

31. System of identical particles

As follows we start to investigate systems of identical particles, assuming that the forces between these particles are absent (similarly, as treating ideal gas, we assume that they are mostly quite apart from each other and we neglect the forces acting between particles).

It appears that there is principal difference between classical and microparticles. Classical particles may be identical, but since they move on determined trajectories, we may observe their motion (at least, in principle) and in each moment say which particles in which points are. Microparticles are not identified in the classical sence, since their wave functions overlap and their position is given only with certain probability. Therefore if we detect particle in some point of space, it is not possible to say which of our particles we have just detected.

Next we denonstrate that in microworld there are two types of microparticles, depending from its spin. The difference is, whether the wave function of a corresponding system of particles is symmetrical or antisymmetrical in replacements of particles.

31.1 Two identical particles. For simplicity we at first treat the system of two identical microparticles. Both of them separately satisfy the equations

$$\hat{H}(1)\psi_{\alpha}(1) = E_1 \psi_{\alpha}(1) ,$$

$$\hat{H}(2)\psi_{\beta}(2) = E_2 \psi_{\beta}(2) ,$$

where $\hat{H}(1)$ is the Hamilton operator of particle 1 and $\hat{H}(2)$ is the same operator for particle 2 . Since we assume that particles are independent and therefore the energy of the first particle E_1 does not depend on the position of the second particle, and so the energy of the second particle E_2 does not depend on the position of the first particle. We use the following notations, indices 1 ja 2 denote the position and quantities which determined the energies of particles, α ja β denote other physical characteristics of particles.

If we, for example have some free particle (electron, proton, ...), then in that case the general form of Hamiltonian operator is $\hat{H} = -\frac{\hbar^2}{2M}\Delta$. Free particle with energy E is described by plane wave

$$\psi_{\alpha}(\vec{r}) = A_{\alpha} e^{i\vec{k}\cdot\vec{r}} ,$$

where $k^2 \equiv \vec{k}^2 = \frac{2ME}{\hbar^2}$, index α characterises other physical quantities (spin projection, as an example).

First of the particles is characterized by its position, therefore $1 = (x_1, y_1, z_1) \equiv \vec{r}_1$, the second one similarly by $2 = (x_2, y_2, z_2) \equiv \vec{r}_2$. The corresponding Hamiltonian operators \hat{H} are

$$\hat{H}(1) = -\frac{\hbar^2}{2M}\Delta_1 \quad \text{and} \quad \hat{H}(2) = -\frac{\hbar^2}{2M}\Delta_2 ,$$

where Δ_1 and Δ_2 are Laplace operators, where derivatives are calculated by corresponding coordinates. Wave functions are

$$\psi_\alpha(1) = A_\alpha e^{i\vec{k}_1 \cdot \vec{r}_1} \quad ja \quad \psi_\beta(2) = A_\beta e^{i\vec{k}_2 \cdot \vec{r}_2} .$$

Now we assume that there are no interactions between these two particles (forces between the particles are absent, or we in some approximation neglect them), then the total Hamiltonian operator of our two particle system is

$$\hat{H}(1,2) = \hat{H}(1) + \hat{H}(2) .$$

What are the wave functions of that two particle system? It is possible to verify that one possible wave function is the product of above given functions

$$\psi(1,2) = \psi_\alpha(1)\psi_\beta(2) .$$

Indeed:

$$\begin{aligned} \hat{H}(1,2)\psi(1,2) &= (\hat{H}(1) + \hat{H}(2))\psi_\alpha(1)\psi_\beta(2) = \\ &= (\hat{H}(1)\psi_\alpha(1))\psi_\beta(2) + \psi_\alpha(1)(\hat{H}(2)\psi_\beta(2)) = (E_1 + E_2)\psi_\alpha(1)\psi_\beta(2) = (E_1 + E_2)\psi(1,2) . \end{aligned}$$

Similarly it is easy to verify that the possible wave function is also

$$\psi(2,1) = \psi_\alpha(2)\psi_\beta(1) ,$$

where we changed the positions of particles. It is physically obvious, since the total energy does not change, if we replace particles.

We have got two different solutions and it is therefore easy to verify that an arbitrary linear combination

$$\psi = a\psi_\alpha(1)\psi_\beta(2) + b\psi_\alpha(2)\psi_\beta(1)$$

is also solution corresponding to the same energy $E = E_1 + E_2$.

Next we demonstrate that not all linear combinations of solutions are allowed, but only these states, which are symmetrical by replacing particles, as

$$\psi_s = \psi_\alpha(1)\psi_\beta(2) + \psi_\alpha(2)\psi_\beta(1) ,$$

or which are antisymmetrical by replacing particles, as

$$\psi_a = \psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1) .$$

31.2 Replacement operator. We define the replacement operator \hat{P}_{12} - which replaces particles. By definition

$$\hat{P}_{12} \psi(1,2) = \psi(2,1) ,$$

(its action means the replacement $1 \leftrightarrow 2$).

