

10. H-atom in quantum mechanics

10.1 Central symmetric field. Consider at first the central symmetric potential energy

$$U = U(r) .$$

The corresponding Schrödinger equation is

$$-\frac{\hbar^2}{2M}\Delta\psi(\vec{r}) + U(r)\psi(\vec{r}) = E\psi(\vec{r}) .$$

Since the potential energy depends on radial variable only, it is useful to use spherical coordinates. Laplace operator in spherical coordinates is

$$\begin{aligned} \Delta &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \equiv \\ &\equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left(-\frac{1}{\hbar^2} \hat{L}^2 \right) . \end{aligned}$$

Dependence on angles is expressed with the help of angular momentum operator..

Schrödinger equation in spherical coordinates is

$$-\frac{\hbar^2}{2M} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \hat{L}_{\theta\varphi}^2 - \frac{2M}{\hbar^2} U(r) \right] \psi(\vec{r}) = E\psi(\vec{r}) ,$$

or

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

where

$$\hat{H} = -\frac{\hbar^2}{2M} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \hat{L}_{\theta\varphi}^2 - \frac{2M}{\hbar^2} U(r) \right] .$$

It is easy to verify, that

$$\left[\hat{H} , \hat{L}^2 \right] = 0 .$$

From the last expression it follows that we have two conserved quantities: energy and angular momentum (of course in addition also the projection of angular momentum is conserved) In classical physics the situation is similar: there are two conserved quantities – energy and angular momentum.

10.2 General form of solution. Since the angular momentum is conserved, we try to find the solution in the following general form

$$\psi(\vec{r}) = R(r)Y_{lm}(\theta, \varphi) .$$

Since $\hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$, we after substitution obtain the differential equation for the radial part of solution $R(r)$

$$-\frac{\hbar^2}{2M} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) \right] + \left[\frac{\hbar^2 l(l+1)}{2M r^2} + U(r) \right] R(r) = E R(r) .$$

It is the general form which is used for every $U(r)$.

10.3 H-atom in quantum mechanics. In hydrogen atom electron has the following potential energy

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \equiv -\frac{be^2}{r} ,$$

Coulomb potential energy (here we use the SI-system and for simplicity denote $b = 1/4\pi\epsilon_0$). Similarly one can treat the more general case – hydrogen like atoms – where the charge of nucleus is Ze and there is only one electron moving around it. Then the potential energy is $U_{vs}(r) = -\frac{bZe^2}{r}$. Since the results for latter case are obtained substituting $e^2 \rightarrow Ze^2$, we treat the hydrogen atom case only.

Differential equation for the radial part

$$-\frac{\hbar^2}{2M} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right) + \left(\frac{\hbar^2 l(l+1)}{2M r^2} - \frac{be^2}{r} \right) R = ER .$$

Since we are interested on the electronic states in hydrogen atom, we choose the total energy to be negative: $E < 0$. Positive energy case we treat later.

In solving the given differential equation we must follow similar steps, as in the case of harmonic oscillator: we change variables, find asymptotical solutions and then use the power series expansion.

If $E < 0$, we define the following variable and constants

$$\rho = \alpha r , \quad \alpha^2 = -\frac{8ME}{\hbar^2} , \quad \lambda = \frac{be^2}{\hbar} \left(-\frac{M}{2E} \right)^{1/2} \equiv \frac{2Mbe^2}{\alpha\hbar^2}$$

and our differential equation is

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R_{\lambda l}(\rho) = 0 .$$

(We added two indices λ and l , because the radial part depends from orbital quantum number and also from λ .) Since $0 \leq \rho < \infty$, we must analyse the cases $\rho \rightarrow \infty$ and $\rho \rightarrow 0$. For $\rho \rightarrow \infty$ we obtain the following equation

$$\frac{d^2 R}{d\rho^2} - \frac{R}{4} = 0 .$$

Special solutions are

$$R \sim e^{\pm \frac{\rho}{2}} .$$

The asymptotical solution for $\rho \rightarrow \infty$ is, of course

$$R \sim e^{-\frac{\rho}{2}} .$$

Next we try to find solution in form

$$R_{\lambda l}(\rho) = \rho^s L_{\lambda l}(\rho) e^{-\frac{\rho}{2}} ,$$

where we choose s , demanding that the solution behaves normally, if $\rho \rightarrow 0$ and $L_{\lambda l}(\rho)$ is power series function

$$L_{\lambda l}(\rho) = a_0 + a_1 \rho + a_2 \rho^2 + \dots = \sum_{k=0} a_k \rho^k .$$

