§5.2. Atomic Structure Inferred from Hydrogen Atom

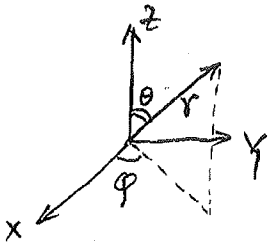
As explained in the last lecture, the atomic structure problems are to solve the energy eigenvalue equations, i.e., the stationary-state Schrödinger equation to derive energy eigenstates and eigenvalues.

Hydrogen atom is the only atomic structure that can be solved from the Schrödinger equation exactly. Therefore, it is representative to illustrate the approaches and fundamental principles in atomic structure study. We will use H to study the energy levels determined by the main force (electrostatic interaction between the nucleus and the electron), the spin-orbit angular momentum coupling, the nuclear spin and electron angular momentum coupling, the isotope shift, the external electric and magnetic field effects.

Then we will use Helium atom as an example to illustrate multielectron's interactions and how they complicate structures.

1. Hydrogen energy eigenvalues and eigenstate in Coulomb potential

* For this problem, we use the $\{|\vec{r}\rangle\}$ representation, and project the states and operators to a spherical coordinate system (r, θ, φ)



$$\hat{H}\psi = E\psi = \left(\frac{\hat{p}^2}{2\mu} + \hat{V}\right)\psi \qquad (1)$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = E\psi \qquad \hat{V} = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\mu = \frac{m_e M}{m_e + M}$$

In the first step, we only consider the electrostatic force (Coulomb) between the nucleus and electron. Write ∇^2 in the spherical coordinates, then we have

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right] - \frac{\hbar^2}{2\mu}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

$$+ V(r)\psi = E\psi. \qquad (2)$$

Recall $\hat{\vec{l}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$, (3)

then the second term on the left side of the hydrogen equation is proportional to $\hat{\vec{l}}^2$. Thus,

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{\hat{\vec{l}}^2}{2\mu r^2}\psi+V(r)\psi=E\psi. \quad (4)$$

On the left side, the 1st and 3rd term only concern r, while the 2nd term is only related to θ and φ. Therefore, we can solve the equation using separation of variables by assuming a solution of the form: $\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$. (5)

Substitute this solution to the above equation, we get

$$\frac{1}{\hbar^2 Y}\hat{\vec{l}}^2 Y=\frac{1}{R}\frac{d}{dr}\left(r^2\frac{d}{dr}R\right)+\frac{2\mu r^2}{\hbar^2}[E-V(r)]=\alpha, \quad (6)$$

where α is a constant for the separation of variables.

Therefore, we get two equations from this:

$$\begin{cases}\left[-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\alpha\hbar^2}{2\mu r^2}+V(r)\right]R(r)=ER(r) & (7)\\ \hat{\vec{l}}^2 Y(\theta,\varphi)=\alpha\hbar^2 Y(\theta,\varphi) & (8)\end{cases}$$

Both are eigenvalue equations; the first is for the radial direction, an energy eigenvalue equation; the second is an eigenvalue equation for the square of angular momentum.

* Let's solve the $\hat{\vec{l}}^2$ eigenvalue equation first. This equation is independent of $V(r)$, thus, a general equation for the central field potential case. We further separate variables:

$$Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi) \quad (9)$$

Substitute this expression and $\hat{\vec{l}}^2$ expression into the $\hat{\vec{l}}^2$ eigenvalue equation, we have

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\alpha\sin^2\theta=-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=\nu \quad (10)$$

where ν is another constant for the separation of variables. Thus, we get another two equations:

$$\begin{cases} \dfrac{d^2\Phi}{d\varphi^2} + \nu\Phi = 0 & (11) \\ \dfrac{\sin\theta}{\Theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right) + \alpha\sin^2\theta = \nu. & (12) \end{cases}$$