Next we solve the eigenvalue problem of replacement operator \hat{P}_{12} and find its eigenvalues and eigenfunctions. If we assume that $\psi(1,2)$ is an eigenfunction of \hat{P}_{12} , then we must get

$$\hat{P}_{12} \psi(1,2) = \lambda \psi(1,2) ,$$

where λ is the corresponding eigenvalue. Next we show that the eigenvalues of \hat{P}_{12} are +1 and -1. Indeed, if we apply to the eigenvalue problem from left operator \hat{P}_{12} and use the eigenvalue equation, we get

$$\hat{P}_{12} (\hat{P}_{12} \psi(1,2)) = \hat{P}_{12} (\lambda \psi(1,2)) = \lambda^2 \psi(1,2) .$$

On the other hand, taking the definition of replacement operator and applying \hat{P}_{12} from left, we obtain

$$\hat{P}_{12} (\hat{P}_{12} \psi(1,2)) = \hat{P}_{12} \psi(2,1) = \psi(1,2) .$$

Comparing the results, it follows that $\lambda^2 = 1$, which gives

$$\lambda = \pm 1 .$$

Next we show that eigenfunctions of operator \hat{P}_{12} are symmetrical or antisymmetrical. First we take eigenfunction corresponding to $\lambda = +1$

$$\hat{P}_{12} \psi(1,2) = \psi(1,2) .$$

Since by definition of \hat{P}_{12} : $\hat{P}_{12} \psi(1,2) = \psi(2,1)$, we get

$$\psi(1,2) = \psi(2,1) ,$$

which means that eigenfunction is symmetrical in replacement $1 \leftrightarrow 2$.

Taking similarly the eigenfunction corresponding to $\lambda = -1$

$$\hat{P}_{12} \psi(1,2) = -\psi(1,2)$$

and using the definition of \hat{P}_{12} , we get

$$\psi(1,2) = -\psi(2,1) ,$$

which means that eigenfunction is antisymmetrical in replacement $1 \leftrightarrow 2$.

31.3 Symmetrical and antisymmetrical wave functions. Now it is easy to demonstrate that wave functions for systems with identical particles are always symmetrical or antisymmetrical by replacements of particles. It follows from the fact that the energy operator

$$\hat{H}(1,2) = \hat{H}(1) + \hat{H}(2)$$

is invariant on replacement $1 \leftrightarrow 2$, therefore it commutes with the replacement operator \hat{P}_{12}

$$[\hat{P}_{12}, \hat{H}(1,2)] = 0 .$$

For that reason both operators have common eigenfunctions. We just demonstrated that the eigenfunctions of replacement operator \hat{P}_{12} are symmetrical or antisymmetrical, therefore the eigenfunctions of Hamilton operator $\hat{H}(1,2)$ are similarly symmetrical or antisymmetrical.

In conclusion. If for two identical particles we have two separate equations

$$\hat{H}(1)\psi_\alpha(1) = E_1 \psi_\alpha(1) ,$$

$$\hat{H}(2)\psi_\beta(2) = E_2 \psi_\beta(2) ,$$

then the energy operator of a given two-particle system is

$$\hat{H}(1,2) = \hat{H}(1) + \hat{H}(2)$$

and its eigenfunctions, corresponding to the total energy $E = E_1 + E_2$ are symmetrical

$$\psi_s = \psi_\alpha(1)\psi_\beta(2) + \psi_\alpha(2)\psi_\beta(1) ,$$

or antisymmetrical

$$\psi_a = \psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)$$

(not normed here).

31.4 System of n identical particles. The result, obtained above is easily generalized to n-identical particles case. The wave function is also symmetrical or antisymmetrical in replacements of arbitrary pair of particles. If we denote the n-particle wave function symbolically as $\psi(1,2,\dots,i,\dots,j,\dots,n)$, we define replacement operator \hat{P}_{ij} , which replaces particles i and j , as follows

$$\hat{P}_{ij}\psi(1,2,\dots,i,\dots,j,\dots,n) = \psi(1,2,\dots,j,\dots,i,\dots,n) .$$

Eigenvalues of all replacement operators are +1 and -1, and the corresponding wave functions are in replacements symmetrical or antisymmetrical.

Operator of total energy

$$\hat{H}(1,2,\dots,i,\dots,j,\dots,n) = \hat{H}(1) + \hat{H}(2) + \dots + \hat{H}(i) + \dots + \hat{H}(j) + \dots + \hat{H}(n)$$

commutes with all replacement operators. Therefore there remains two possibilities: wave

function is symmetrical in all replacements, or it is antisymmetrical in all replacements. All nonsymmetrical combinations are not allowed, since then the particles are not identical as assumed (assuming, for example, that our wave function is symmetrical with respect to the replacement $1 \leftrightarrow 3$, but antisymmetrical with respect to the replacement $2 \leftrightarrow 3$, then the particles are not totally identical and some of them distinguish from others).

General symmetrical wave function is written symbolically as

$$\psi_s = \sum_P \psi_{\alpha_1}(1) \psi_{\alpha_2}(2) \dots \psi_{\alpha_i}(i) \dots \psi_{\alpha_j}(j) \dots \psi_{\alpha_n}(n),$$

where P denotes the sum over all permutations of indices $1, 2, \dots, n$. Antisymmetrical wave function is written as

$$\psi_a = \sum_P (-1)^P \psi_{\alpha_1}(1) \psi_{\alpha_2}(2) \dots \psi_{\alpha_i}(i) \dots \psi_{\alpha_j}(j) \dots \psi_{\alpha_n}(n),$$

where for even permutations there is plus, and for odd permutations minus sign. The latter may be written as determinant (called Slater determinant)

$$\psi_a = \begin{vmatrix} \psi_{\alpha_1}(1) & \psi_{\alpha_1}(2) & \dots & \psi_{\alpha_1}(n) \\ \psi_{\alpha_2}(1) & \psi_{\alpha_2}(2) & \dots & \psi_{\alpha_2}(n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{\alpha_n}(1) & \psi_{\alpha_n}(2) & \dots & \psi_{\alpha_n}(n) \end{vmatrix}.$$

These functions are not normed. For normed functions we must add the normalization factor $1/\sqrt{n!}$.