Substituting $R_{\lambda l}(\rho)$ we get the differential equation

$$\rho^2 \frac{d^2 L}{d\rho^2} + \rho(2(s+1) - \rho) \frac{dL}{d\rho} + (\rho(\lambda - s - 1) + s(s+1) - l(l+1))L = 0 .$$

We see that when $\rho \rightarrow 0$, the following expression must be equal to zero

$$s(s+1) - l(l+1) = 0 .$$

We have two solutions

$$s = l \quad \text{and} \quad s = -(l+1) .$$

The second solution is not applicable (it is negative) and we must take $s = l$. Our equation is simplified

$$\rho \frac{d^2 L}{d\rho^2} + (2(l+1) - \rho) \frac{dL}{d\rho} + (\lambda - l - 1)L = 0 .$$

Substituting the power series function, we get

$$a_{p+1} = \frac{p+l+1-\lambda}{(p+1)(p+2l+2)} a_p .$$

As in the previous cases, the power serie must be finite (infinite serie behaves as e^ρ). Assuming that the power series function is polynomial and

$$a_p \neq 0 \quad ja \quad a_{p+1} = 0 ,$$

we get

$$\lambda = p + l + 1 \equiv n , \quad \text{where} \quad n = 1, 2, 3, \dots .$$

New quantum number n , is called principal quantum number and it determiner energy in hydrogen atom.

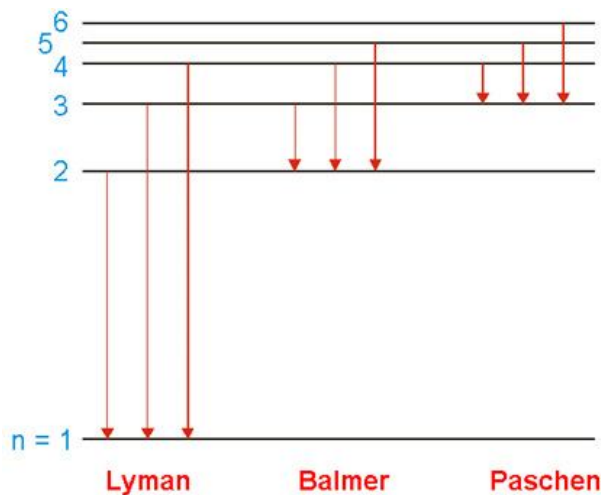
Since $p = 0, 1, 2, \dots$, we from the definition of principal quantum number get the following restrictions to possible values of angular quantum number

$$l + 1 \leq n .$$

Therefore, for a given n , orbital quantum number has values $l = 0, 1, 2, \dots, n - 1$.

10.4 Energy levels in hydrogen atom. From the definition of λ we have

$$E = -\frac{M b^2 e^4}{2 \hbar^2 \lambda^2} ,$$



and since $\lambda = n$, we get the energy values

$$E_n = -\frac{M b^2 e^4}{2 \hbar^2} \frac{1}{n^2} , \quad n = 1, 2, \dots .$$

Using Rydbergi constant

$$R = \frac{M b^2 e^4}{2 \hbar^3} \approx 2,07 \cdot 10^{16} \text{ s}^{-1} ,$$

energy is expressed as

$$E_n = -R \hbar \frac{1}{n^2} .$$

Later we see that the next important constant is Bohr radius

$$r_0 = \frac{\hbar^2}{M b e^2} \approx 0,53 \text{ \AA}$$

(in Bohr's theory it is the radius of the first stationary orbit).

