19. Time independent perturbation theory

There are not much problems which have general analytical solutions. There 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.

Here 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 energy E_n^0 and corresponding eigenfunctions ψ_n^0, also we assume 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 analysed). 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 setup. In order to follow our step by step solving method more easily, we write the energy operator in form

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

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

We write down the following series expansion

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

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

After substitution to the original eigenvalue problem

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

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

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

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

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

and so on

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

19.2 First order approximation. The next, i.e. the first order approximation is possible to 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 series

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

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

After substitutions 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 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 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

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

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 (*λ* = 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 represent ψ_n^2 as a power series

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

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

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

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

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

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

$$U=-F\ x \quad .$$

It is added to energy operator which we write as

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

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

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

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

From the previous paragraphs we know, that we have nonzero elements, if $m=n\pm1$. Therefore the nonzero matrix elements are

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

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

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

Therefore we must examine the next approximation

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

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

Here we have used that $E_n^0=\hbar\omega(n+1/2)$ 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

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

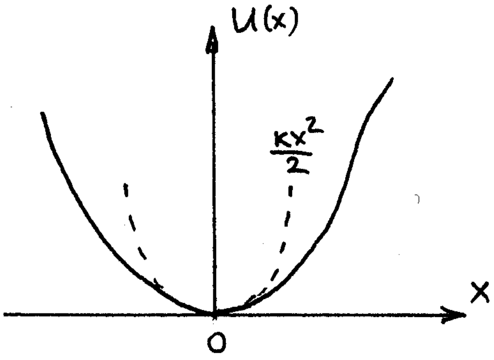
It means that in the case of additional constant force the equilibrium point of oscillator is shifted and also the equilibrium point of energy is shifted.

Example 2. Anharmonic oscillator. Assume that the following perturbation

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

is added to the harmonic oscillator, where α and β are some small coefficients. We call it anharmonic oscillator, since the 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



$$U(x) = U_0 + \frac{dU}{dx}x + \frac{1}{2!}\frac{d^2U}{dx^2}x^2 + \frac{1}{3!}\frac{d^3U}{dx^3}x^3 + \frac{1}{4!}\frac{d^4U}{dx^4}x^4 + \ldots \ .$$

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

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

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

Atvery small deviations 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

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

For the next term we have $(x^4)_{nn} \neq 0$. Its matrix elements are calculated 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 of the same order and must be treated together.

The final result is

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

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

It 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 initial system energy level E_n^0 there corresponds several independent states

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

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

Now we have

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

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 added some samaal perturbation operator $\hat{H}'$. 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 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 orde 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. 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 then 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 in general also coincident ones). Therefore, all nonzero solutions ε_i give us new energy level

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

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 zero 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) 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 $\mathrm{E} = (0, 0, \mathrm{E})$ directed along the z-axis. Electrical potential is expressed as

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

therefore the additional potential energy is $\Delta U = e\mathrm{E}z$. 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 mackroscopic field stregth quite large value $\mathrm{E} = 10^6\ V/m$, 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

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

2*s* and 2*p* 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

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

As we see, we must calculate the matrix elements from z-coordinate. In §22 (treating the selection rules) we calculate the matrix elements of x, y and z separately, therefore we here use the rules which we obteined 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

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

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

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 by φ gives 2π, by 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 gives 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

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

Nonzero matrix elements of perturbation Hamiltonian therefore are

$$H'_{12} = H'_{21} = -3er_0\,\mathrm{E} \ .$$

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

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

Somple calculation gives

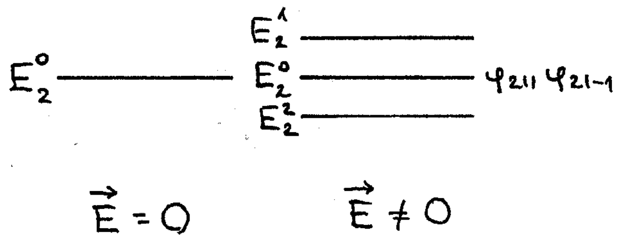
$$\varepsilon^2(\varepsilon^2 - H'^2_{12}) = 0 \ .$$

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

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

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 $\psi_4 = \psi_{21\text{-}1}$. For $\varepsilon_{1,2} = \pm 3 e\, r_0\, \mathrm{E}$ we correspondingly get