31.5 Connection between spin and statistics. It appears that the symmetry of wave functions corresponding to systems of identical particles depends on spin. Particles with even integer spin ($0, 1, 2, \dots$) are described by symmetrical wave functions (we denote them ψ_s), particles with half-odd integer spin ($1/2, 3/2, \dots$) are described by antisymmetrical wave functions (we denote ψ_a). Since particles with integer spin are described by Bose-Einstein statistics and particles with half-odd integer spin are described with Fermi-Dirac statistics, then it is sometimes called the connection between spin and statistics. As we know, particles with integer spin are called bosons and particles with half odd integer spin are called fermions.

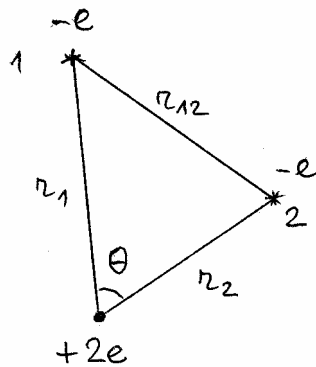
The strict proof of connection between spin and statistics is given in quantum field theory. Here we give it as a known fact. Here we give only a trivial example that in the case of two electrons its wave function must be antisymmetrical. As we know, for electrons Pauli formulated the exclusion principle (there are no two electrons in the same quantum state), therefore it is described by antisymmetrical wave function $\psi_a = \psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)$. Indeed, if we take $\alpha = \beta$, we get $\psi_a = 0$, which means that the probability that two electrons are exactly in the same state is equal to zero. For the integer spin particles there are no such restrictions and if we take the symmetrical wave function, then the state with $1=2$ and $\alpha = \beta$ is allowed and $\psi_s = 2\psi_1(\alpha)\psi_1(\alpha)$ is nonzero.

32. Helium atom

Next we consider the Helium atom and possibilities to find its energy levels and states. Since there are two electrons connected with nucleus and also with each other by electrical forces, the problem is very complicated and there are no analytical solutions for the corresponding Schrödinger equation. For that reason some approximation methods are needed. Next we use not the best one, since it gives not the best values for energies, but on the other hand it gives quite simple picture for the energy levels structure and explains the new type of forces (exchange forces) which are specific to the microworld and have no classical analog.

32.1 Hamilton operator of He-atom. To simplify the problem we take into consideration only electrical forces. Electrons energy operator is the following

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta_1 - \frac{\hbar^2}{2M} \Delta_2 + U(1) + U(2) + U(1,2) .$$



Two first terms are electrons kinetic energy operators, two next terms - $U(1)$ and $U(2)$ - are potential energies of electrons and nucleus

$$U(1) = -\frac{b2e^2}{r_1} , \quad U(2) = -\frac{b2e^2}{r_2}$$

and $U(1,2)$ is the potential energy of two electrons

$$U(1,2) = \frac{be^2}{r_{12}} .$$

Before we go further, one general remark. Total energy does not depend on spin. That means that the total spin is a conserved quantity and characterizes the helium states. General wave function is written as a product of spin function and coordinate dependent wave function. Since the energy operator is symmetrical with respect to the replacement of electrons, the total wave function must be antysymmetrical.

The complications in solving eigenvalue problem arise mainly from to the interaction between electrons, since their potential energy depends on the distance r_{12} between electrons, which is a function of distances r_1 and r_2 , and also on the angle θ between their segments. Therefore there do not exist any closed analytical solutions and approximation methods are needed.

Next we use the most simple approximation, we call it the zeroth approximation, where we neglect the interaction between electrons. In the He-atom case that is not the best one, since the forces between two electrons are not too small (in comparison with forces between electrons and nucleus), but it gives the simple explanation to the general structure of energy levels .

32.2 Zeroth approximation. We begin with approximation where we take the potential energy $U(1,2)$ to be equal to zero. Then we must solve the eigenvalue problem of the

following energy operator

$$\hat{H} = -\frac{\hbar^2}{2M}\Delta_1 + U(1) - \frac{\hbar^2}{2M}\Delta_2 + U(2) .$$

It is written as

$$\hat{H} = \hat{H}(1) + \hat{H}(2) ,$$

where $\hat{H}(1)$ and $\hat{H}(2)$ are energy operators of hydrogen like atoms (now $Z = 2$).

In our new problem there are two independent electrons moving around the same nucleus. Total energy E is the sum of its energies

$$E = E_1 + E_2 .$$

Solutions of equations $\hat{H}(1)\psi_\alpha(1) = E_1\psi_\alpha(1)$ and $\hat{H}(2)\psi_\beta(2) = E_2\psi_\beta(2)$ are known. Energies of electrons depend on two principal quantum numbers, which we denote as n_1 and n_2

$$E_1 = -\frac{4R\hbar}{n_1^2} , \quad E_2 = -\frac{4R\hbar}{n_2^2} ,$$

therefore the total energy is

$$E = -\frac{4R\hbar}{n_1^2} - \frac{4R\hbar}{n_2^2} ,$$

where $n_1, n_2 = 1, 2, \dots$.