10.5 Eigenfunctions. The radial part of eigenfunctions

$$R_{nl}(\rho) = \rho^l L_{nl}(\rho) e^{-\frac{\rho}{2}} ,$$

where $L_{nl}(\rho)$ are polynomials

$$L_{nl}(\rho) = \sum_{p=0}^{n-l-1} a_p \rho^p ,$$

which satisfy

$$\rho \frac{d^2 L_{nl}}{d\rho^2} + (2(l+1) - \rho) \frac{dL_{nl}}{d\rho} + (n-l-1) L_{nl} = 0$$

and are called Laquerre'i polynomials. $R_{nl}(\rho)$ is polymial ending on power $n-1$.

Normalization of radial functions we introduce tha normalization coefficient

$$R_{nl}(\rho) = N_{nl} \rho^l L_{nl}(\rho) e^{-\frac{\rho}{2}} .$$

Since

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

we must demand that

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi_{nlm}(r, \theta, \varphi)|^2 r^2 dr \sin \theta d\theta d\varphi = 1 .$$

Since the spherical functions were normalized, we for the radial part get

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1$$

and therefore N_{nl} is obtained from

$$|N_{nl}|^2 \int_0^\infty \left(\frac{2r}{nr_0}\right)^{2l} \left(L_{nl}\left(\frac{2r}{nr_0}\right)\right)^2 e^{-\frac{2r}{nr_0}} r^2 dr = 1 .$$

Here we do not perform the calculations and give only the final result

$$N_{nl} = \sqrt{\left(\frac{2}{nr_0}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} .$$

Next we write down radial functions for the lower states in hydrogen atom ($n = 1, 2, 3$)

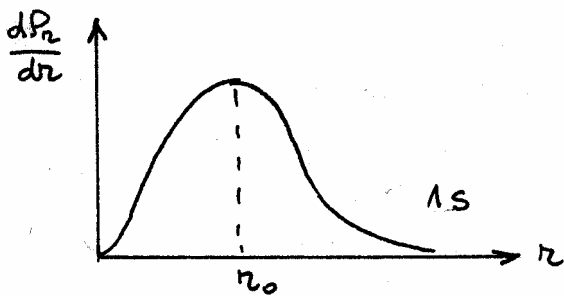
$$R_{10}(r) = \frac{2}{\sqrt{r_0^3}} e^{-\frac{r}{r_0}} ,$$

$$R_{20}(r) = \frac{1}{2\sqrt{2r_0^3}} \left(2 - \frac{r}{r_0}\right) e^{-\frac{r}{2r_0}} , \quad R_{21}(r) = \frac{1}{2\sqrt{6r_0^3}} \frac{r}{r_0} e^{-\frac{r}{2r_0}} ,$$

$$R_{30}(r) = \frac{2}{81\sqrt{3}r_0^3} \left(27 - 81\frac{r}{r_0} + 2\left(\frac{r}{r_0}\right)^2 \right) e^{-\frac{r}{3r_0}},$$

$$R_{31}(r) = \frac{2\sqrt{2}}{81\sqrt{3}r_0^3} \left(6 - \frac{r}{r_0} \right) \frac{r}{r_0} e^{-\frac{r}{3r_0}}, \quad R_{32}(r) = \frac{2\sqrt{2}}{81\sqrt{15}r_0^3} \left(\frac{r}{r_0} \right)^2 e^{-\frac{r}{3r_0}}.$$

Radial functions which are nonzero values at $r = 0$ are $R_{n0}(0) = \frac{2}{n\sqrt{n}r_0^3}$.



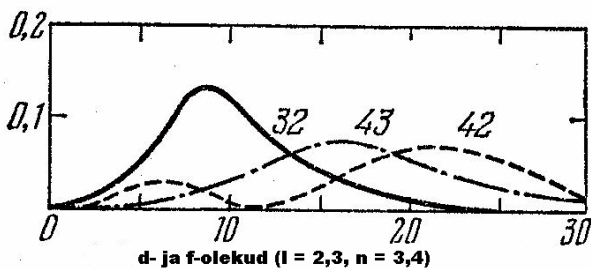
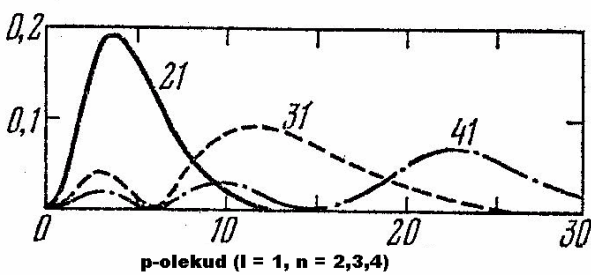
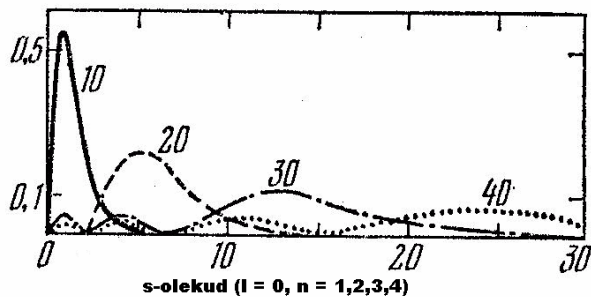
10.6 Radial probability density. Radial probability ($r, r+dr$)