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

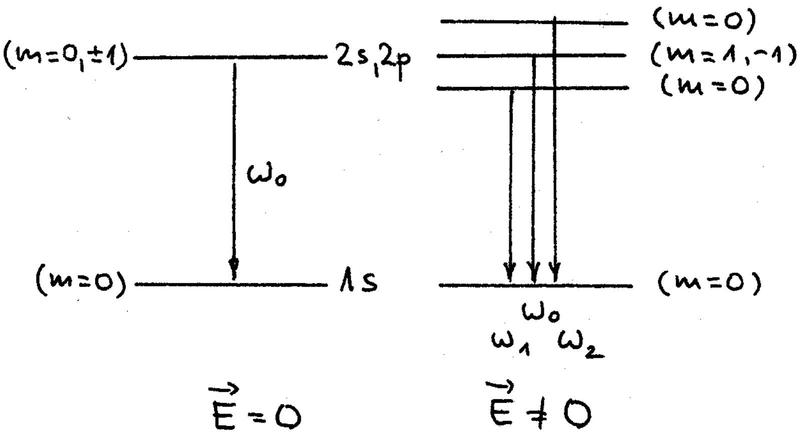
(unnormed). These functions must be used for the next approximation.

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

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

(there is odd function by z).

Next are given the energy levels befor and after splitting. Instead of one 2p → 1s spectral line we in electrical field have spectral lines.



Example 3. Elementary Zeeman effect (zero spin electron). Suppose we had an atom and its states are found from

$$\hat{H}_0 \psi_{nlm}^0 = E_{nl}^0 \psi_{nlm}^0 \ .$$

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

In homogeneous magnetix 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

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

The 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

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

The eigenfunctions remain the same, since from

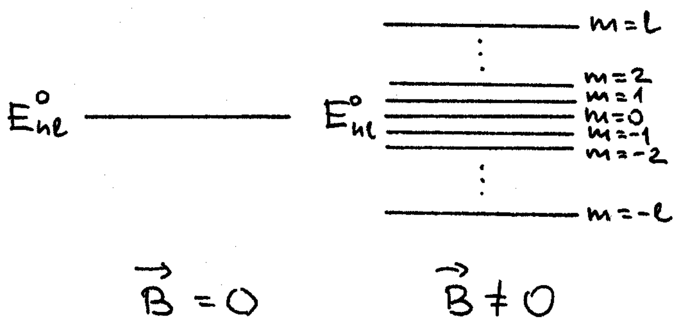
$$(\varepsilon - H'_{mm})c_m = 0$$

that for each $\varepsilon = \varepsilon_m$ we have $c_m \neq 0$, the others are zero.

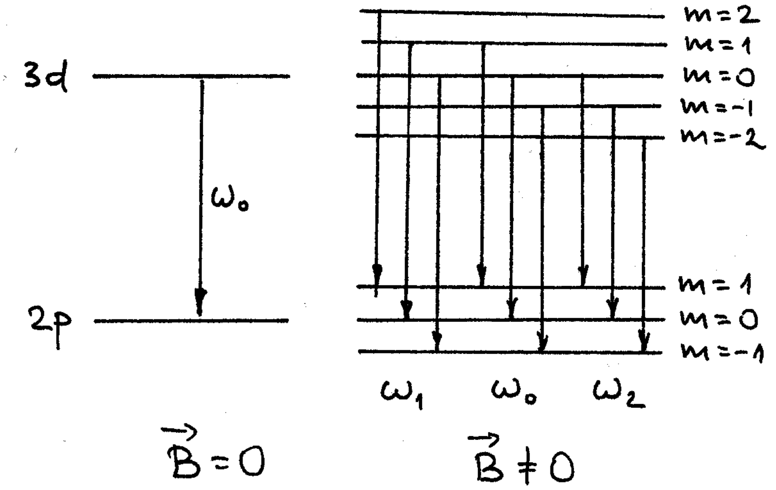
The result is that each energy level E^0_{nl} splits in magnetic field to 2*l*+1 levels having energies

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

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 → 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 due to its spin.