32.3 Electronic states. Since there are two identical electrons, the total wave function is antisymmetric. Next we find the general structure of wave functions. Since the energy does not depend on spin, electron wave function is a product of two independent functions

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

where the wave function which depends on space coordinates is in turn the product of radial and spherical functions.

As a shorthand, we write the wave functions of electrons, as

$$\psi_\sigma(1) = \psi(1) \chi_\sigma^1 , \quad \psi_{\sigma'}(2) = \psi(2) \chi_{\sigma'}^2 .$$

(where the $\psi(1)$ and $\psi(2)$ depend on coordinates). From products of such functions we must construct antisymmetrical wave functions.

As we told, energy does not depend on spin and therefore one of the quantities that determine electron states is total spin. For that reason we at first analyse the spin states of these two electrons. Since electrons have spin $1/2$ the total spin is 0 or 1 . Next we write down the corresponding state functions (see §17).

We denote the state, corresponding to spin projection $\sigma = +1/2$, by α and the state,

corresponding to spin projection $\sigma = -1/2$ by β . If spin projections of both electrons are equal to $+1/2$, then $\chi_{+1/2}^1 = \alpha(1)$ and $\chi_{+1/2}^2 = \alpha(2)$, and analogically, if the spin projections are $-1/2$, then $\chi_{-1/2}^1 = \beta(1)$ and $\chi_{-1/2}^2 = \beta(2)$. The normed wave function, corresponding to the total spin $s = 0$, is written as

$$S(0) = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1)),$$

and in the case of total spin $s = 1$, we, depending on spin projection, have three orthonormed wave functions

$$\begin{aligned} S_{+1}(1) &= \alpha(1)\alpha(2), \\ S_0(1) &= \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1)), \\ S_{-1}(1) &= \beta(1)\beta(2). \end{aligned}$$

In the first case spins are antiparallel (opposite directed), in the second case they are parallel (had the same direction).

As we see, the spin dependent functions have different symmetry in replacement $1 \leftrightarrow 2$, if total spin is 0, it is antisymmetrical and if total spin is 1, it is symmetrical. The total wave function of two electron is antisymmetrical. Since the the total wave function is a product of spin function to the space dependent function, then we have two diffent types of functions. The states with the total spin 0, have antisymmetrical spin function, therefore the corresponding space part must be symmetrical, therefore the wave function is written as

$$\psi_{00}(1,2) = \psi_s(1,2)S(0),$$

where $\psi_s(1,2)$ is symmetrical in space coordinates in replacement $1 \leftrightarrow 2$. The states with the total spin 1 have symmetrical spin function, therefore the corresponding total wave function is written as

$$\psi_{1\sigma}(1,2) = \psi_a(1,2)S_\sigma(1),$$

where $\psi_a(1,2)$ is antisymmetrical in replacement $1 \leftrightarrow 2$ (σ denotes spin projection of total spin ($\sigma = +1, 0, -1$)). The states with the total spin 0 and 1 are correspondingly called singlet and triplet states.

Next we shortly analyse the space part of wave functions. The space part of both electrons are determined by the location and three quantum numbers n, l ja m : $\psi_{nlm}(\vec{r})$, then it is obvious that it is always possible to construct symmetrical wave functions, but not always antisymmetrical functions. If the wave functions of two electrons are

$$\psi_{nlm}(\vec{r}_1) \text{ ja } \psi_{n'l'm'}(\vec{r}_2),$$

then the simple symmetrization (independently on the values of corresponding quantum numbers) gives

$$\psi_s(1,2) = \frac{1}{\sqrt{2}} (\psi_{nlm}(\vec{r}_1)\psi_{n'l'm'}(\vec{r}_2) + \psi_{nlm}(\vec{r}_2)\psi_{n'l'm'}(\vec{r}_1)) .$$

It means that singlet states exist in the case of all possible electron states. Antisymmetrical wave function exists for these states only, in which electrons are in different states ($n \neq n'$, $l \neq l'$, $m \neq m'$)

$$\psi_a(1,2) = \frac{1}{\sqrt{2}} (\psi_{nlm}(\vec{r}_1)\psi_{n'l'm'}(\vec{r}_2) - \psi_{nlm}(\vec{r}_2)\psi_{n'l'm'}(\vec{r}_1)) .$$

Therefore the triplet states exist only in cases when electrons are in states with different quantum numbers.

Next we write down some special wave functions and calculate the energy correction due the interactions between electrons themselves.

32.4 Ground state. The ground state corresponds to minimal energy. In that case both electrons are in ground state ($n_1 = n_2 = 1$). Ground state energy is

$$E_0 = -2(4R\hbar) = -8R\hbar .$$

Next we find the corresponding wave function. Since for both electrons $l = m = 0$, the space dependent wave functions are

$$\psi_{100}(\vec{r}_1) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{r_0} \right)^{3/2} e^{-\frac{2r_1}{r_0}} \quad \text{and} \quad \psi_{100}(\vec{r}_2) = \frac{1}{\sqrt{\pi}} \left(\frac{2}{r_0} \right)^{3/2} e^{-\frac{2r_2}{r_0}} .$$

