}Y_{l+1\,m\mp1} + \beta_{\mp}\,Y_{l-1\,m\mp1}\ ,$$

where

$$\alpha_z = \sqrt{\frac{3}{4\pi}}\sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}\,, \qquad \beta_z = \sqrt{\frac{3}{4\pi}}\sqrt{\frac{l^2-m^2}{(2l+1)(2l-1)}}$$

$$\alpha_{\mp} = \sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l\mp m)(l+1\mp m)}{(2l+1)(2l+3)}}\,, \qquad \beta_{\mp} = \sqrt{\frac{3}{8\pi}}\sqrt{\frac{(l\pm m)(l+1\pm m)}{(2l+1)(2l-1)}}\ .$$

18. Elektron spin, Pauli equation

18.1 Elektron spin. In their year 1922 experiment Stern and Gerlach demonstrated that the magnetic moment of electron is quantized and has only two projections

$$+\mu_z \qquad and \qquad -\mu_z\ .$$

The answer was given in year 1925 by Uhlenbeck and Goudsmidt, assuming that electron had intrinsic angular momentum, later called spin. From the general analysis it follows that we have

two projections, if $s = 1/2$, i.e. the intrisic angular momentum has quantum number 1/2 (usually we say, that electron's spin is 1/2).

Thefore we must describe it by two-component matrix

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix},$$

where the components describe two different spin projections.

Next we use the repseentation, given in §16. Spin $s = 1/2$ operators we take in form $\vec{s} = \dfrac{\hbar}{2}\vec{\sigma}$:

$$s_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad s_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad s_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

One of the s_z eigenfunctions is

$$\chi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and has spin projection $\sigma = +1/2$ ($s_z = \dfrac{\hbar}{2}$, but usually we omit the Planck constant and say that the projection is one half (in units of $\hbar$)). Indeed

$$s_z \chi_{1/2} = \frac{\hbar}{2}\chi_{1/2},$$

and

$$\chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

is another s_z eigenfunction and has spin projection $\sigma = -1/2$

$$s_z \chi_{-1/2} = -\frac{\hbar}{2}\chi_{-1/2}.$$

For some normed state χ which is expressed as

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_{1/2} + b\chi_{-1/2}$$

we get that with porobability $|a|^2$ spin projection is $\sigma = +1/2$ and with probability $|b|^2$ spin projection is $\sigma = -1/2$.

Next some useful relations for Pauli matrices:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I , \quad \sigma_x \sigma_y = i\sigma_z , \quad \sigma_y \sigma_z = i\sigma_x , \quad \sigma_z \sigma_x = i\sigma_y ,$$

$$\sigma_x \sigma_y + \sigma_y \sigma_x = 0 , \quad \sigma_z \sigma_y + \sigma_y \sigma_z = 0 , \quad \sigma_x \sigma_z + \sigma_z \sigma_x = 0 .$$

Pauli matrices are Hermitean

$$(\sigma_x)^+ = \sigma_x , \quad (\sigma_y)^+ = \sigma_y , \quad (\sigma_z)^+ = \sigma_z .$$

If we have $\vec{a} \cdot \vec{\sigma}$, where $\vec{a} = (a_x , a_y , a_z)$ is some arbitrary vector, then the 2x2 form of it is

$$\vec{a} \cdot \vec{\sigma} = \begin{pmatrix} a_z & a_x - ia_y \\ a_x + ia_y & -a_z \end{pmatrix} .$$

From the Stern-Gerlach experiment it follows that spin and the corresponding magnetic moment $\vec{\mu}_s$ which is due to spin, are connected, as follows

$$\vec{\mu}_s = -\frac{e}{M} \vec{s} .$$

Comparing it with the relation

$$\vec{\mu} = -\frac{e}{2M} \vec{L}$$

we see, that the coefficients for angular and spin moments are different. It leads to some physical effects (anomalous Zeeman effect, for example).

Electron orbital magnetic moment was equal to Bohr magneton $\mu_B = e\hbar/2M$, spin magnetic moment is expressed as follows

$$\vec{\mu}_s = -\frac{e\hbar}{2M} \vec{\sigma} = -\mu_B \vec{\sigma} .$$

18.2 Pauli equation. Pauli generalized Schrödinger equation to the form which takes into consideration electron spin and its magnetic moment.

Schrödinger equation for an electron in external electromagnetic field, which we obtained previously, was

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi ,$$

where

$$\hat{H}_0 = \frac{1}{2M} (-i\hbar\nabla + e\vec{A})^2 + U$$

(U is the potential energy of mechanical forces and also electrical forces).

That equation do not take into account the intrinsic magnetic moment of electron, which was connected with its spin. The absent term was added by Pauli. He used the fact that in classical electrodynamics every magnetic moment $\vec{\mu}$ has in magnetic field $\vec{B}$ energy

$$\Delta U = -\vec{\mu} \cdot \vec{B} .$$

and used the same expression for spin magnetic moment. He therefore added to Hamiltonian operator the following term

$$\hat{H}' = -\hat{\vec{\mu}}_s \cdot \vec{B} = \frac{e}{M} \vec{s} \cdot \vec{B} = \mu_B \vec{\sigma} \cdot \vec{B} .$$

Since the term, added, is a 2x2 matrix, we must go over to two component wave functions

$$\Psi = \begin{pmatrix} \psi_1(\vec{r},t) \\ \psi_2(\vec{r},t) \end{pmatrix} ,$$

where the upper component $\psi_1(\vec{r},t)$ describes spin projection $\sigma = +1/2$ and the lower component $\psi_2(\vec{r},t)$ spin projection $\sigma = -1/2$.