21. Time dependent perturbation theory

Next we start to analyse the perturbations when the perturbation operator depends explicitly from time

$$\hat{H}' = \hat{H}'(t) \ .$$

The total Hamilton operator

$$\hat{H} = \hat{H}_0 + \hat{H}(t)$$

depends on time and it means that the total energy of a given system is not conserved (see § 26). For that reason there are no energy level changes or splittings, but there appear transitions between different energy levels (radiation or absorption).

21.1 General solution of Schrödinger equation without perturbation. At first we analyse the solutions without perturbation. If we have eigenvalue problem for $\hat{H}_0$

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

and we assume that it is solved. Then the possible energy values

$$E_1, E_2, \ldots$$

and the corresponding stationary eigenfunctions

$$\psi_1, \psi_2, \dots .$$

are given.

The general solution of the time dependent Schrödinger equation

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

is an arbitrary linear combination

$$\Psi(\vec{r}, t) = \sum c_n e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) ,$$

where c_1 , c_2 , ... are some arbitrary constants.

21.2 General solution for the time dependent perturbation. Next we assume, that from some moment, for example, from $t = 0$ to our system starts to act some time dependent perturbation $\hat{H}'(t)$. We have to solve the next equation

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

where

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$$

Since for $t < 0$ the solution is expressed as an above given linear combination, we start to search the solution in form

$$\Psi(\vec{r}, t) = \sum c_n(t) e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) ,$$

where coefficients $c_n(t)$ depend on time.

Now we get some differential equation for $c_n(t)$. Calculating separately both sides of Schrödinger equation, we have

$$i\hbar \frac{\partial \Psi}{\partial t} = \sum_n e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) \left(E_n c_n(t) + i\hbar \frac{d c_n(t)}{d t} \right) ,$$

$$(\hat{H}_0 + \hat{H}'(t))\Psi = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} (E_n + \hat{H}'(t)) \psi_n(\vec{r}) .$$

Equalizing, we get

$$i\hbar \sum_n \frac{d c_n(t)}{d t} e^{-\frac{i}{\hbar} E_n t} \psi_n(\vec{r}) = \sum_n c_n(t) e^{-\frac{i}{\hbar} E_n t} \hat{H}'(t) \psi_n(\vec{r}) .$$

Multiplying from left to $\psi_m{}^*(r)$ and integrating, we get the following equation

$$i\hbar \frac{d c_m(t)}{d t} e^{-\frac{i}{\hbar} E_m t} = \sum c_n(t) e^{-\frac{i}{\hbar} E_n t} H'_{mn} ,$$

where

$$H'_{mn} = \int \psi_m * \hat{H}'(t)\, \psi_n\, dV = \langle \psi_m |\, \hat{H}'(t)\, | \psi_n \rangle$$

are the matrix elements of perturbation operator (which, of course, depend on time).

At last we move the exponent from left to the right side. Denoting

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \ ,$$

we write the equations for $c_m(t)$ in its final form

$$i\hbar \frac{d\, c_m(t)}{d\, t} = \sum_n e^{i\, \omega_{mn}\, t}\, H'_{mn}\, c_n(t) \ ,$$

where $m = 1, 2, \ldots$.

The last system of equations is exact and applicable for all perturbations, since we have made no additional restrictions.

21.3 Small time dependent perturbation. Next we assume that $\hat{H}'(t)$ is some small perturbation. Coefficients $c_n(t)$ are expanded as series

$$c_n(t) = c_n^0 + c_n^1 + c_n^2 + \ldots \ ,$$

where each next term is one order of values smaller. Small perturbation means, that nonzero matrix elements H'_{mn} are of the same order of values, as c_n^1. Substituting coefficients and equating the terms with the same order of value, we get the next equations

$$i\hbar \frac{d\, c_m^0}{d\, t} = 0 \ ,$$

$$i\hbar \frac{d\, c_m^1}{d\, t} = \sum_n e^{i\, \omega_{mn}\, t}\, H'_{mn}\, c_n^0 \ ,$$

$$i\hbar \frac{d\, c_m^2}{d\, t} = \sum_n e^{i\, \omega_{mn}\, t}\, H'_{mn}\, c_n^1 \ ,$$

$$\ldots$$

From the first equation it follows that

$$c_m^0 = const.$$

Therefore choosing c_m^0 we are able to calculate step by stem other coefficients c_n^1 , c_n^2 , … .