$$dP_r = R_{nl}^2(r) r^2 dr,$$

gives for probability density

$$\rho(r) = R_{nl}^2(r) r^2.$$

Analyse the probability distribution for the ground state $1s$ ($n = 1, l = 0$). Probability maximum correspond to the Bohr radius.



The following graphs represent radial probability distributions for some lower lying energy levels : n ja l values are 10, 20, 21, 30, 31, 32, etc). Distance unit on these graphs is Bohr radius. Vertical axis represents probability density.

Comments:

1. For the hydrogen-like atoms one must do the change $e^2 \rightarrow Ze^2$, which in turn means, that in eigenfunctions Bohr radius $r_0 = \frac{\hbar^2}{Mbe^2}$ is changed to $\frac{r_0}{Z} = \frac{\hbar^2}{MbZe^2}$.

2. Mean values of r^{-1} , r^{-2} and r^{-3} . In § 29 we need the mean values of r^{-1} , r^{-2} and r^{-3} . These are

$$\langle r^{-1} \rangle = \frac{1}{r_0 n^2}, \quad \langle r^{-2} \rangle = \frac{1}{r_0^2 n^3 (l + 1/2)}, \quad \langle r^{-3} \rangle = \frac{1}{r_0^3 n^3 l (l + 1/2)(l + 1)}.$$

3. Positive total energy. We shortly deal with the $E > 0$ and demonstrate that energy is continuous, and electron and proton do not form a connected system (atom), since electron may move to infinity.

For $E > 0$ we introduce new variable and new constant

$$\rho = \alpha r, \quad \alpha^2 = \frac{8ME}{\hbar^2}, \quad \lambda = \frac{be^2}{\hbar} \left(\frac{M}{2E}\right)^{1/2} \equiv \frac{2Mbe^2}{\alpha \hbar^2},$$

which give the following equation for the radial part

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \frac{\lambda}{\rho} + \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0.$$

For $\rho \rightarrow \infty$ it gives

$$\frac{d^2 R}{d\rho^2} + \frac{1}{4} R = 0.$$

The general asymptotical solution is

$$R_\infty = A \sin \frac{\rho}{2} + B \cos \frac{\rho}{2}.$$

Since it is finite for every E the energy is not restricted may have arbitrary nonnegative values.

11. Energy levels of atoms

In hydrogen atom energy depends only from the principal quantum number n . To each energy level E_n there are n^2 different states:

$$E_n, \quad \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad l = 0, 1, \dots, n-1.$$

It appears that energy depends on principal number only for Coulomb potential energy (potential energy is reciprocal to distance r). For other atoms, since there are more electrons, electron potential energy is different from the Coulomb one, energy depends on two two quantum numbers – principal and orbital quantum numbers. As the first approximation, we assume that the potential energy is central symmetric ($U = U(r)$), therefore energy and states have the following general form

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

For a given n we similarly have $l = 0, 1, \dots, n-1$, but for each l the energy value is different and increasing with l .