Their product is obviously symmetrical

$$\psi_s(1,2) = \frac{8}{\pi r_0^3} e^{-\frac{2(r_1+r_2)}{r_0}} .$$

Therefore the ground state corresponds to the total spin $s = 0$, since now the spin part must be antisymmetrical. Therefore the ground state wave function is

$$\psi_{00}(1,2) = \frac{8}{\pi r_0^3} e^{-\frac{2(r_1+r_2)}{r_0}} \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) .$$

Energy correction to the ground state. Next we use simple perturbation theory to calculate the energy correction due to the forces between two electrons. The perturbation operator is now $\hat{H}' = U(1,2)$. First order energy correction is given by the diagonal matrix element

$$\Delta E_0 \equiv \langle \psi_{00}(1,2) | U(1,2) | \psi_{00}(1,2) \rangle = b e^2 \langle \psi_{00}(1,2) | \frac{1}{r_{12}} | \psi_{00}(1,2) \rangle .$$

Since the function under the integral ($1/r_{12}$) does not depend on spin and spin functions are

normed, the integral is over the space coordinates only

$$\Delta E_0 = b e^2 \langle \psi_s(1,2) | \frac{1}{r_{12}} | \psi_s(1,2) \rangle,$$

which in our case means integral

$$\Delta E_0 = \frac{64 b e^2}{\pi^2 r_0^6} \int e^{-\frac{4r_1}{r_0}} \frac{1}{r_{12}} e^{-\frac{4r_2}{r_0}} dV_1 dV_2$$

Calculation of that integral is quite complicated, since $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos\theta}$, therefore we give here the final result (which one may find in textbooks)

$$\Delta E_0 = -\frac{5}{16} E_0 .$$

The ground state energy is therefore

$$E = E_0 + \Delta E_0 = \frac{11}{16} E_0 .$$

The quantity, measured in experiments, is usually the ionization energy. That is

$$E_i = \frac{1}{2} E_0 - \frac{11}{16} E_0 = -\frac{3}{16} E_0 \equiv \frac{3}{2} R\hbar = 20,4 \text{ eV} .$$

If we compare it with the experimental result 24,6 eV, we see that our approximation is not quite good and for that reason better approximation methods are needed. Our main goal here was to clarify the general structure of energy levels and therefore we here limit ourselves with the given results.

It appears that for other helium-like atoms - Li^+ , Be^{++} , ..., the same method gives quite good results, since there the interaction between two electron is smaller and smaller than the interaction between electrons and nucleus.

32.5 First excited state. To clarify the structure of He energy levels and corrections to energy we next consider the first excited state. In the zeroth-order the first excited state corresponds to $n_1 = 1$ ja $n_2 = 2$ or $n_1 = 2$ ja $n_2 = 1$ (one of the electrons is in the first excited state). Its energy is

$$E_1 = -4R\hbar - \frac{4R\hbar}{2^2} = -5R\hbar .$$

For simplicity we assume that both electrons are in s-state ($l = 0$). Then the corresponding wave functions are

$$\psi_{1s} = \frac{1}{2\sqrt{\pi}} R_{10}(r) \chi_\alpha \quad \text{and} \quad \psi_{2s} = \frac{1}{2\sqrt{\pi}} R_{20}(r) \chi_\beta .$$

Since the radial functions are different, its possible to find both, symmetrical and antisymmetrical radial functions:

$$R_s = \frac{1}{4\sqrt{2}\pi} (R_{10}(r_1)R_{20}(r_2) + R_{10}(r_2)R_{20}(r_1)),$$

$$R_a = \frac{1}{4\sqrt{2}\pi} (R_{10}(r_1)R_{20}(r_2) - R_{10}(r_2)R_{20}(r_1)) .$$

The first one corresponds to the singlet state ($s = 0$), since it must be combined with antisymmetrical spin function, and the second one to the triplet state ($s = 1$), since it is combined with the symmetrical spin function.

Next we consider the energy corrections to the E_1 . The general expression of it is

$$\Delta E = \langle \psi | U(1,2) | \psi \rangle ,$$

We treat symmetrical and antisymmetrical cases simultaneously. Since $U(1,2)$ does not depend on spin (transitions are allowed between the states with the same spin), we must calculate integrals

$$\Delta E = \frac{1}{32\pi^2} \iint (R_{10}(r_1)R_{20}(r_2) \pm R_{10}(r_2)R_{20}(r_1)) \frac{be^2}{r_{12}} (R_{10}(r_1)R_{20}(r_2) \pm R_{10}(r_2)R_{20}(r_1)) dV_1 dV_2$$

We do not calculate them directly, but give only the general analysis of results. Simple arithmetics gives the following general form

$$\Delta E = Q \pm A ,$$

where the plus sign is in the case of symmetrical and the minus sign in the case of antisymmetrical radial functions. Quantities Q and A are integrals

$$Q = \frac{1}{16\pi^2} \iint R_{10}^2(r_1) \frac{be^2}{r_{12}} R_{20}^2(r_2) dV_1 dV_2 ,$$

$$A = \frac{1}{16\pi^2} \iint R_{10}(r_1)R_{10}(r_2) \frac{be^2}{r_{12}} R_{20}(r_1)R_{20}(r_2) dV_1 dV_2 .$$

The first term Q has simple physical meaning, it is the total potential energy of two electrons. The charge of the 1s electron in the volume element dV_1 is $dq_1 = e R_{10}^2(r_1) dV_1$, and similarly the charge of the 2s electron in volume element dV_2 is $dq_2 = e R_{20}^2(r_2) dV_2$. If the distance between them is r_{12} their potential energy is expressed as

$$\frac{bdq_1 dq_2}{r_{12}}$$

The second term - A - has a direct quantum mechanical origin and has no classical analog. The corresponding energy correction is called the exchange energy and follows from the demand that the wave function must be antisymmetrical in replacement of electrons. It has no classical analog since the radial part of $1s$ electron must be taken at the same time with the argument r_1 and also with r_2 , similarly the radial part of $2s$, which seems that due to the “exchange” of particles they are at the same time on both places. But that “exchange” gives us some additional energy – exchange energy – which in classical meaning is connected with some extra force, and therefore the corresponding forces are called exchange forces. The physical origin of exchange energy is due to the fact that microparticles are identical and therefore it is not possible to distinguish states, in which the particles are replaced.