21.4 First order approximation. At first we start to analyse the situation, when before the perturbation starts to act ($t < 0$) our system was in some stationary state with energy E_n. Therefore we assume, that

$$c_n^0 = 1 \ ,$$

and other coefficients $c_m^0 = 0 \quad (m \neq n)$.

The equations for the first approximation then are

$$i\hbar\frac{dc_m^1}{dt} = e^{i\omega_{mn}t}H'_{mn} \ ,$$

and the simple integration gives

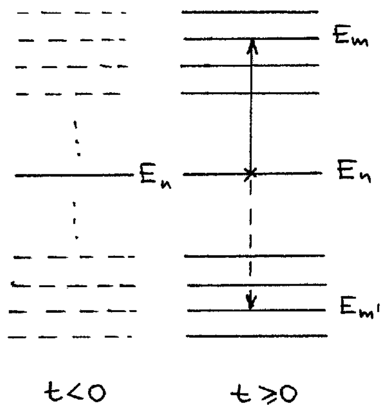
$$c_m^1 = \frac{1}{i\hbar}\int_0^t e^{\,i\omega_{mn}\tau}\,H'_{mn}d\tau \ .$$

Since $H'_{mn} = H'_{mn}(t)$, it is not possible to integrate without the exact form for these matrix elements.

In textbooks the above given expression is freguently written as

$$c_m^1 = \frac{1}{i\hbar}\int_0^t e^{\,i\omega_{mn}t}\,H'_{mn}dt \ ,$$

which is mathematically not quite correct. We have denoted the time under the integral by τ.



One interesting and important conclusion. If our system is in some stationary state with energy E_n, then after the time dependent perturbation is applied there open the possibilities for transitions to other states with other energies E_m ($E_m > E_n$ or $E_m < E_n$) if $c_m^1 \neq 0$. The probability of transition n → m depends on $|c_m^1|^2$.

21.5 Harmonic perturbation. Next we specify the perturbation operator $\hat{H}'(t)$. We assume that the perturbation is harmonic with frequency ω (for example, the external electromagnetic wave with frequency ω and wave lenght λ is applied) and write $\hat{H}'(t)$ as

$$\hat{H}'(t) = \hat{h}e^{-i\omega t} + \hat{h}^+ e^{i\omega t} \ ,$$

where $\hat{h}$ is some time independent operator. Matrix elements of our perturbation operator are

$$H'_{mn} = h_{mn}e^{-i\omega t} + h_{mn}^+ e^{i\omega t} \ ,$$

where $h_{mn} = \langle\varphi_m|\hat{h}|\varphi_n\rangle = (h_{nm}^+)^*$. In order to find c_m^1 one must calculate integral

$$c_m^1 = \frac{1}{i\hbar}\int_0^t (e^{i(\omega_{mn}-\omega)\tau}\,h_{mn} + e^{i(\omega_{mn}+\omega)\tau}\,h_{mn}^+)\,d\tau \ .$$

These integrals are quite elementary:

$$\int_0^t e^{i(\omega_{mn}\mp\omega)\tau}\,d\tau = \left.\frac{e^{i(\omega_{mn}\mp\omega)\tau}}{i(\omega_{mn}\mp\omega)}\right|_0^t = \frac{e^{i(\omega_{mn}\mp\omega)t}-1}{i(\omega_{mn}\mp\omega)} \ .$$

The final result is

$$c_m^1 = -\frac{1}{\hbar}\left(h_{mn}\,\frac{e^{i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega} + h_{mn}^{+}\,\frac{e^{i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega} \right) .$$

Next we must calculate the probabilities $|c_m^1|^2$ of transitions $n \to m$, but before it we give some general remarks. Usually the frequency ω is large (in the visible light case, for example $\omega \sim 10^{15}$ 1/s), and therefore for $\omega \neq \pm\omega_{mn}$ both summands are very small, but if $\omega \to \omega_{mn}$ (and $\omega_{mn} > 0$), the first summand is large and the second summand is small and it should be omitted. Therefore, in that case one may analyse the first summand only. Since $\omega_{mn} = (E_m - E_n)/\hbar$, then in the case $\omega_{mn} > 0$ there is induced transition from some low energy level to some higher energy level and the system adsorbs from external radiation one photon with frequency $\omega = \omega_{mn}$. But when $\omega_{mn} < 0$ we get induced (stimulated) radiation. Now the first summand is small and the second one large. The frequency of external radiation equals to $\omega = -\omega_{mn}$.