There is no general proof that $E = E_{nl}$, but as we see later it explains the periodic properties of atoms. Here we treat one specific example which demonstrates that if the Coulomb potential is modified (dipole approximation) energy also depends on orbital quantum number. We take the following potential energy

$$U(r) = -\frac{be^2}{r} - \frac{de^2}{r^2},$$

where d is some constant and assume that the second term is very small compared with the first one. Since

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

we analyse only the radial part R_{nl} , which must satisfy

$$-\frac{\hbar^2}{2M} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right) + \left(\frac{\hbar^2 l(l+1)}{2M r^2} - \frac{be^2}{r} - \frac{de^2}{r^2} \right) R = ER.$$

Next we use the following trick: we try to write the above given equation in similar form, as it was in the hydrogen atom case. For that we write $1/r^2$ terms in the following form

$$\frac{\hbar^2 l'(l'+1)}{2Mr^2} = \frac{\hbar^2 l(l+1)}{2Mr^2} - \frac{de^2}{r^2},$$

which gives

$$l'(l'+1) = l(l+1) - \frac{2M d e^2}{\hbar^2}.$$

Next, l' is expressed via l . Solving the quadratic equation, we get

$$l' = -\frac{1}{2} \pm \frac{1}{2} \sqrt{(2l+1)^2 - \frac{8Mde^2}{\hbar^2}} .$$

We take the + sign (l' similarly to l is nonnegative). Assuming that the dipole term is small, we may write

$$l' = -\frac{1}{2} + \frac{1}{2} \sqrt{(2l+1)^2 - \frac{8Mde^2}{\hbar^2}} = -\frac{1}{2} + \frac{2l+1}{2} \left(1 - \frac{4Mde^2}{\hbar^2(2l+1)^2}\right)$$

and get the final result

$$l' = l - \frac{2Mde^2}{\hbar^2(2l+1)} .$$

We write it more shortly

$$l' = l - \sigma_l ,$$

where

$$\sigma_l = \frac{2Mde^2}{\hbar^2(2l+1)} .$$

The equation for radial part via l' is

$$-\frac{\hbar^2}{2M} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \right) + \left(\frac{\hbar^2 l'(l'+1)}{2M r^2} - \frac{be^2}{r} \right) R = ER .$$

In the hydrogen atom case we had the same equation, except that instead of l' there was orbital quantum number l . Since in hydrogen case we obtained energy

$$E_n = -\frac{R\hbar}{(p+l+1)^2} \equiv -\frac{R\hbar}{n^2} ,$$

then now we had similarly

$$E_{nl} = -\frac{R\hbar}{(p+l'+1)^2} \equiv -\frac{R\hbar}{n^{*2}} .$$

But now the quantum number n^* depends from the principal quantum number also from the orbital quantum number

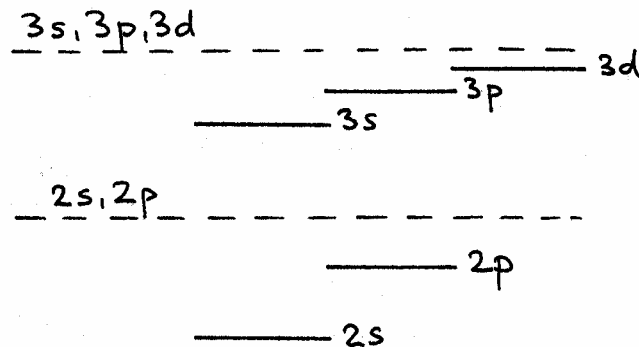
$$n^* = p + l' + 1 = p + l + 1 - \sigma_l \equiv n - \sigma_l ,$$

and so does energy

$$E_{nl} = -\frac{R\hbar}{(n - \sigma_l)^2} .$$

From the expression for σ_l we see that energy increases with l .

The above given simple example qualitatively explains the general structure of valence electron energy levels in alkali-metals (Li, K, Na, ...). Lithium (${}_3\text{Li}$) has three electrons, two which fill the K-shell, but the third one is on the outer L-shell. The ground state of the third electron is therefore 2s and its excited states are 2p, 3s, 3p, 3d. The corresponding energy levels from our dipole approximation model are shown in the following figure (dotted line gives energies corresponding to the Coulomb potential energy).



Such level structure qualitatively explains the spectral lines of alkali-metals.