The general solution for the first equation is given by

$$\begin{cases} \Phi = Ae^{i\sqrt{\nu}\varphi} + Be^{-i\sqrt{\nu}\varphi}, & \text{for } \nu \neq 0 \\ \Phi = C + D\varphi, & \text{for } \nu = 0 \end{cases} \quad \begin{matrix} A.B.C.D \\ \text{are constants.} \end{matrix} \quad (13)\ (14)$$

As a wavefunction, $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, i.e., single value in space. Thus, for $\nu = 0$, we must have $D = 0$; for $\nu \neq 0$, we must have $\sqrt{\nu} = m$, where m is an integer. This gives us a special solution to the first equation as:

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \cdots \qquad (15)$$

Here, the coefficient $\frac{1}{\sqrt{2\pi}}$ is obtained by the normalization condition

$$\int_0^{2\pi} \Phi_m^* \Phi_m \, d\varphi = 1. \qquad (16)$$

Apparently, Φ_m is an eigenvalue function for $\hat{l}_z = -i\hbar\frac{\partial}{\partial\varphi}$:

$$\hat{l}_z\Phi_m = -i\hbar\frac{\partial}{\partial\varphi}\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\Phi_m \qquad (17)$$

∴ the eigenvalues of $\hat{l}_z$ is $l_z = m\hbar$, $m = 0, \pm 1, \pm 2, \cdots$ (18)

$\hat{l}_z$ is the z-component of the angular momentum vector.

* Substitute $\sqrt{\nu} = m$ into the second equation above, we obtain

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \alpha\sin^2\theta = m \qquad (19)$$

Let $u = \cos\theta$, then $\Theta(\theta) = P(u)$. The above equation becomes

$$\frac{d}{du}\left[(1-u^2)\frac{dP}{du}\right] + \left(\alpha - \frac{m^2}{1-u^2}\right)P = 0 \qquad (20)$$

This equation can be solved analytically, but we only list the results here. The solution requires

$$\alpha = l(l+1), \quad l = 0, 1, 2, \cdots \tag{21}$$

$$|m| \leq l, \quad m = 0, \pm 1, \pm 2, \cdots, \pm l. \tag{22}$$

∴ From $\hat{\vec{l}}^2$ equation, we get

$$\hat{\vec{l}}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m} \tag{23}$$

i.e; $Y_{l,m}$ is an eigen function of $\hat{\vec{l}}^2$, and the corresponding eigen-value is $l^2 = l(l+1)\hbar^2$. (24)

l is called the quantum number of angular momentum.

The solution to equation (20) is

$$P(u) = P_l^{|m|}(u) \tag{25}$$

where $$P_l^{|m|}(u) = (1-u^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{du^{|m|}} P_l(u) \tag{26}$$

and $$P_l(u) = \frac{1}{2^l l!} \frac{d^l}{du^l} (u^2-1)^l \tag{27}$$

From above, we obtain the eigen function for $\hat{\vec{l}}^2$ as

$$Y_{l,m}(\theta, \varphi) = N_{lm} P_l^{|m|}(\cos\theta) e^{im\varphi} \tag{28}$$

where N_{lm} is the normalization constant and obtained by

$$\int_0^{2\pi} \int_0^{\pi} Y_{l,m}^*(\theta,\varphi)\, Y_{l,m}(\theta,\varphi) \sin\theta \, d\theta \, d\varphi = 1. \tag{29}$$

$$\Rightarrow N_{lm} = \sqrt{\frac{(l-|m|)!\,(2l+1)}{4\pi\,(l+|m|)!}}. \tag{30}$$

For $l = 0, 1, 2$, the states are called s, p, d states.

$l=0$: $Y_{0,0} = \frac{1}{\sqrt{4\pi}}$; $l=1$, $Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$, $Y_{1,\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$

$l=2$: $Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$, $Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$

and $Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$

Notice that $|Y_{l,m}|^2$ is independent of φ, but only dependent on θ. This implies that the probability of electron appearance is rotational symmetric about the z-axis.