Next we analyse the abroption ($\omega_{mn} > 0$). Omitting in c_m^1 the second summand, we have

$$c_m^1 = -\frac{h_{mn}}{\hbar}\,\frac{e^{i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega} .$$

The corrsponding transition probability is

$$\left|c_m^1\right|^2 = \frac{|h_{mn}|^2}{\hbar^2}\,\frac{(e^{i(\omega_{mn}-\omega)t}-1)(e^{-i(\omega_{mn}-\omega)t}-1)}{(\omega_{mn}-\omega)^2} = \frac{2|h_{mn}|^2}{\hbar^2}\,\frac{(1-\cos(\omega_{mn}-\omega)t)}{(\omega_{mn}-\omega)^2} =$$

$$= \frac{4|h_{mn}|^2}{\hbar^2}\,\frac{\sin^2\frac{(\omega_{mn}-\omega)t}{2}}{(\omega_{mn}-\omega)^2} .$$

Let us analyse the result more closely. Transition probability depends on the modulus square $|h_{mn}|^2$ of matrix element h_{mn} and also from the rapidly oscillating function of frequency ω

$$\frac{\sin^2\frac{(\omega_{mn}-\omega)t}{2}}{(\omega_{mn}-\omega)^2} ,$$

which is nonzero near $\omega = \omega_{mn}$. Since the perturbation is small, the transition probability becomes essential after longer time intervals (theoretically, if $t \to \infty$). Next we demonstrate the in the limit $t \to \infty$ the transition probability is proportional to time and we have the resonance transition, where kus $\omega = \omega_{mn}$.

To prove it, we use the following definition of δ -function

$$\delta(x) = \lim_{A\to\infty}\frac{\sin^2 Ax}{\pi A x^2} ,$$

which in our case gives

$$\lim_{t\to\infty}\frac{\sin^2\frac{\omega_{mn}-\omega}{2}t}{\pi\frac{(\omega_{mn}-\omega)^2}{4}t}=\delta(\frac{\omega_{mn}-\omega)}{2})=2\delta(\omega_{mn}-\omega)\ .$$

Therefore, for long time intervals we have

$$P_{mn}=\lim_{t\to\infty}\left|c_m^1\right|^2=\frac{2\pi\left|h_{mn}\right|^2 t}{\hbar^2}\delta(\omega_{mn}-\omega)\ \cdot$$

21.6 Transition probability per time unite. Since the transition probability is proportional to time, we usually talk about transition probablity per time unit

$$\frac{d\,P_{mn}}{d\,t}=\frac{2\pi\left|\,h_{mn}\right|^2}{\hbar^2}\,\delta\,(\omega_{mn}-\omega)\ \cdot$$

From here it follows that the transition takes place in frequency $\omega=\omega_{mn}$, which is the resonance frequency and the probability is proportional to $\left|\,h_{mn}\right|^2$ (and which also gives the intensity of corresponding spectral line).

Instead of frequency one must use energy. Then

$$\frac{d\,P_{mn}}{d\,t}=\frac{2\pi\left|\,h_{mn}\,\right|^2}{\hbar}\,\delta\,(E_m-E_n-\hbar\,\omega)\ ,$$

which means that $E_m=E_n+\hbar\,\omega$.

It is obvious, that analyzing similarly the radiation processes, we get

$$\frac{d\,P_{mn}}{d\,t}=\frac{2\pi\left|\,h_{mn}^+\,\right|^2}{\hbar}\,\delta\,(E_m-E_n+\hbar\,\omega)\ \cdot$$

In the next paragraph we take a closer look to radiation processes and derive the selection rules for spectral transitions.