Pauli equation for two component wave fuction Ψ is written as follows

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi + \mu_B \vec{\sigma} \cdot \vec{B} \Psi .$$

Of course, we have here two equations for two components $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$

$$i\hbar \frac{\partial \psi_1(\vec{r},t)}{\partial t} = \hat{H}_0 \psi_1(\vec{r},t) + \mu_B \left(B_z \psi_1(\vec{r},t) + (B_x - iB_y)\psi_2(\vec{r},t) \right) ,$$

$$i\hbar \frac{\partial \psi_2(\vec{r},t)}{\partial t} = \hat{H}_0 \psi_2(\vec{r},t) + \mu_B \left((B_x + iB_y)\psi_1(\vec{r},t) - B_z \psi_2(\vec{r},t) \right) .$$

In general we try to operate with two component quantities. In order to practice it, we derive the continuity equation. At first, scalar product of Ψ is

$$\Psi^+ \Psi = \begin{pmatrix} \psi_1* & \psi_2* \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \psi_1 * \psi_1 + \psi_2 * \psi_2 .$$

Since it is nonnegative, we treat it as probability density for two component wave function.

Proceeding from Pauli equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi + \mu_B \vec{\sigma} \cdot \vec{B} \Psi ,$$

we derive equation for Ψ^+. It means to take complex conjutates and transposition of matrices. We get

$$-i\hbar\frac{\partial\Psi^+}{\partial t} = \hat{H}_0 * \Psi^+ + \mu_B\Psi^+\vec{\sigma}\cdot\vec{B} \ ,$$

since $(\vec{\sigma})^+ = \vec{\sigma}$ and for matrices $(AB)^+ = B^+A^+$.

Now we multiply tha starting equation from the left to Ψ^+ and subract the second equation which is multiplied from right to Ψ . The result is

$$i\hbar(\Psi^+\frac{\partial\Psi}{\partial t} + \frac{\partial\Psi^+}{\partial t}\Psi) = \Psi^+\hat{H}_0\Psi - (\hat{H}_0 * \Psi^+)\Psi + \mu_B(\Psi^+(\vec{\sigma}\cdot\vec{B})\Psi - \Psi^+(\vec{\sigma}\cdot\vec{B})\Psi) \ ,$$

which is written as

$$i\hbar\frac{\partial}{\partial t}(\Psi^+\Psi) = \Psi^+\hat{H}_0\Psi - (\hat{H}_0 * \Psi^+)\Psi \ .$$

From the latter expression follows the continuity relation

$$\frac{\partial\rho}{\partial t} + div\vec{j} = 0 \ ,$$

where

$$\rho = \Psi^+\Psi = \psi_1 * \psi_1 + \psi_2 * \psi_2$$

and

$$\vec{j} = \frac{i\hbar}{2M}((\nabla\Psi^+)\Psi - \Psi^+(\nabla\Psi)) - \frac{e}{M}\vec{A}\Psi^+\Psi =$$

$$= \frac{i\hbar}{2M}((\nabla\psi_1*)\psi_1 - \psi_1*(\nabla\psi_1) + (\nabla\psi_2*)\psi_2 - \psi_2*(\nabla\psi_2)) - \frac{e}{M}\vec{A}(\psi_1*\psi_1 + \psi_2*\psi_2) \ .$$

Since ψ_1 and ψ_2 depend on each other, it is not easy to solve Pauli equation in the general case. If we treat problems, where atom is in some external electromagnetic field, the problem is simplified, since the extenal field in atoms may be assumed to be homogeneous ($\vec{B} = const$). If we take the z-axis in the direction of magnetic field $\vec{B} = (0, 0, B)$, we for ψ_1 and ψ_2 get independent equations

$$i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t} = \hat{H}_0\psi_1(\vec{r},t) + \mu_B B\psi_1(\vec{r},t) \ ,$$

$$i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t} = \hat{H}_0\psi_2(\vec{r},t) - \mu_B B\psi_2(\vec{r},t)) \ ,$$

or in the two component form

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}_0\Psi + \mu_B B\sigma_z\Psi \ .$$

Example. Atomic electron in external homogeneous magnetic field. Let us treat atomic electron in homogeneous external magnetic field. We choose the following vector potential

$$\vec{A} = \frac{1}{2}(-yB,\, xB,\, 0) \quad .$$

We omit the A^2 term, as small (external fields are not strong compared with fields in atom). Hamilton operator $\hat{H}_1$, where spin is yet not taken into account, is (see 13.4)

$$\hat{H}_1 = -\frac{\hbar^2}{2M}\Delta + U + \frac{eB}{2M}\hat{L}_z \quad .$$

If we add the term with spin magnetic moment

$$\hat{H}_2 = \mu_B \sigma_z B \quad,$$

we must solve the problem

$$\hat{H}\Psi = E\Psi \quad,$$

where $\hat{H} = \hat{H}_1 + \hat{H}_2$. Next we write Hamilton operator $\hat{H}$ as

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad,$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2M}\Delta + U$$

and

$$\hat{H}' = \frac{eB}{2M}\hat{L}_z + \mu_B \sigma_z B \quad .$$

In the absence of magnetic field we assume, that electron's potential energy is central symmetric: $U = U(r)$. Then energy depends on two quantum numbers and states (without spin) depend on three quantum numbers, therefore

$$\hat{H}_0 \psi_{nlm} \equiv (-\frac{\hbar^2}{2M}\Delta + U)\psi_{nlm} = E_{nl}\psi_{nlm} \quad,$$

where

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) \quad .$$

Taking into account spin, we must find solutions for two-component wave function. Upper component ψ_1 describes states with spin projection $\sigma = +1/2$ and lower component ψ_2 states with spin projection $\sigma = -1/2$. We assume that these solutions are also in form

$$\psi_{1nlm}(r,\theta,\varphi) = R_{1nl}(r)Y_{1lm}(\theta,\varphi) \quad,$$

$$\psi_{2nlm}(r,\theta,\varphi) = R_{2nl}(r)Y_{2lm}(\theta,\varphi) \quad .$$

Since $\hat{L}_z \varphi_{1,2} = \hbar m \varphi_{1,2}$, we for $\sigma = +1/2$ have