Periodic table. Energy dependence E_{nl} allows to explain the periodic table of chemical elements. It is based on two principles: 1. Pauli exclusion principle, which states that each quantum state (n, l, m) may be occupied as maximum by two electron (and differ by spin projection σ (which we discuss later)); 2. In ground state energy is minimal. It means that electrons occupy the possible energy levels step by step, starting from the minimal energy.

To E_{nl} there corresponds $2l+1$ states ψ_{nlm} . Since the spin projection doubles the number of states, the total number of states is $2(2l+1)$. Maximal number of electrons on E_{nl} is therefore also $2(2l+1)$ and is determined by the orbital quantum number l . These states are also denoted by letters s, p, d, f, \dots (whic correspond to $l = 0, 1, 2, 3, \dots$). Therefore we have:

s – level	max	2 electrons,
p – level	max	6 electrons,
d – level	max	10 electrons,
f – level	max	14 electrons.

Electrons in atoms form electron shells, inside one shell difference between levels is small, but energy difference between shells are much greater. Each shell starts from some ns level and ends with np . The general strcture of shells is the following.

K – shell	$1s$	2 elektrons
L – shell	$2s, 2p$	8 elektrons
M – shell	$3s, 3p$	8 elektrons

<i>N</i> – shell	4 <i>s</i> , 3 <i>d</i> , 4 <i>p</i>	18 elektrons
<i>O</i> – shell	5 <i>s</i> , 4 <i>d</i> , 5 <i>p</i>	18 elektrons
<i>P</i> – shell	6 <i>s</i> , 5 <i>d</i> , 4 <i>f</i> , 6 <i>p</i>	32 elektrons
<i>Q</i> – shell	7 <i>s</i> , 6 <i>d</i> , 5 <i>f</i> , 7 <i>p</i>	32 elektrons .

Of course in each atom the energies are different. For example energy of 2*s* level in Lithium differs from that one in Boron, and so on.

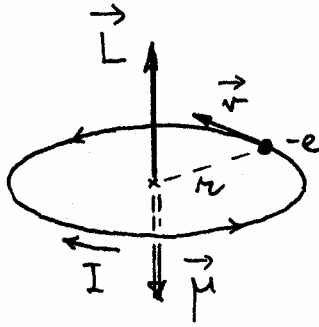
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

12. Atomar currents

In central symmetric field $U(r)$ elektron's energy depends on two quantum numbers n and l , elektron's state from three quantum numbers n, l ja m

$$E = E_{nl} , \quad \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi) = R_{nl}(r)P_{lm}(\theta)e^{im\varphi} .$$

From each elektron the exact value of energy depends on concrete form of $U(r)$, and similarly radial part $R_{nl}(r)$, but the general structure of wave function is always $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)P_{lm}(\theta)e^{im\varphi}$ (and we always choose $R_{nl}(r)$ and $P_{lm}(\theta)$ to be real valued functions).



Next we analyse the magnetic properties of electrons „moving“ in atoms. In classical physics one can find magnetic moment for electron moving on circular orbit in central symmetri field. Since the moving electron is at the same time electrical current, it has some magnetic moment which is expressed as

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

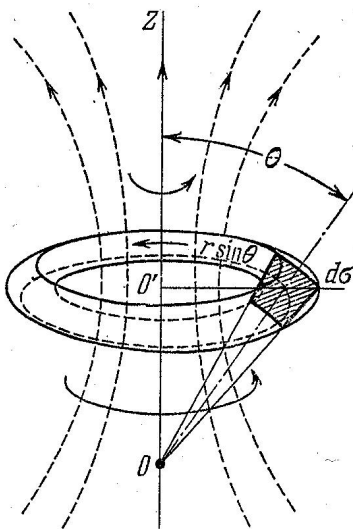
Since it depends on angular momentum, it is natural to assume that also in the microworld electrons have magnetic moments depending on their orbital quantum numbers. Next we prove that similar expression is also valid in quantum mechanics, but we must replace the physical quantities by its operators.