22. Radiation transitions, selection rules

22.1 Perturbation due to the external electromagnetic field. Assume, that on atom there acts some monochromatic electromagnetic wave (for example light wave), whic has the electric field strength

$$\mathrm{E}=\mathrm{E}_0\cos(\omega t-k\cdot r)\ .$$

Since the atomic diameter ($d\sim 10^{-10}\ m$) is small, comparing the wave length of light (in the case of visible light $\lambda\sim 10^{-7}\ m$), the quantity $k\cdot r=k\,r\cos\alpha=2\pi\,r\cos\alpha/\lambda$ in atomic region does not practically change and we therefore take $k\cdot r$ to be constant (dipole approximation). In that case $k \cdot r$ is some constant phase constant, we for simplicity take it equal to zero. Electrical field strength then changes harmonically having frequency ω

$$\mathrm{E} = \mathrm{E}_0 \cos \omega t \ .$$

Connecting the starting point of our coordinate system with nucleous, the electrical potential of external field is

$$\phi(r) = - r \cdot \mathrm{E} \ .$$

(Indeed, if $\phi(r) = -(x\mathrm{E}_x + y\mathrm{E}_y + z\mathrm{E}_z)$, then from $\mathrm{E} = - \, grad \, \phi(r)$ we obtain the above given field strength.)

If we assume that electrical field is directed along the z-axis: $\mathrm{E} = (0, 0, \mathrm{E})$, then

$$\phi(z) = - z \cdot \mathrm{E} = - z \mathrm{E}_0 \cos \omega t \ ,$$

and it gives to electron the additional energy

$$\Delta U(t) = - e\phi(z) = e z \mathrm{E}_0 \cos \omega t \ .$$

The last expression gives us the following time dependent perturbation operator

$$\hat{H}'(t) = e z \mathrm{E}_0 \cos \omega t = \frac{e z \mathrm{E}_0}{2} (e^{i\omega t} + e^{-i\omega t}) \ ,$$

which in turn gives us

$$\hat{h} = \hat{h}^+ = \frac{e z \mathrm{E}_0}{2} \ .$$

22.2 Transition probability. In induced transitions, both for $\omega = \omega_{mn}$ and also for $\omega = - \omega_{mn}$ the transition probability is expressed via the matrix elements of z, as

$$\frac{d P_{mn}}{d t} = \frac{\pi e^2 \mathrm{E}_0^2}{\hbar^2} | z_{mn} |^2 \ ,$$

where

$$z_{mn} = \langle \psi_m | z | \psi_n \rangle = \int \psi_m {}^* z \psi_n \, dV \ .$$

Directing the field along the x- or y-axis, we analogically obtain

$$\frac{d P_{mn}}{d t} = \frac{\pi e^2 \mathrm{E}_0^2}{\hbar^2} | x_{mn} |^2 \ , \quad \frac{d P_{mn}}{d t} = \frac{\pi e^2 \mathrm{E}_0^2}{\hbar^2} | y_{mn} |^2 \ .$$

It means that the transition probabilities are directly connected with matrix elements of radius vector $r = (x, y, z)$

$$r_{mn} = (x_{mn,} \ y_{mn,} \ z_{mn}) \ .$$

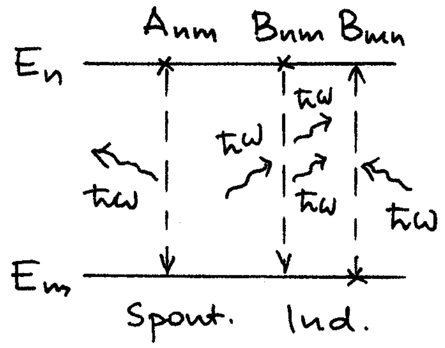
It is obvious that the transition is possible (allowed) only in cases, where $r_{mn} \neq 0$. If $r_{mn} = 0$, the transition probability is equal to zero and there are no such transition. Therefore the investigation of matrix elements r_{mn} gives us information which transitions are possible and which ones are forbidden. The restrictions on transitions are called selection rules.

The radiation, we analyze here, is usually called the dipole radiation, since the selection rules depend on the matrix elements $d_{mn} = e\, r_{mn}$ of dipole moment

$$d = e\, r$$

In addition to dipole radiation there are another ones: elctrical quadrupole, magnetical dipole and another radiations which depend on the corresponding parameters. Since these have intensities which are five to six orders of magnitude smaller from dipole radiation, we do not analyse then here.