$$\hat{H}' = \mu_B B(m+1)$$

and for $\sigma = -1/2$

$$\hat{H}' = \mu_B B(m-1) \ .$$

Therefore in the case of ψ_1

$$\hat{H}\psi_1 = (\hat{H}_0 + \mu_B B(m+1))\psi_1 = E\psi_1$$

and since $\hat{H}_0\psi_1 = E_{nl}\psi_1$, we get that

$$E = E_{nl} + \mu_B B(m+1), \qquad m = +l, l-1, \dots, 0, \dots, -l \ .$$

Analogically in the case of ψ_2 we get

$$(\hat{H}_0 + \mu_B B(m-1))\psi_2 = E\psi_2 \ ,$$

and

$$E = E_{nl} + \mu_B B(m-1), \qquad m = +l, l-1, \dots, 0, \dots, -l \ .$$

For both projections there are $2l+1$ close lying energy levels with energy difference $\mu_B B$, for $\sigma = +1/2$ the levels are shifted one $\mu_B B$ up, for $\sigma = -1/2$ similarly one $\mu_B B$ down. Since $\mu_B \approx 10^{-23} \ J/T$, then for $B = 1 \ T$ we have $\mu_B B \approx 10^{-4} \ eV$. It means that energy shift is quite small.

Next figures illustrate the splitting of 2s and 2p levels in external magnetic field.
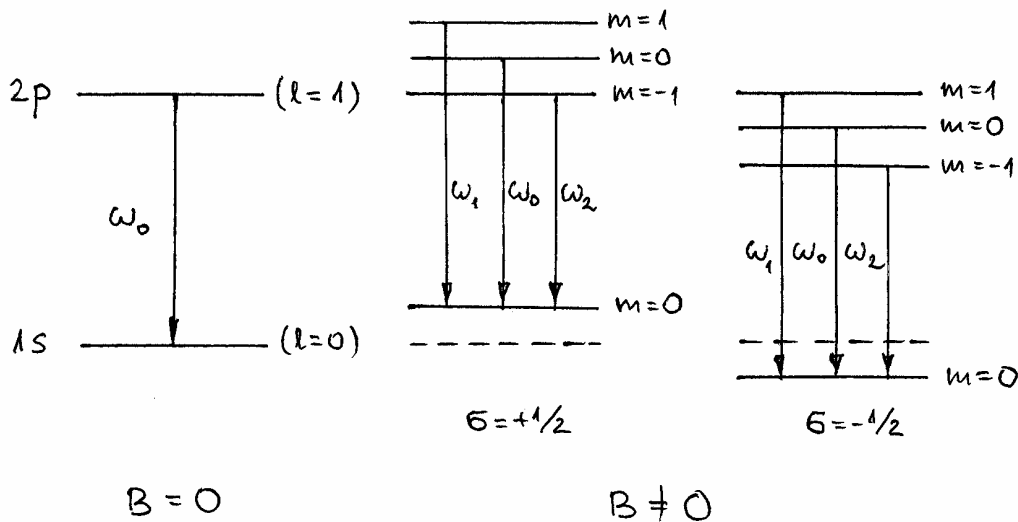
More throughly we analyse the results, obtained here, in §24. As we see, we get three close lying spectral lines (transitions between $\sigma = +1/2$ and $\sigma = -1/2$ are forbidden).

19. Time independent perturbation theory

There are not much problems which have general analytical solutions. But there are different possibilities to solve them using different approximation methods. Here we start with problems where there are some small perturbations acting in addition to usual forces.

We treat the following problem. We assume that we have solved the eigenvalue problem

$$\hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0$$

(we know energies E_n^0 and corresponding eigenfunctions ψ_n^0, also we assume here that for each E_n^0 there is only one eigenfunction ψ_n^0). We have to solve the next eigenvalue problem

$$\hat{H}\psi_n = E_n \psi_n$$

where

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

and the additional term $\hat{H}'$ may be treated as a small perturbation (in each case the smallness of perturbation must be separately verified). In general, we assume that the additional energy due to the perturbation, is very small compared to energies E_n^0 and energy differences between levels.

19.1 Problem set up. In order to follow our step by step solving method more easily, we write the energy operator in form

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

where λ is some helping parameter, which is useful to to compare the terms of the same order of value. After solving the problems we at the end take $\lambda = 1$.

We write down the following series expansion

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \ ,$$

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \ .$$

After substitution to the original eigenvalue problem

$$(\hat{H}_0 + \lambda \hat{H}')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots)$$

and equating the the terms with the same powers of λ, we get

$$\lambda^0 : \qquad \hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0 \ ,$$

$$\lambda : \qquad \hat{H}_0 \psi_n^1 + \hat{H}' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \ ,$$

$$\lambda^2 : \quad \hat{H}_0 \psi_n^2 + \hat{H}' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \ ,$$

and so on.

The first of equations is satisfied, since we assumed that the starting eigenvalue problem has been solved.

19.2 First order approximation. The next, i.e. the first order approximation we find from

$$\hat{H}_0 \psi_n^1 + \hat{H}' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \quad or \quad (\hat{H}_0 - E_n^0) \psi_n^1 = (E_n^1 - \hat{H}') \psi_n^0 .$$

From here we find the first approximation to energy and wave function. The first order to wave function we express as a serie

$$\psi_n^1 = \sum_m a_m^1 \psi_m^0$$

(ψ_n^0 is a complete ON system of functions).

After substitutings and using the fact that ψ_n^0 are the eigenfunctions of $\hat{H}_0$, we get

$$\sum_m a_m^1 (E_m^0 - E_n^0) \psi_m^0 = (E_n^1 - \hat{H}') \psi_n^0 .$$

Multiplying from left to the ψ_k^0 conjugated and integrating, we obtain

$$a_k^1 (E_k^0 - E_n^0) = E_n^1 \delta_{kn} - H'_{kn} ,$$

where

$$H'_{kn} = \int (\psi_k^0)^* \hat{H}' \psi_n^0 dV$$

are the matrix elements of perturbation operator.