* Parity of states: When making an operation of inversion transformation ($x \to -x$, $y \to -y$, $z \to -z$, i.e., $\vec{r} \to -\vec{r}$) on a state wave function $\psi(\vec{r})$, if $\psi(\vec{r})$ and $\psi(-\vec{r})$ have the following relations

$$\psi(\vec{r}) = -\psi(-\vec{r}) \qquad (31)$$

$$\text{or } \psi(\vec{r}) = +\psi(-\vec{r}) \qquad (32)$$

then we say the state has parity: odd parity for (31) and even parity for (32).

"Parity is a measure of the symmetry of interactions under spatial inversion". In QM, parity is defined as an operator $\hat{\Pi}$, that

$$\left.\begin{aligned} \hat{\Pi}\,|\vec{r}\rangle &= |-\vec{r}\rangle \\ \text{or } \hat{\Pi}\,\psi(\vec{r}) &= \psi(-\vec{r}) \end{aligned}\right\} \quad (33)$$

Apparently, $\hat{\Pi}^2 \psi(\vec{r}) = \hat{\Pi}\,\psi(-\vec{r}) = \psi(\vec{r})$

$\therefore$ $\hat{\Pi}^2$ has an eigenvalue of 1, and $\hat{\Pi}$ has eigenvalues of ± 1.

For the $Y_{l,m}$ we obtained above, in spherical coordinates, under the spatial inversion ($r \to r$, $\theta \to \pi - \theta$, $\varphi \to \varphi + \pi$), we have

$$Y_{l,m}(\pi-\theta, \varphi+\pi) = (-1)^l Y_{l,m}(\theta, \varphi) \qquad (34)$$

So, when l is even number, $Y_{l,m}$ has even parity;
when l is odd number, $Y_{l,m}$ has odd parity.

In general, if there is no external force, Hamiltonian operator $\hat{H}$ remains unchanged under parity operator, therefore, the parity of state wave function is constant, and does not change with time.

* Now let's solve the energy eigenvalue equation (7).

Let $K^2 = -\frac{2\mu E}{\hbar^2}$, $\gamma = \frac{\mu e^2 Z}{4\pi\varepsilon_0 k\hbar^2}$, $\rho = 2kr$. (35)

then Equation (7) becomes $\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{\gamma}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R = 0$ (36)

This equation is solved under the boundary condition

$$R(r) \to \infty \text{ as } r \to \infty. \quad (37)$$

We skip the procedure of solving this equation, but list results as follows: the eigenvalues of energy are

$$E_n = -\frac{\mu e^4 Z^2}{32\pi^2\varepsilon_0^2\hbar^2 n^2}, \quad n = 1, 2, 3, \cdots \quad (38)$$

The normalized eigenvalue radial wave function $R_{n,l}(r)$ is

$$R_{n,l}(r) = -\left\{\left(\frac{2Z}{na_1}\right)^3 \frac{[n-(l+1)]!}{2n[(n+l)!]^3}\right\}^{1/2} \times \exp\left(-\frac{Zr}{na_1}\right)\left(\frac{2Zr}{na_1}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_1}\right) \quad (39)$$

where a_1 is the first Bohr radius, L is the associated Laguerre function. We also have

$$n \geq l+1 \quad (40).$$

Note: $a_1 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \approx 0.053\text{nm}$.

Normalization condition for $R(r)$ is $\int |R|^2 \, dr = 1$.

Note: In this whole procedure, we used $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$.

This is for not only hydrogen atom itself, but also for other hydrogen-like ion, e.g., He^+, Li^{++}, Be^{+++}

In other words, the nucleus charge is Ze, and electron charge is $-e$. $Z = 1, 2, 3, 4, \cdots$ for H, He^+, Li^{++}, Be^{+++}, $\cdots$.

The reduced mass $\mu = \frac{meM}{me+M}$, where M will be different for different nucleus.