22.3 Radiation transitions. The elementary radiation theory, given in 1917 by A. Einstein, it follows that for induced radiation the probabilities are connected as follows



$$\frac{d\, P_{mn}}{d\, t} = B_{mn}\, \rho(\omega) = B_{nm}\, \rho(\omega) = \frac{d\, P_{nm}}{d\, t} \ ,$$

where $\rho(\omega)$ was the intensity of external radiation and $B_{mn} = B_{nm}$ is the probability of inner (induced) transitions. We derived the same result from quantum mechanics

$$\frac{d\, P_{mn}}{d\, t} = \frac{\pi\, e^2\, \mathrm{E}_0^2}{\hbar^2} |\, z_{mn}\, |^2 = \frac{d\, P_{nm}}{d\, t} \ ,$$

since $|\, z_{mn}\, |^2 = |\, z_{nm}\, |^2$. As E_0^2 characterizes the intensity of external radiation, we have, that the probability of aromic transitions

$$B_{mn} = B_{nm} \approx |\, z_{mn}\, |^2 \ .$$

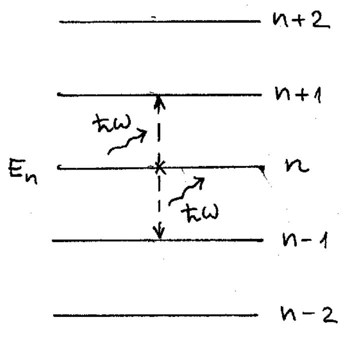
Therefore, quantum mechanics gives us the prescription to calculate Einstein coefficients.

Einstein theory gives also the relation between spontaneous and induced transitions

$$A_{nm} = \frac{2\pi\, \hbar\, \omega^3}{c^2} B_{mn} \ .$$

Therefore the calculation of matrix elements of coordinates allows also to analyze the spontaneous radiation (for example the mean life of exited state).

Näide 1. Harmonic oscillator. In the case of harmonic oscillator the selection rules are determined by the matrix elements of *x*-coordinate



$$x_{mn} = \langle \psi_m | x | \psi_n \rangle \cdot$$

Using the results of §6 it follows that

$$x_{mn} \neq 0 , \quad kui \quad m = n \pm 1 \cdot$$

From that it is obvious that transitions are allowed between neighbouring levels. In radiation the possible transitions are $n \to n-1$ and in absorbing $n \to n+1$. In the first case energy $\hbar\omega$ is radiated, in the second case the same energy is absorbed. In conclusion: harmonic oscillator radiates and absorbes energy which is equal to $\hbar\omega$ (Planck's energy quantum).

Näide 2. Atomic transitions. Next we analyse transitions in atoms, when there is transition from the state $| n\, l\, m\, \sigma \rangle$ with energy E_{nl} to the state $| n'\, l'\, m'\, \sigma' \rangle$ with energy $E_{n'l'}$. Since the transition probabilities are determined by the matrix elements of x, y and z, it is easy to verify that the spin projection on transitions cannot change. Indeed, if we write the states as

$$|n\, l\, m\, \sigma \rangle = \psi_{nlm}(r, \theta, \varphi) Y_{1/2\sigma} \ ,$$

$$|n' l' m' \sigma' \rangle = \psi_{n'l'm'}(r, \theta, \varphi) Y_{1/2\sigma'} \ ,$$

we, for example, for x_{ij} have

$$x_{ij} = \langle n' l' m' \sigma' | x | n l m \sigma \rangle = (\int \psi_{n'l'm'} {}^* x \psi_{nlm} \, dV) Y_{1/2\sigma'} {}^* Y_{1/2\sigma} \ .$$

From the orthonormality of spin functions: $Y_{1/2\sigma'} {}^* Y_{1/2\sigma} = \delta_{\sigma'\sigma}$ it follows, that in all transitions $\sigma' = \sigma$. Therefore it remains to calculate matrix element

$$x_{ij} = \int \psi_{n'l'm'} {}^* x \psi_{nlm} \, dV$$

and analogically

$$y_{ij} = \int \psi_{n'l'm'} {}^* y \psi_{nlm} \, dV \qquad \text{ja} \qquad z_{ij} = \int \psi_{n'l'm'} {}^* z \psi_{nlm} \, dV \ .$$

As follows, we demonstrate that from these integrals we get the following selection rules for spectral transitions

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

In all cases there are three integrals, over *r*, θ and φ, because

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

In spherical coordinates we have

$$x = r \sin\theta \cos\varphi , \quad y = r \sin\theta \sin\varphi , \quad z = r \cos\theta \ .$$