Taking $k = n$, we obtain the first order correction to energy

$$E_n^1 = H'_{nn} ,$$

(these are the diagonal elements of perturbation operator).

If $k \neq n$, we obtain the coefficients to the first approximation of wave function

$$a_k^1 = \frac{H'_{kn}}{E_n^0 - E_k^0} .$$

As we see, one of the coefficients - a_n^1 - remains undetermined. It is determined from the normalization of the first order wave function

$$\int (\psi_n^0 + \lambda \sum_m a_m^1 \psi_m^0)^* (\psi_n^0 + \lambda \sum_m a_m^1 \psi_m^0) dV = 1 .$$

In the first order approximation of λ coefficient a_n^1 must satisfy

$$a_n^1 + (a_n^1)^* = 0 .$$

As we see, it is imaginary and for simplicity we may take it equal to zero, therefore we shall take $a_n^1 = 0$.

In conclusion, the first order approximation ($\lambda = 1$) is

$$E_n = E_n^0 + H'_{nn} ,$$

$$\psi_n = \psi_n^0 + \sum_{k \neq n} \frac{H'_{kn}}{E_n^0 - E_k^0} \psi_k^0 .$$

19.3 Second order approximation. Let's calculate the second order energy correction. It is needed mostly in that case when the first order approximation is equal to zero.

For the second order approximation we use the equation

$$\hat{H}_0 \psi_n^2 + \hat{H}' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 .$$

We repsesent ψ_n^2 as a power serie

$$\psi_n^2 = \sum_m a_m^2 \psi_m^0$$

and substitute it together with the first order approximation to the above given equation. We get

$$\sum_m E_m^0 a_m^2 \psi_m^0 + \hat{H}' \sum_{k \neq n} \frac{H'_{kn}}{E_n^0 - E_k^0} \psi_k^0 = E_n^0 \sum_m a_m^2 \psi_m^0 + H'_{nn} \sum_{k \neq n} \frac{H'_{kn}}{E_n^0 - E_k^0} \psi_k^0 + E_n^2 \psi_n^0$$

Multiplying from the left with the ψ_r^0 conjugated and integrating, we have

$$E_r^0 a_r^2 + \sum_{k \neq n} \frac{H'_{rk} H'_{kn}}{E_n^0 - E_k^0} = E_n^0 a_r^2 + H'_{nn} \sum_{k \neq n} \frac{H'_{kn}}{E_n^0 - E_k^0} \delta_{rk} + E_n^2 \delta_{rn} .$$

Taking $r = n$, we get the second order energy approximation

$$E_n^2 = \sum_{k \neq n} \frac{H'_{nk} H'_{kn}}{E_n^0 - E_k^0} \equiv \sum_{k \neq n} \frac{|H'_{nk}|^2}{E_n^0 - E_k^0} .$$

Taking $r \neq n$, we get the second order coefficients for wave function

$$a_r^2 = \sum_{k \neq n} \frac{H'_{rk} H'_{kn}}{(E_n^0 - E_k^0)(E_n^0 - E_r^0)} - \frac{H'_{rn} H'_{nn}}{(E_n^0 - E_r^0)^2} .$$

Analogically to the first order approximation a_n^2 remains to be underdetermined and its is determined from the normalization condition

$$\int (\psi_n^0 + \lambda \sum_{k \neq n} a_k^1 \psi_k^0 + \lambda^2 \sum_k a_k^2 \psi_k^0) * (\psi_n^0 + \lambda \sum_{k \neq n} a_k^1 \psi_k^0 + \lambda^2 \sum_k a_k^2 \psi_k^0) dV = 1 ,$$

whic for the second order terms gives

$$\sum_{k \neq n} \left| a_k^1 \right|^2 + ((a_n^2)^* + a_n^2) = 0 \ .$$

If we take a_n^2 to be real, we have

$$a_n^2 = -\frac{1}{2} \sum_{k \neq n} \left| a_k^1 \right|^2 = -\frac{1}{2} \sum_{k \neq n} \frac{\left| H'_{nk} \right|^2}{(E_n^0 - E_k^0)^2} \ .$$

Example 1. Oscillator in constant force field. Assume that in addition to elastic force there acts some constant force F. Its potential energy is

$$U = -F x \ .$$

Then the following perturbation operator is added

$$\hat{H}' = -F x \ .$$

Next we treat it as a small perturbation (assuming that F is small).

To find corrections to energy, one must calculate the matrix elements

$$H'_{nm} = -F \int_{-\infty}^{+\infty} \psi_n(x) \, x \, \psi_m(x) \, dx \equiv -F \, x_{nm} \ .$$

From the previous paragraphs we know, that we have nonzero elements, iff $m = n \pm 1$. The exact form of these elements is

$$x_{n,n+1} = \sqrt{\frac{\hbar}{2M\omega}} \sqrt{n+1} \quad , \qquad x_{n,n-1} = \sqrt{\frac{\hbar}{2M\omega}} \sqrt{n} \ .$$

Here we see that the first order energy coreection is equal to zero

$$E_n^1 = H'_{nn} = 0 \ .$$

Therefore we must examine the next approximation

$$E_n^2 = \sum_{k \neq n} \frac{\left| H'_{nk} \right|^2}{E_n^0 - E_k^0} = \frac{\left| H'_{n\,n+1} \right|^2}{E_n^0 - E_{n+1}^0} + \frac{\left| H'_{n\,n-1} \right|^2}{E_n^0 - E_{n-1}^0} =$$

$$= \frac{F^2}{\hbar\omega} \left(-\left| x_{n,n+1} \right|^2 + \left| x_{n,n-1} \right|^2 \right) = -\frac{F^2}{2M\omega^2} \ .$$

Here we have used $E_n^0 = \hbar\omega(n + 1/2)$ and the above given matrix elements. As a result we see, that the energy of all energy levels decreases to the same amount.