Direct calculation gives that both integrals are positive and so the corresponding energies. Therefore the energy corrections are: in the case of symmetrical R_s

$$\Delta E_s = Q + A$$

$$s = 0 \text{ ————— } Q + A$$

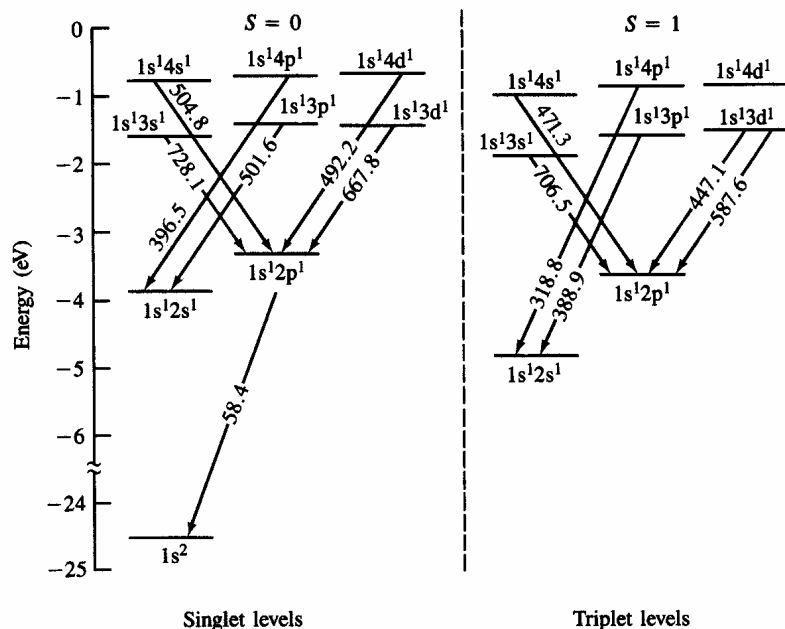
and in the case of antisymmetrical R_a

$$s = 1 \text{ ————— } Q - A$$

$$\Delta E_a = Q - A$$

Distance between levels is $2A$ and is therefore determined by the exchange forces. The results are valid also for the other states, therefore the singlet states energy (antiparallel spins) is higher than the corresponding energy of triplet states (parallel spins).

The energy level structure of He-atom and possible optical transitions are presented on figure (on right). Depending on the total spin of electrons there are two kinds of helium – parahelium ($s = 0$) and orthohelium ($s = 1$).



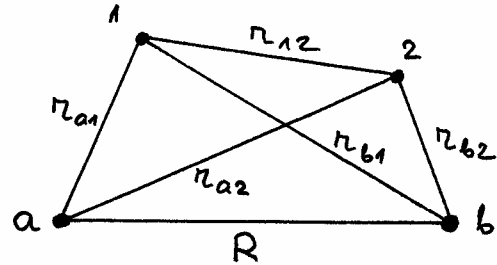
33. Hydrogen molecule

Here we treat the simplest molecule, hydrogen molecule H_2 , and try to explain the conditions for binding of two hydrogen atoms. Mathematically the problem is very complicated (two nucleus and two electrons) and there are no analytical solutions. We mostly analyse the qualitative side of problem and do not perform direct calculations.

33.1 Hamiltonian operator. Next we restrict ourselves to the electrical forces only. Using the adiabatical approximation (see Appendix) the Hamiltonian operator for electrons in fixed distance R between two nucleus is

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta_1 - \frac{\hbar^2}{2M} \Delta_2 - \frac{be^2}{r_{a1}} - \frac{be^2}{r_{a2}} - \frac{be^2}{r_{b1}} - \frac{be^2}{r_{b2}} + \frac{be^2}{r_{12}} + \frac{be^2}{R} ,$$

where nuclei are denoted by a and b, electrons are denoted by 1 and 2, R is distance between two nucleus and r (with different indices) denote different distances of electrons



Since there are no analytical solutions, approximation methods must be used. At first we treat it as the system of two independent hydrogen atoms. As in the helium atom case we have two electrons and the total spin has two values $s = 0$ and $s = 1$, therefore the space coordinates dependent part of wave function must be correspondingly symmetrical or antisymmetrical. Therefore the function, depending on space coordinates, we started with, is written as

$$\psi = \alpha (a(1)b(2) \pm a(2)b(1)) ,$$

where

$$\begin{aligned} a(1) &= \psi_{nlm}(r_{a1}, \theta_1, \varphi_1) , & a(2) &= \psi_{nlm}(r_{a2}, \theta_2, \varphi_2) , \\ b(1) &= \psi_{n'l'm'}(r_{b1}, \theta'_1, \varphi'_1) , & b(2) &= \psi_{n'l'm'}(r_{b2}, \theta'_2, \varphi'_2) \end{aligned}$$

and α is normalization factor. We assumed, that electron 1 may “move” around the first or the second hydrogen nucleus, and similarly electron 2.