Thus, from the QM calculation, we obtain three quantum numbers (n, ℓ, and m) and three eigenvaluation equations:

$$\begin{cases} \hat{H}\psi_{n,\ell,m} = +E_n \psi_{n,\ell,m} \\ \hat{\vec{L}}^2 \psi_{n,\ell,m} = \ell(\ell+1)\hbar^2 \psi_{n,\ell,m} \\ \hat{L}_z \psi_{n,\ell,m} = m\hbar \psi_{n,\ell,m} \end{cases}$$

where $\psi_{n,\ell,m} = R_{n,\ell}(r)\, Y_{\ell,m}(\theta,\phi)$, $E_n = -\dfrac{\mu z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$, $n = 1, 2, 3, \cdots$

Only under the central field Coulomb force, although the wave function depends on 3 quantum numbers (n, ℓ, m), the energy eigenvalues are only dependent on n. This means that eigenvalue functions are degenerate, i.e., many different wave functions correspond to the same energy eigenvalue.

For each n, $\because n \geq \ell+1$, $\therefore \ell = 0, 1, 2, 3, \cdots, n-1$,

For each ℓ, $\because \ell \geq |m|$ $\therefore m = -\ell, -\ell+1, \cdots, 0, \cdots \ell-1, \ell$.

i.e., there are n of ℓ, and $2\ell+1$ of m.

Thus, the degeneracy factor for each n is given by

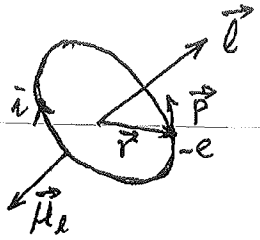
$$\sum_{\ell=0}^{n-1} (2\ell+1) = n^2.$$

i.e., the degeneracy for hydrogen atom and hydrogen-like ions is n^2 for the principal quantum number n.

2. Electron Spin-Orbit Interaction and Energy Fine Structure

An electron moves around a nucleus — what's going to happen?

(1) From Classical Physics, (see figure on the left)



If looking from mechanical aspect, there is angular momentum given by $\vec{l} = \vec{r} \times \vec{p}$,

where $\vec{l}$ is electron orbital angular moment

($\vec{l}$ direction is given by the right-hand law)

$\vec{r}$ is the position vector of the electron relative to the nucleus

$\vec{p}$ is the electron momentum.

When looking from electromagnetic theory, a current in circle will produce a magnetic dipole moment $\vec{\mu}_l$ given by

$$\vec{\mu}_l = i S \vec{n}_0$$

where i is the current, S is the area of the circle, and $\vec{n}_0$ is the unit vector perpendicular to the circle surface.

$\vec{\mu}_l$ direction is also given by the right-hand law, i.e., close your right hand in the current direction, then your thumb points to the direction of the magnetic field produced by the current. Since the electron has negative charge, the current is in opposite direction of electron movement. Thus, the magnetic moment $\vec{\mu}_l$ points to the opposite direction of the angular momentum $\vec{l}$. In classical physics, we can get

$$\vec{\mu}_l = i S \vec{n}_0 = -ef \cdot \pi r^2 \cdot \vec{n}_0 = -\frac{ev}{2\pi r} \pi r^2 \vec{n}_0$$

$$= -\frac{e}{2} v r \vec{n}_0 = \frac{-e}{2m_e} \cdot \underbrace{m_e v r}_{\Rightarrow l} \vec{n}_0 = -\frac{e}{2m_e} \vec{l}$$

Let $\gamma = \frac{e}{2m_e}$, $\therefore \vec{\mu}_l = -\gamma \vec{l}$ (γ is called gyromagnetic ratio)

In a homogeneous magnetic field, a magnetic moment will experience a moment of force: $\vec{\tau} = \vec{\mu}_l \times \vec{B}$, (also called torque)

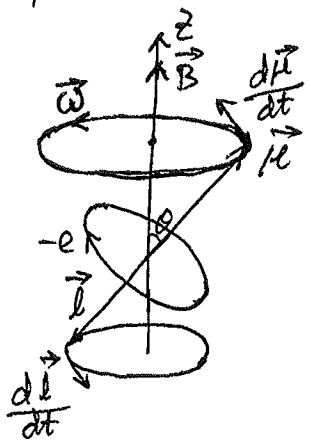
where $\vec{\tau}$ is the moment of force, $\vec{B}$ is the magnetic field.