Our example was trivial, since the problem can be solved exactly, transforming the general expression of the total energy

$$H = \frac{p^2}{2M} + \frac{M\omega^2 x^2}{2} - Fx \equiv \frac{p^2}{2M} + \frac{M\omega^2}{2}(x - \frac{F}{M\omega^2})^2 - \frac{F^2}{2M\omega^2} \ .$$

It means that in the case of additional constant force the equilibrium point of oscillator is shifted and also the equilibrium point of energy is shifted.

Example 2. Anharmonic oscillator. Assume that the following perturbation

$$\hat{H}' = \alpha x^3 + \beta x^4$$

is added, where α and β are some small coefficients. We call it anharmonic oscillator, since the total potential energy is not parabolic.

These anharmonic terms simply follow from the next physical considerations. Let us take some arbitrary potential energy which is in zero point minimal. In small deviations from the equilibrium we may it expand as
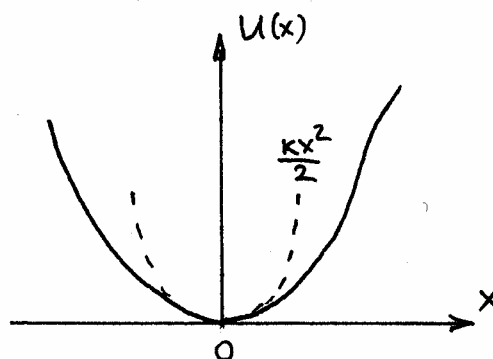
$$U(x) = U_0 + \frac{dU}{dx}x + \frac{1}{2!}\frac{d^2U}{dx^2}x^2 + \frac{1}{3!}\frac{d^3U}{dx^3}x^3 + \frac{1}{4!}\frac{d^4U}{dx^4}x^4 + \dots \ .$$

Since $U_0 = 0$ and in the minimum point also $dU/dx = 0$ and $d^2U/dx^2 = k > 0$ we have

$$U(x) = \frac{kx^2}{2} + \alpha x^3 + \beta x^4 + \dots \ ,$$

where in higher powers the coefficients are denoted by α and β.

At very small deviations from the rest we may it approximate with parabolic potential energy, but if the deviations increase we must take into account also the next terms.

We start from the cubic term. Since

$$(x^3)_{nn} = \int_{-\infty}^{+\infty} x^3 \psi_n^2 \, dx = 0$$

we must use the following, second order approximation

$$E''_n = \frac{\alpha^2}{\hbar\omega} \sum_{n'} \frac{(x^3)_{nn'}(x^3)_{n'n}}{(n - n')} \ .$$

Using the x^3 matrix elements, given in §15, we after some simple calculations have

$$E''_n = -\frac{15\hbar^2\alpha^2}{4M^3\omega^4}(n^2 + n + \frac{11}{30}) \ .$$

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For the next, x^4 -term the matrix elements are nonzero: $(x^4)_{nn} \neq 0$. Its matrix elements are calculated, using the matrix elements of x^2, as

$$(x^4)_{nn} = \sum (x^2)_{nn'}(x^2)_{n'n} = ((x^2)_{nn-2})^2 + ((x^2)_{nn})^2 + ((x^2)_{nn+2})^2$$

and gives that the corresponding energy approximation is

$$E'_n = \frac{3\hbar^2 \beta}{2M^2\omega^2}(n^2 + n + \frac{1}{2})^2 .$$

Since it is also proportional to the Planck constant square, the both approximations are usually of the same order and must be treated together.

The final result is

$$E_n = \hbar\omega(n + \frac{1}{2}) + E''_n + E'_n =$$

$$= \hbar\omega(n + \frac{1}{2}) - \frac{15\hbar^2 \alpha^2}{4M^3\omega^4}(n^2 + n + \frac{11}{30}) + \frac{3\hbar^2 \beta}{2M^2\omega^2}(n^2 + n + \frac{1}{2})^2 .$$

The exact resut, of course, depends on α and β, and on their signs.

20. Time independent perturbation theory(degenerate case)

Next we consider the case, where to the energy level E_n^0 there corresponds several independent states

$$\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr} .$$

(In H-aatom, for example to E_n corresponds n^2 different states.)

Now we have

$$\hat{H}_0 \psi_{ni} = E_n^0 \psi_{ni} , \qquad i = 1, 2, \ldots, r ,$$

but also an arbitrary linear combination

$$\psi_n^0 = \sum_{i=1}^{r} c_i \psi_{ni}$$

satisfies the same eigenvalue problem

$$\hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0 .$$

20.1 Problem set up. Let us take a new problem where to the pevious Hamiltonian operator there is some small perturbation operator $\hat{H}'$ added. The total energy operator is

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

and we are interested in problem

$$\hat{H}\psi = E\psi \ .$$

In general the degeneracy of states are connected with some symmetries (central symmetry or others). Usually the perturbation has no such symmetry and for that reason the symmetry is breaked and it leads to the splitting of energy levels E_n^0 and we get some set of closely laying energy levels $E_n^0 + \Delta E_n$.

Next we analyse of how the energies E_n^0 are splitted. We restrict ourselves to the first order approximation, which was given in the previous paragraph

$$(\hat{H}_0 - E_n^0)\psi_n^1 = (E_n^1 - \hat{H}')\psi_n^0 \ .$$

where ψ_n^1 and E_n^1 are the first order improvements to the wave equation and energy eigenvalues. Since we operate in the subspace, corresponding to E_n^0, we take zeroth order wave function ψ_n^0 as an arbitrary linear combination of functions $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$. Therefore we analyse the equation

$$(\hat{H}_0 - E_n^0)\psi_n^1 = \sum_{j=1}^{r} c_j(E_n^1 - \hat{H}')\psi_{nj} \ .$$

Multiplying from left to $\psi_{ni}{}^*$, we integrate and use $\int \psi_{ni}{}^* \psi_{nj}\, dV = \delta_{ij}$.