Electron current density equals the probability current density multiplied to charge $q = -e$

$$\vec{j} = -\frac{ie\hbar}{2M} (\psi_{nlm} (\nabla \psi_{nlm}^*) - \psi_{nlm}^* (\nabla \psi_{nlm}))$$

We calculate its components in spherical coordinates, where the components of gradient are

$$\nabla_r = \frac{\partial}{\partial r}, \quad \nabla_\theta = \frac{1}{r} \frac{\partial}{\partial \theta}, \quad \nabla_\varphi = \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} .$$



Simple calculation gives that the only nonzero component is the axial one

$$j_r = j_\theta = 0, \quad j_\varphi = -\frac{em\hbar}{M r \sin \theta} |\psi_{nlm}|^2 .$$

Next we calculate the magnetic moment. At first we consider the axial current pipe having its cross section area $d\sigma$. Current in pipe

$$dI = j_\varphi d\sigma .$$

Its magnetic moment is

$$\begin{aligned} d\mu_z &= dI \cdot S = dI \pi r'^2 = j_\varphi \pi (r \sin \theta)^2 d\sigma = \\ &= -\frac{em\hbar \pi}{M} r \sin \theta |\psi_{nlm}|^2 d\sigma . \end{aligned}$$

The total magnetic moment is sum over all possible current pipes, which is integral

$$\mu_z = -\frac{em\hbar}{2M} \int |\psi_{nlm}|^2 2\pi r \sin \theta d\sigma = -\frac{em\hbar}{2M} .$$

($dV = 2\pi r \sin \theta d\sigma$ is a volume of current pipe and wave function is normed).

Therefore electron's magnetic moment in a state (n, l, m) is

$$\mu_z = -\frac{e\hbar}{2M} \cdot m \equiv -\mu_B m ,$$

where $\mu_B = e\hbar/2M$ is Bohr magneton ($\mu_B = 9,23 \cdot 10^{-24} \text{ J/T}$). μ_z depends on the projection of angular momentum and for that reason the quantum number m is called magnetic quantum number.

Since $L_z = \hbar m$, we have

$$\mu_z = -\frac{e}{2M} L_z .$$

In operator form it is written as

$$\hat{\mu}_z = -\frac{e}{2M} \hat{L}_z ,$$

or more generally

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

Electron has also intrinsic angular momentum – spin and intrinsic magnetic moment. The role of spin and its magnetic moment we treat later.

13. Schrödinger equation (external electromagnetic field)

We started with Schrödinger equation

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

where the Hamilton operator is

$$\hat{H} = -\frac{\hbar^2}{2M} \Delta + U(\vec{r}, t) = \frac{1}{2M} (-i\hbar \nabla)^2 + U(\vec{r}, t) .$$

It is applicable in the case of classical nonrelativistic conservative force field. In order to apply it in the case of external electromagnetic field we next modify it.

13.1 Electric and magnetic fields, potentials. Electric and magnetic fields are characterized by two vectors

$$\vec{E} \quad \text{and} \quad \vec{B} ,$$

which on the other hand are described by two potentials \vec{A} and ϕ , whereas

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} - \text{grad} \phi, \quad \vec{B} = \text{rot } \vec{A}.$$

In Schrödinger equation we use potential functions and therefore the Schrödinger equation is modified using the following substitutions (q is electrical charge of particle)

$$\hat{p} \rightarrow \hat{p} - q\vec{A} \equiv -i\hbar\nabla - q\vec{A}$$

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$$\hat{E} \equiv i\hbar \frac{\partial}{\partial t} \rightarrow \hat{E} - q\phi \equiv i\hbar \frac{\partial}{\partial t} - q\phi.$$

We obtain the following

$$i\hbar \frac{\partial \Psi}{\partial t} - e\phi \Psi = \frac{1}{2M} (-i\hbar\nabla - e\vec{A})^2 \Psi + U(\vec{r}, t) \Psi.$$

Usually it is written in “traditional” form

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2M} (-i\hbar\nabla - e\vec{A})^2 \Psi + e\phi \Psi + U(\vec{r}, t) \Psi \equiv \hat{H} \Psi,$$

Where the Hamilton operator in the presence of external electromagnetic field is the following

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

In the last equality we denoted the sum of potential energies simply by U' (later we omit prim, but remember that it is sum of classical mechanical potential energy and electrostatical potential energy).