To simplify calculations it is useful instead of *x* and *y* take the new variables

$$\xi = x + iy = r\sin\theta\, e^{i\varphi} \ , \quad \eta = x - iy = r\sin\theta\, e^{-i\varphi} \ ,$$

since now ξ, η and *z* are expressed via the spherical functions $Y_{1m}(\theta,\varphi)$ and use the properties of spherical functions. The result is

$$\xi = -\sqrt{\frac{8\pi}{3}}\, r\, Y_{11}(\theta,\varphi) \ , \quad \eta = \sqrt{\frac{8\pi}{3}}\, r\, Y_{1-1}(\theta,\varphi) \ , \quad z = \sqrt{\frac{4\pi}{3}}\, r\, Y_{10}(\theta,\varphi) \ .$$

Next we must calculate the following types of integrals

$$(\xi_{ij}\ , \eta_{ij}\ , z_{ij}\ ) = \alpha \int_0^\infty R_{n'l'}(r) R_{nl}(r)\, r^3 dr \cdot \int_{4\pi} Y_{l'm'}\, Y_{1m''}\, Y_{lm}\, d\Omega \ ,$$

where α is correspondingly $-\sqrt{8\pi/3}$, $\sqrt{8\pi/3}$ or $\sqrt{4\pi/3}$.

At first we treat the integrals over the variables θ ja φ, which are integrated over the solid angle.

Starting from the matrix elements of *z*-coordinate, we must calcutale the integral

$$\int Y_{l'm'}\, Y_{10}\, Y_{lm}\, d\Omega \ .$$

Using the relation between spherical functions (§ 17 Example 6), we get

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

(we do not write here the exact values of α_z and β_z, since we are interested mainly in selection rules). Using these relations, we have

$$\int_{4\pi} Y_{l'm'}\, Y_{10}\, Y_{lm}\, d\Omega = \alpha_z \int_{4\pi} Y_{l'm'}\, Y_{l+1m}\, d\Omega + \beta_z \int_{4\pi} Y_{l'm'}\, Y_{l-1m}\, d\Omega \ .$$

From the orthonormality of spherical functions, we get, that the result is nonzero, iff

$$m' = m \quad \text{and} \quad l' = l \pm 1 \ ,$$

or otherwise written

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

In he case of matrix elements of ξ and η we must calculate the integrals

$$\int Y_{l'm'}\, Y_{1\pm 1}\, Y_{lm}\, d\Omega \ ,$$

which using

$$Y_{1\pm 1}\, Y_{l\,m} = \alpha_\pm Y_{l+1m\pm 1} + \beta_\pm Y_{l-1m\pm 1} \ ,$$

give

$$\int Y_{l'm'}\, Y_{1\pm 1}\, Y_{lm}\, d\Omega = \alpha_\pm \int Y_{l+1m\pm 1}\, Y_{lm}\, d\Omega + \beta_\pm \int Y_{l-1m\pm 1}\, Y_{lm}\, d\Omega \ .$$

From those integrals it follows that the result is nonzero, iff

$$m' = m \pm 1 \quad \text{ja} \quad l' = l \pm 1 \ ,$$

or

$$\Delta l = \pm 1 \ , \ \Delta m = \pm 1 \ .$$

In conclusion we get the general selection rules for dipole transitions

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

(all other dipole transitions are forbidden).

These selection rules are general, since for the quantum number *n* there are no restrictions, since the integrals

$$\int_0^\infty R_{n'l\pm 1} \, R_{nl} \, r^3 \, dr$$

are nonzero for every *n* and *n'* (since the radial functions in some regions always overlapped and the product is nonzero). From these integrals depend the intensities of corresponding spectral lines.

Condition $\Delta l = \pm 1$, $\Delta m = 0$ means, that the radiation along the z-axis is linearly polarized, the radiation along the *x*- and *y*-plane has circular polarization ($\Delta l = \pm 1$, $\Delta m = \pm 1$).

In many cases we use the total angular momentum

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

but the selection rules for *l* and *m* are the same. Since spin projection does not change, we get the selection rules

$$\Delta j = \pm 1 \ , \ \Delta m_j = 0 \, , \pm 1 \ .$$

Since $j = l \pm 1/2$, the rule $\Delta l = \pm 1$ allows also the transition

$$\Delta j = 0 \ ,$$

(the same *j* give different *l* values (for example *j* = *l* + ½ and *j* = (*l*+1) – ½)).