At first we demonstrate that the left side of the previous equality is equal to zero, i.e.

$$\int \psi_{ni}{}^* (\hat{H}_0 - E_n^0)\psi_n^1\, dV = 0 \ .$$

If follows from the fact that $\hat{H}_0$ is Hermitean

$$\int \psi_{ni}{}^* (\hat{H}_0 - E_n^0)\psi_n^1\, dV = \int ((\hat{H}_0 - E_n^0)\psi_{ni})^* \psi_n^1\, dV = 0 \ .$$

For that reason the integral from the right side is also equal to zero

$$\sum_{j=1}^{r} c_j \int \psi_{ni}{}^* (E_n^1 - \hat{H}')\psi_{nj}\, dV = 0 \ .$$

Introducing matrix elements

$$H'_{ij} = \int \psi_{ni}{}^* \hat{H}' \psi_{nj}\, dV$$

(matrix elements in the subspace of functions $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$) and taking into account the orthonormality of $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$, we get he following equations

$$\sum_{j=1}^{r} (E_n^1 \delta_{ij} - H'_{ij}) c_j = 0 , \qquad i = 1, 2, \ldots, r \ .$$

It is the linear homogeneous system for coefficients c_j, which is written in the matrix form as

$$
\begin{pmatrix}
E_n^1 - H'_{11} & -H'_{12} & \cdots & -H'_{1r} \\
-H'_{21} & E_n^1 - H'_{22} & \cdots & -H'_{2r} \\
\vdots & \vdots & \ddots & \vdots \\
-H'_{r1} & -H'_{r2} & \cdots & E_n^1 - H'_{rr}
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
\vdots \\
c_r
\end{pmatrix} = 0 \ .
$$

20.2 Approximations to energy. There are nontrivial solutions, if the determinant of the system is equal to zero. Denoting $\varepsilon = E_n^1$, we have

$$
\begin{vmatrix}
\varepsilon - H'_{11} & -H'_{12} & \cdots & -H'_{1r} \\
-H'_{21} & \varepsilon - H'_{22} & \cdots & -H'_{2r} \\
\vdots & \vdots & \ddots & \vdots \\
-H'_{r1} & -H'_{r2} & \cdots & \varepsilon - H'_{rr}
\end{vmatrix} = 0 \ .
$$

From it we have some r-th order equation for ε

$$
\varepsilon^r + \alpha_1 \varepsilon^{r-1} + \ldots + \alpha_r = 0 \ ,
$$

which has r real valued solutions (roots)

$$
\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_r
$$

(there are in general also coincident ones). Therefore, all nonzero solutions ε_i give us new energy levels

$$
E_n^i = E_n^0 + \varepsilon_i \ .
$$

For each ε_i one can solve the system and find the corresponding $c_1^i, c_2^i, \ldots, c_r^i$, which in turn gives the wave function

$$
\psi_n^i = \sum_{j=1}^{r} c_j^i \psi_{nj} \ .
$$

That is the first approximation which must be further used to calculate ψ_n^1 and E_n^2, if needed.

Example 1. Double degeneration. Assume that for E_n^0 we have two states ψ_{n1}, ψ_{n2}. Then

$$
\psi_n^0 = c_1 \psi_{n1} + c_2 \psi_{n2} \ .
$$

One must calculate the determinant

$$
\begin{vmatrix}
\varepsilon - H'_{11} & -H'_{12} \\
-H'_{21} & \varepsilon - H'_{22}
\end{vmatrix} = 0
$$

and solve the equation $(\varepsilon - H'_{11})(\varepsilon - H'_{22}) - H'_{12} H'_{21} = 0$, or

$$\varepsilon^2 - \varepsilon\,(H'_{11} + H'_{22}) + H'_{11}\,H'_{22} - H'_{12}\,H'_{21} = 0 \,.$$

We got the quadratic equation $\varepsilon^2 - b\,\varepsilon + c = 0$, which has two real number solutions.

Example 2. Stark effect: splitting of spectral lines in external electric field.

As an example we treat the two lowest energy levels of the H-aatom ($n = 1$ and $n = 2$) in external electric field and demonstrate that there are no splitting for $n = 1$, but $n = 2$ level splits to three levels.

Assume that in addition to Coulomb force on electron acts small external homogeneous electrical force, caused by the electrical field $\vec{E} = (0, 0, E)$ directed along the z-axis. Electrical potential is expressed as

$$\phi(z) = -z\,E \,,$$

therefore the additional potential energy is $\Delta U = e\,E\,z$. It means that the following perturbation

$$\hat{H}' = e\,E\,z$$

is added. That perturbation is indeed small: if we take $z = r_0$ (Bohr's radius) and for macroscopic field stregth quite large value $E = 10^6 \ V/m$, we get $\Delta U \approx 10^{-5} \ eV$, Coulomb energy due to the nuclear charge is at the same distance approximately 18 eV.

We consider the splitting of energy levels for $n = 2$. It has energy

$$E_2^0 = -\frac{R\hbar}{4} \,.$$

$2s$ and $2p$ give us four total states. We denote them

$$\psi_1 = \psi_{200} \,, \quad \psi_2 = \psi_{210} \,, \quad \psi_3 = \psi_{211} \,, \quad \psi_4 = \psi_{21-1} \,.$$

Next we must calculate the matrix elements of perturbation Hamiltonian, which in our case are the following integrals

$$H'_{ij} = e\,E \int \psi_i^* \, z\,\psi_j \, dV = e\,E\,z_{ij} \,.$$

As we see, we must calculate the matrix elements of z-coordinate. In §22 (selection rules) we calculate the matrix elements of x, y and z separately, therefore we here use the rules which we shall derive in §22, that for z-coordinate the only nonzero matrix elements are those, for which $\Delta m = 0$ and $\Delta l = \pm 1$. In our case it means that the only nonzero matrix elements are

$$z_{12} \quad and \quad z_{21} = z_{12}^* \,.$$

Next, using the explicit expressions of wave fuctions, we calculate z_{12}. The corresponding wave functions are

$$\psi_1(r,\theta,\varphi) \equiv \psi_{200}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi r_0^3}}\left(2 - \frac{r}{r_0}\right)e^{-\frac{r}{2r_0}} \,,$$

$$\psi_2(r,\theta,\varphi) \equiv \psi_{210}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi r_0^3}}\frac{r}{r_0}e^{-\frac{r}{2r_0}}\cos\theta \ .$$