Next we find the normalization factor α . Here we must take into account that the wave functions of atoms a and b are not mutually orthogonal.

$$\int |\psi|^2 dV_1 dV_2 = 1 = |\alpha|^2 \int (a(1)b(2) \pm a(2)b(1))^* (a(1)b(2) \pm a(2)b(1)) dV_1 dV_2$$

Rewriting the right hand side, we get

$$|\alpha|^2 2 (\int |a(1)|^2 dV_1 \int |b(2)|^2 dV_2 \pm \int a^*(1)b(1) dV_1 \int a(2)b^*(2) dV_2) = |\alpha|^2 2(1 \pm |\beta|^2) = 1 ,$$

where $\beta = \int a^*(1)b(1)dV_1$. If we choose the normalization factor to be real, we have

$$\alpha = \frac{1}{\sqrt{2(1 \pm |\beta|^2)}} .$$

We next consider the ground state only ($n = n' = 1, l = 0, m = 0$), the radial wave functions are

$$a(1) = \frac{1}{2\sqrt{\pi}} R_{10}(r_{a1}) , \quad a(2) = \frac{1}{2\sqrt{\pi}} R_{10}(r_{a2}) ,$$

$$b(1) = \frac{1}{2\sqrt{\pi}} R_{10}(r_{b1}) , \quad b(2) = \frac{1}{2\sqrt{\pi}} R_{10}(r_{b2}) .$$

These satisfy

$$\left(-\frac{\hbar^2}{2M}\Delta_1 - \frac{be^2}{r_{a1}}\right)a(1) = E_1 a(1) , \quad \left(-\frac{\hbar^2}{2M}\Delta_2 - \frac{be^2}{r_{b2}}\right)b(2) = E_1 b(2) ,$$

(analogically also $a(2)$ and $b(1)$, where one must replace indices 1 and 2). $E_1 = -R\hbar$ is the ground state energy of hydrogen atom. In a given approximation the ground state energy of whole system is

$$E_0 = 2 E_1 = -2 R \hbar$$

Next we analyse the energy corrections and find the possibilities to form the hydrogen molecule. We in principle must use modified perturbation theory (since $a(1)$ ja $b(1)$ are not orthogonal)

$$\beta = \int a(1)b(1)dV_1 \neq 0 ,$$

but since β is small we may restrict ourselves to the ordinary perturbation theory. We rewrite the energy operator as

$$\hat{H} = \hat{H}_0(1,2) + \hat{H}' ,$$

where

$$\hat{H}_0(1,2) = \hat{H}_0(1) + \hat{H}_0(2) = \left(-\frac{\hbar^2}{2M}\Delta_1 - \frac{be^2}{r_{a1}}\right) + \left(-\frac{\hbar^2}{2M}\Delta_2 - \frac{be^2}{r_{b2}}\right)$$

is the sum of two independent energy operators of hydrogen atoms and take

$$\hat{H}' = -\frac{be^2}{r_{a2}} - \frac{be^2}{r_{b1}} + \frac{be^2}{r_{12}} + \frac{be^2}{R}$$

as perturbation. From here we separate the potential energy of two nucleus (we treat the distance R between them as an independent parameter), and write

$$\hat{H}' = \frac{be^2}{R} + \hat{H}'' ,$$

where we treat

$$\hat{H}'' = -\frac{be^2}{r_{a2}} - \frac{be^2}{r_{b1}} + \frac{be^2}{r_{12}}$$

as a “real” perturbation.

The total energy of the ground system is expressed as

$$E = E_0 + \frac{be^2}{R} + \Delta E ,$$

where ΔE is a diagonal matrix element of perturbation operator \hat{H}'' . The general form of it is

$$\begin{aligned} \Delta E &= \frac{1}{2(1 \pm \beta^2)} \int (a(1)b(2) \pm a(2)b(1)) \hat{H}'' (a(1)b(2) \pm a(2)b(1)) dV_1 dV_2 = \\ &= \frac{1}{(1 \pm \beta^2)} \left\{ \int a^2(1)b^2(2) \hat{H}'' dV_1 dV_2 \pm \int a(1)a(2)b(1)b(2) \hat{H}'' dV_1 dV_2 \right\} \end{aligned}$$

We rewrite it as

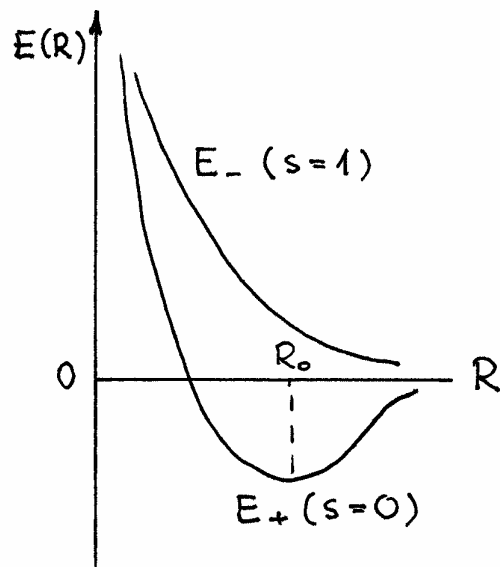
$$\Delta E = \frac{1}{1 \pm \beta^2} (Q \pm A) ,$$

where

$$Q = \int a^2(1)b^2(2) \hat{H}'' dV_1 dV_2 \quad \text{and} \quad A = \int a(1)a(2)b(1)b(2) \hat{H}'' dV_1 dV_2 .$$

The first term Q is the Coulomb potential energy (potential energy of electrons themselves and potential energies between electron and other nucleus). The second term A is similarly treated as an exchange energy which is due to the replacement of electrons and has no classical analog. Both terms of course depend on the distance R between the two nucleus. Direct calculations demonstrate, and that is the most important result here, that A is always negative (in the He-atom case it was positive).