(See appendix), $\frac{d\vec{l}}{dt} = \vec{\tau} = \vec{\mu}_l \times \vec{B}$

$$\therefore \frac{d\vec{\mu}_l}{dt} = -\gamma \frac{d\vec{l}}{dt} = -\gamma \vec{\mu}_l \times \vec{B} = \vec{\omega} \times \vec{\mu}$$

where $\vec{\omega} \equiv \gamma \vec{B}$ is the angular speed of the magnetic moments precession around $\vec{B}$.

The classical picture is that the electron moves around the nucleus, producing a magnetic moment $\vec{\mu}_l$, and then the $\vec{\mu}_l$ precesses around an external magnetic field $\vec{B}$ with an angle of θ and angular speed of ω.



(2) From Quantum mechanics: Similar to classical physics, the QM magnetic moment $\mu_l \propto l$, but its magnitude is quantized and given by $\sqrt{l^2} = \sqrt{l(l+1)}\,\hbar$.

Therefore, in QM, magnetic moment is given by

(orbital magnetic moment) $\mu_l = -\gamma \mathbf{l} = -\sqrt{l(l+1)}\,\hbar\gamma = -\sqrt{l(l+1)}\,\frac{e\hbar}{2m_e}$.

Define Bohr magneton $\mu_B = \frac{e\hbar}{2m_e} = 0.9274 \times 10^{-23}\ J \cdot T^{-1}$

(Bohr magneton is the minimum unit of orbital magnetic moment — an important constant) $= 0.9274 \times 10^{-23}\ A \cdot m^2$

$= 0.009274\ mA \cdot (nm)^2$

$= 0.5788 \times 10^{-4}\ eV \cdot T^{-1}$

$$\therefore \mu_l = -\sqrt{l(l+1)}\,\mu_B = -\sqrt{l(l+1)}\,g_l\,\mu_B$$

z-component: $\mu_z = -m_l \mu_B = -m_l g_l \mu_B$ $(l_z = m_l \hbar)$

Here, g_l is call the g-factor for orbital magnetic moment

$$g_l = \frac{\text{measure } \mu_z \text{ in } \mu_B \text{ unit (component of } \mu \text{ in } z\text{-direction)}}{\text{projection of angular moment in } z\text{-direction (in } \hbar \text{ unit)}}$$

$$g_l = 1.$$

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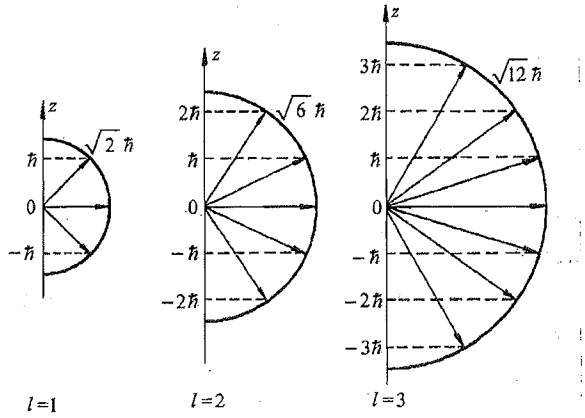
(3) Quantization of angular momentum / magnetic moment:

1). The magnitude of angular momentum is quantized

$$l^2 = l(l+1)\hbar^2$$

$$\mu_l = -\sqrt{l(l+1)}\,\mu_B\, g_l.$$

2). The spatial direction of angular momentum is also quantized



Orbital Angular momentum and its z-component (Both are quantized)

Since $l = 0, 1, 2, 3 \cdots$

$$l = \sqrt{l^2} = \sqrt{l(l+1)}\,\hbar \text{ — quantized.}$$

Since $m_l = l, l-1, \cdots, 0, \cdots, -l+1, -l.$

$$\therefore l_z = m_l \hbar \text{ — quantized.}$$

For $l=1$, $m_l = 1, 0, -1$

For $l=2$, $m_l = 2, 1, 0, -1, -2$

For $l=3$, $m_l = 3, 2, 1, 0, -1, -2, -3.$