Since $dV = r^2 dr \sin\theta\, d\theta\, d\varphi$ and $z = r\cos\theta$, we have to calculate three integrals

$$z_{12} = \frac{1}{32\pi r_0^3}\int_0^\infty (2-\frac{r}{r_0})\frac{r^4}{r_0}e^{-\frac{r}{r_0}}dr \cdot \int_0^\pi \cos^2\theta \sin\theta\, d\theta \cdot \int_0^{2\pi} d\varphi \ .$$

Integral over φ gives 2π, over θ gives 2/3 (using the substitution $u = \cos\theta$). The remaining integral is

$$z_{12} = \frac{1}{24}\int_0^\infty (2-\frac{r}{r_0})(\frac{r}{r_0})^4 e^{-\frac{r}{r_0}}dr \ .$$

Next we substitute $x = r/r_0$ and use integrals

$$\int_0^\infty x^n e^{-x}dx = \Gamma(n+1) = n! \ ,$$

which give us

$$\int_0^\infty (2-\frac{r}{r_0})(\frac{r}{r_0})^4 e^{-\frac{r}{r_0}}dr = r_0\int_0^\infty (2-x)x^4 e^{-x}dx = -72\,r_0 \ .$$

The final result is

$$z_{12} = z_{21} = -3\,r_0 \ .$$

Nonzero matrix elements of perturbation Hamiltonian therefore are

$$H'_{12} = H'_{21} = -3\,e\,r_0\,\mathrm{E} \ .$$

In order to find energy corrections $\varepsilon = E_2^1$ we must calculate the following 4x4 determinant and equal it to zero

$$\begin{vmatrix} \varepsilon & -H'_{12} & 0 & 0 \\ -H'_{12} & \varepsilon & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \varepsilon \end{vmatrix} = 0 \ .$$
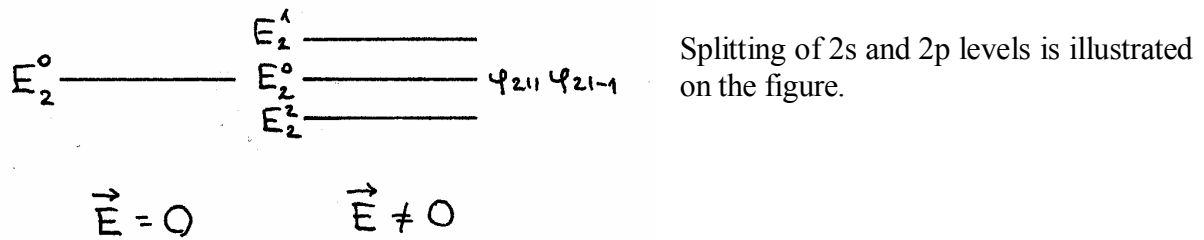
Simple calculation gives

$$\varepsilon^2(\varepsilon^2 - H'^2_{12}) = 0 \ .$$

We have two solutions $\varepsilon = 0$, which mean that the energies of states $\psi_3 = \psi_{211}$ and $\psi_4 = \psi_{21-1}$ do not change. The remaining two solutions

$$\varepsilon_{1,2} = \pm\sqrt{H'^2_{12}} = \pm 3\,e\,r_0\,\mathrm{E}$$

mean that in the subspace of states $\psi_1 = \psi_{200}$ and $\psi_2 = \psi_{210}$ energy levels split and the energies are

$$E_2^1 = -\frac{R\hbar}{4} + 3er_0\,\mathrm{E}\;, \quad E_2^2 = -\frac{R\hbar}{4} - 3er_0\,\mathrm{E}\;.$$

Splitting of 2s and 2p levels is illustrated on the figure.

Next we find the corresponding wave functions. For that we must solve the equation

$$\begin{pmatrix} \varepsilon & 3er_0\mathrm{E} & 0 & 0 \\ 3er_0\mathrm{E} & \varepsilon & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

which reduses to

$$\varepsilon\,c_1 + 3er_0\mathrm{E}\,c_2 = 0\;,$$

$$3er_0\mathrm{E}\,c_1 + \varepsilon\,c_2 = 0\;,$$

$$\varepsilon\,c_3 = 0\;,$$

$$\varepsilon\,c_4 = 0\;.$$

We see that for $\varepsilon = 0$ we may take the same functions $\psi_3 = \psi_{211}$ and $\psi_4 = \psi_{21-1}$. For $\varepsilon_{1,2} = \pm 3er_0\,\mathrm{E}$ we correspondingly get

$$\psi' = \psi_{200} - \psi_{210} \quad \text{ja} \quad \psi'' = \psi_{200} + \psi_{210}$$

(unnormed). These functions must be used for the next approximations.

Ground state $n = 1$. Its energy does not change, because due to the previous conditions ($\Delta m = 0$ and $\Delta l = \pm 1$) the matrix element z_{11} is equal to zero

$$z_{11} = \int z\psi_{100}^2\,dV = 0$$

(it is odd function of z).