As we already mentioned Q and A depend on R . For that reason the total energy $E = E(R)$ of the ground state depends also from the distance R between the two nucleus. The result of direct calculations of total energy of ground state is presented on figure and shows that when the total spin $s = 1$ (the radial wave function is antisymmetrical), no molecule forms (in all distances the forces between hydrogen atoms are repulsive, but in the total spin $s = 0$ case (radial function is symmetrical) appears the binding between two hydrogen atoms and they form the hydrogen molecule.



In chemistry it is called the covalent binding.

Physically it is explained in the following way: if spins are antiparallel, the radial wave function is symmetrical and that means that the probability to find electrons between two

nucleus is not small and therefore the electrons “moving” between two nucleus compensate the repulsive forces acting between the two nucleus themselves. Moreover in that case electrons are common and do not “move” around one atom only, but around both atoms.

Appendix.

Adiabatical approximation. In the case of molecules and especially in the solid state case we have the particle systems which consists of electrons and nuclei. Therefore it is impossible directly solve corresponding equations and we must use some approximations. Since the mass of nucleus is usually more than 2000 times greater, it is logical to assume that nuclei move slowly comparing with electrons. It allows us to assume that in the zeroth approximation nuclei do not move and calculate electron states for fixed positions of nuclei and in the next approximations use the motion of nuclei as some perturbation. The above given method is called adiabatical approximation.

Assume that we have the system of identical electrons and identical nuclei. Their Hamiltonian operator is written symbolically as

$$\hat{H} = T_R + T_r + U(r, R) ,$$

where R is a shorthand of all coordinates of nuclei, r is a shorthand of all electron coordinates. T_R and T_r are the corresponding kinetic energy operators

$$T_R = -\frac{\hbar^2}{2M_i} \sum_i \Delta_{R_i}, \quad T_r = -\frac{\hbar^2}{2M} \sum_j \Delta_{r_j}$$

and $U(r, R)$ is the total potential energy of whole system.

Assuming that nuclei move slowly, we treat its motion as a small perturbation and write energy operator as

$$\hat{H} = \hat{H}_0 + T_R ,$$

where $\hat{H}_0 = T_r + U(r, R)$ and for zeroth-order approximation take the equation

$$\hat{H}_0 \psi_n(r, R) = \varepsilon_n(R) \psi_n(r, R) .$$

In the last equation coordinates of nuclei R are fixed (we treat them as parameters)

Suppose the last equation is solved. Then the solution of the problem, we are interested in

$$\hat{H} \psi(r, R) = E \psi(r, R)$$

is given in the following form

$$\psi(r, R) = \sum_n \Phi_n(R) \psi_n(r, R) .$$

If we put the solution back to our equation, multiplying from left to $\psi_k^*(r, R)$ and integrating over the coordinates of electrons, we get the following equation

$$(T_R + \varepsilon_n - E) \Phi_k(R) = \hat{C} \Phi_k(R) ,$$

where

$$\hat{C} \Phi_k(R) = \sum \left\{ \frac{\hbar^2}{2M} \Phi_n(R) \int \psi_k^* \Delta_{R_i} \psi_n dV + \frac{\hbar^2}{M} \int \psi_k^* \text{grad}_{R_i} \psi_n \cdot \text{grad}_{R_i} \Phi_n(R) dV \right\} .$$

The equation, we just derived, is equivalent to the equation we started with. Adiabatical approximation means that the term on the right side $\hat{C} \Phi_k(R)$ is small and we therefore take it equal to zero.

In conclusion, using the adiabatical approximation, we replace our equation we started with

$$\hat{H} \psi(r, R) = E \psi(r, R) ,$$

or, as written more precisely

$$\left(-\frac{\hbar^2}{2M_t} \sum_i \Delta_{R_i} - \frac{\hbar^2}{2M} \sum_j \Delta_{r_j} + U(r, R) \right) \psi(r, R) = E \psi(r, R) ,$$

with the following two equations

$$\left(-\frac{\hbar^2}{2M} \sum_j \Delta_{r_j} + U(r, R) \right) \psi_n(r, R) = \varepsilon(r, R) \psi_n(r, R) ,$$

$$\left(-\frac{\hbar^2}{2M_t} \sum_i \Delta_{R_i} + \varepsilon(r, R) \right) \Phi_n(R) = E \Phi_n(R) .$$

(The general solution is in form $\psi(r, R) = \sum_n \Phi_n(R) \psi_n(r, R)$.) The first equation gives states of electrons when the positions of nuclei R_i are fixed and corresponding energies of electrons. The second equation describes nuclei, where the role of potential energy is energy of electrons $\varepsilon_n(r, R)$.