13.2 Minimal replacement. Usually the above given replacement is called minimal replacement, since it is the simplest possibility to introduce external field. What is the physical meaning of our replacement. We start with

$$\hat{p} \rightarrow \hat{p} - q\vec{A} \equiv -i\hbar\nabla - q\vec{A}.$$

From electrodynamics we know that if we consider a system of charged particles and electric and magnetic fields, we must take into consideration momentum and energy of particles and also momentum and energy of field, in other words we consider the total momentum and total energy. Total momentum is the sum

$$\vec{P} = \vec{p} + q\vec{A}.$$

($q\vec{A}$ is momentum of field). Since Schrödinger equation describes particles in external field, the must be momentum of particles described, which means that the momentum operator is

$$\vec{p} = \vec{P} - e\vec{A}$$

(now the operator of total momentum is $-i\hbar\nabla$).

13.3 Hamilton operator. If we express the square of momentum, we get

$$\hat{H} = -\frac{\hbar^2}{2M}\Delta + \frac{iq\hbar}{M}\vec{A}\cdot\nabla + \frac{iq\hbar}{2M}\text{div}\vec{A} + \frac{q^2}{2M}\vec{A}^2 + U .$$

Of course our new equation is quite complicated, concerning especially the vector potential terms. In electrodynamics different restrictions on potentials (gauges) are used. In the case of static fields the gauge $\text{div}\vec{A} = 0$ is mostly used. In the weak fields usually the term with vector potential square, as small, is also omitted.

In the following we mostly assume that $\text{div}\vec{A} = 0$. The Hamilton operator is

$$\hat{H} = -\frac{\hbar^2}{2M}\Delta + U + \frac{iq\hbar}{M}\vec{A}\cdot\nabla + \frac{q^2}{2M}\vec{A}^2 \equiv \hat{H}_0 + \hat{H}(\vec{A}) ,$$

where

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

is the “standard” Hamiltonian operator, we used previously, and

$$\hat{H}(\vec{A}) = \frac{iq\hbar}{M}\vec{A}\cdot\nabla + \frac{q^2}{2M}\vec{A}^2$$

is the part depending on vector potential.

Probability density current is (prove)

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

13.4 Elektron Hamiltonian operator for external homogeneous magnetic field. In our quantum mechanics course we mostly analyse electrons in atoms and external fields, therefore the electric charge in our equations is $q = -e$. External field in atoms is practically homogeneous and therefore we mostly treat external fields, acting on electrons in atoms as homogeneous.

Next we assume that external homogeneous magnetic field is directed towards the z-axis. Therefore the magnetic field (magnetic induction) is

$$\vec{B} = (0, 0, B) .$$

That field is described with the help of different vector potentials. We use mostly the following three ones

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

(Prove that they all satisfy $\text{div}\vec{A} = 0$ and give the same magnetic field). Which of them to use depends on problem we had to solve.

Using the first vector potential we calculate $-i\hbar\vec{A}\cdot\nabla$:

$$-i\hbar\vec{A}\cdot\nabla = -i\hbar\left(A_x\frac{\partial}{\partial x} + A_y\frac{\partial}{\partial y}\right) = \frac{i\hbar B}{2}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right).$$

Since $\hat{L}_z = -i\hbar(x\partial/\partial y - y\partial/\partial x)$, we can write it as

$$-i\hbar\vec{A}\cdot\nabla = \frac{B}{2}\hat{L}_z.$$

Since $\vec{A}^2 = B^2(x^2 + y^2)/4$, we get the following Hamilton operator for electrons in homogeneous magnetic field

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M}\Delta + U - \frac{ie\hbar}{M}\vec{A}\cdot\nabla + \frac{e^2}{2M}\vec{A}^2 = \\ &= -\frac{\hbar^2}{2M}\Delta + U + \frac{eB}{2M}\hat{L}_z + \frac{e^2 B^2}{8M}(x^2 + y^2).\end{aligned}$$

We use it in paragraphs 24,25. As we see, our equation takes into consideration electron's orbital magnetic moment, since

$$\hat{\mu}_z = -\frac{e}{2M}\hat{L}_z.$$

Electron has due to its spin also intrinsic magnetic moment $\vec{\mu}_s$, and we in paragraph 18 introduce electron spin and once more modify our equation to take into account also intrinsic magnetic moment.