Next we give the energy levels before and after splitting. Instead of one 2p $\rightarrow$ 1s spectral line we in electrical field have three spectral lines.
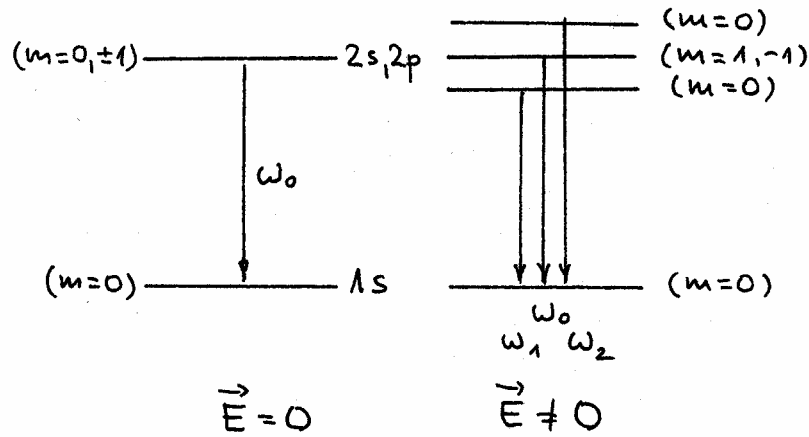
Example 3. Elementary Zeeman effect (zero spin electron). Suppose we had an atom and its states are found from

$$\hat{H}_0 \psi^0_{nlm} = E^0_{nl} \psi^0_{nlm} \; .$$

For each energy E^0_{nl} there are on $2l+1$ states ψ^0_{nlm} (degenerate by m).

In homogeneous magnetic field directed along the z-axis the following perturbation operator (see §13)

$$\hat{H}' = \frac{eB}{2M} \hat{L}_z$$

must be added. Supposing that the perturbation is small we next find the corrections to energy level E^0_{nl}. At first, one must find the matrix elements $H'_{m'm}$. It is easy to verify that the only nonzero matrix elements are diagonal, i.e. if $m' = m$. Indeed

$$H'_{m'm} = \frac{eB}{2M}\int \psi_{nlm'}{}^{*} \hat{L}_z \psi_{nlm}\, dV = \frac{e\hbar B m}{2M}\int \psi_{nlm'}{}^{*} \psi_{nlm}\, dV = \frac{e\hbar B}{2M} m\, \delta_{m'm} \; .$$

Energy corrections are calculated from

$$\begin{vmatrix} \varepsilon - H'_{11} & 0 & \cdots & 0 \\ 0 & \varepsilon - H'_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \varepsilon - H'_{rr} \end{vmatrix} = 0 \; ,$$

which reduces to

$$(\varepsilon - H'_{11})(\varepsilon - H'_{22}) \cdot \ldots \cdot (\varepsilon - H'_{rr}) = 0$$

We see that first order energy corrections (as in the nondegenerate case) are given in the following way

$$\varepsilon_m = H'_{mm} = \frac{e\hbar B}{2M} m = \mu_B B m , \qquad m = l, l-1, \ldots, -l \; .$$

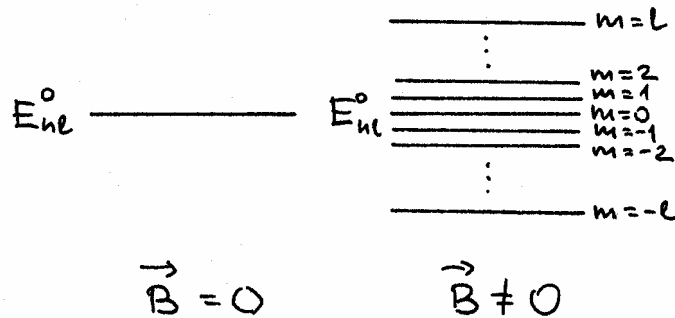The eigenfunctions remain the same, since from

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$$(\varepsilon - H'_{mm})c_m = 0$$

it follows, that for each $\varepsilon = \varepsilon_m$ we have $c_m \neq 0$, the others c_n are zero.
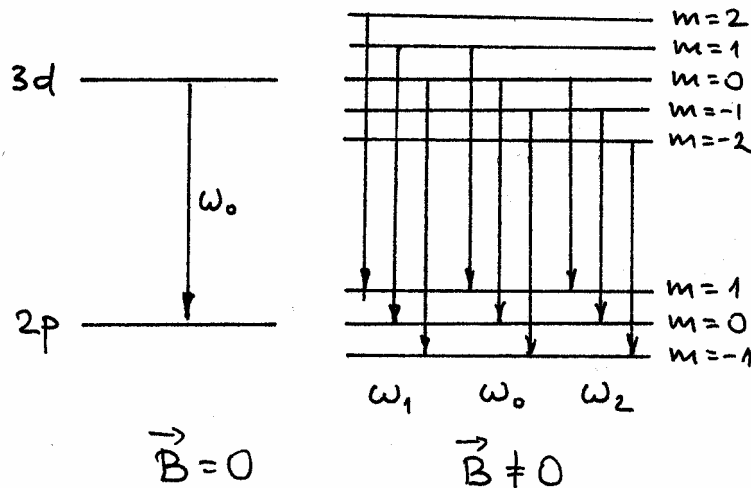
The result is that each energy level E^0_{nl} splits in magnetic field to $2l+1$ levels having energies

$$E_{nlm} = E^0_{nl} + \mu_B B m .$$

Difference between the neighboring levels $\Delta E = \mu_B B$ is in all cases the same.

It is interesting to note that due to the selection rules $\Delta l = \pm 1$, $\Delta m = 0$, ± 1 (see §22) we instead of one spectral line get always three spectral lines (normal Zeeman effect). Example: transition $3d \rightarrow 2p$.

In conclusion we estimate the magnitude of energy splitting. Since $\Delta E = \mu_B B$ the distance between levels is small in not very small magntic fields. If, for example, $B = 1$ T ,we get $\Delta E = 9{,}3 \cdot 10^{-24}$ J $\approx 6 \cdot 10^{-5}$ eV, which is in most cases smaller than the distance between $E_{n+1l} - E_{nl}$.

More detailly we analyse Zeeman effect in §24. Here we neglected the electron intrisic magnetic moment which exists due to its spin.