Fine Structure of a Hydrogen Atom

Recap Chapter 4.2 Hydrogen Atom

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{1}{r}$$

$\Longrightarrow$ Bohr energy

$$E_0 = -\frac{13.6}{n^2}\mathrm{eV}$$

Hierarchy Bohr

Bohr	$\alpha^2 \mathrm{MC}^2$
Fine Structure	$\alpha^4 \mathrm{MC}^2$
Lamb Shift	$\alpha^5 \mathrm{MC}^2$
Hydro splitting	$\left(\frac{m}{m_p}\right)\alpha^7 \mathrm{MC}^2$

Table 1.

Fine structure = (spinless) relativistic + spin-orbit coupling

Problem. (6.11) Express Bohr energy in terms of α and MC^2

Page 149 Eq [4.70]

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = -\frac{\mathrm{MC}^2}{2}\left(\frac{e^2}{4\pi\epsilon_0\pi C}\right)^2\frac{1}{n^2} = -\frac{1}{2}\mathrm{MC}^2\alpha^2\frac{1}{n^2}$$

1 Spinless Relativistic Correction

In QM, Kinetic energy $T = {}^{p^2}\!/_{2m} \to -{}^{\hbar^2}\!/(2m)\nabla^2$, where $\vec{p} = -\mathrm{i}\hbar\vec{\nabla}$, $\hat{\vec{p}}e^{\mathrm{i}\vec{p}\cdot\vec{x}/\hbar}$

Relativistic kinetic energy

$$T = \frac{mv^2}{\sqrt{1-\left(\frac{v}{c}\right)^2}} - mc^2, \quad p = \frac{mv}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$$

Note that

$$p^2c^2 + m^2c^4 = \frac{m^2v^2c^2}{1-\left(\frac{v}{c}\right)^2} + m^2c^4 = \frac{m^2v^2c^2 + m^2c^4\left(1-\left(\frac{v}{c}\right)^2\right)}{1-\left(\frac{v}{c}\right)^2}$$

gives us

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 = mc^2\left(\sqrt{1+\left(\frac{p}{mc^2}\right)^2} - 1\right).$$

By Taylor expansion

$$\begin{aligned} T &= mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc^2}\right)^2 - \frac{1}{8}\left(\frac{p}{mc^2}\right)^4 + \cdots - 1\right] \\ &= \underbrace{\frac{p^2}{2m}}_{\text{unperterbed term}} - \frac{p^4}{8m^3c^2} + \cdots. \end{aligned}$$

Therefore,

$$H'_r = -\frac{p^4}{8m^3c^2} = \frac{\left(\frac{p^2}{2m}\right)^2}{2mc^2} \approx -\frac{(10\text{eV})^2}{10^6\text{eV}}$$

1st order correction to energy

$$E_r^{(1)} \equiv \langle \psi_{nlm} | H'_r | \psi_{nlm} \rangle \tag{1}$$

$n=1, \quad l=0, \quad m=0$

$n=2, \quad l=0,1, \quad m=0,\pm 1$ Degenerate case.

Question 1. *Why the non-degenerate correction (1) can be used in hydrogen atom?*

To answer Question 1, we prove the following theorem:

Theorem 1. *Given Hermitian operator $\hat{A}$ and $[\hat{A}, H^{(0)}]=0$, $[\hat{A}, H']=0$. If $\psi_a^{(0)}$ and $\psi_b^{(0)}$ are the eigenstate of $\hat{A}$ with distinct eigenstates*

$$\hat{A}\psi_a^{(0)} = \mu\psi_a^{(0)}, \quad \hat{A}\psi_b^{(0)} = \nu\psi_b^{(0)}, \quad \text{and} \quad \mu \neq \nu$$

then

$$\left\langle \psi_a^{(0)} | H' | \psi_b^{(0)} \right\rangle = 0.$$

Proof. Note that

$$[\hat{A}, H'] = 0 \Longrightarrow \left\langle \psi_a^{(0)} | [\hat{A}, H'] | \psi_b^{(0)} \right\rangle = 0$$

which implies

$$\left\langle \psi_a^{(0)} | \hat{A} H' | \psi_b^{(0)} \right\rangle - \left\langle \psi_a^{(0)} | H' \hat{A} | \psi_b^{(0)} \right\rangle = 0.$$

Therefore,

$$(\mu - \nu)\left\langle \psi_a^{(0)} | H' | \psi_b^{(0)} \right\rangle = 0.$$

The proof is finished by the fact that $\mu - \nu \neq 0$. □

In the present case,

$$\hat{A} \to L^2, L_z, \quad H' \propto p^4, \quad H^{(0)} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}.$$

We need

$$[H^{(0)}, L^2] = 0, \quad [H^{(0)}, L_z] = 0.$$

This is known because $H^{(0)}, L^2$ and L_z share ψ_{nlm} as eigenstate.

Also, we need

$$[p^4, L^2] = 0, \quad [p^4, L_z] = 0. \tag{2}$$

To show Eq. (2) holds, we note that

$$\boxed{[AB, C] = A[B, C] + [A, C]B}$$

which implies

$$[p^4, L_z] = p^2[p^2, L_z] + [p^2, L_z]p^2.$$

In page 167 Problem 4.19 (c), we proved $[p^2, L_z] = 0$.

Recap

$$[L_z, p^2] = [L_z, p_x^2] + [L_z, p_y^2] + [L_z, p_z^2]$$

where

$$L_z = xp_y - yp_x \Longleftarrow \vec{L} = \vec{r} \times \vec{p}.$$

The last term $[L_z, p_z^2]$ vanishes by definition of L_z. Thus,

$$[L_z, p^2] = [L_z, p_x]p_x + p_x[L_z, p_x] + [L_z, p_y]p_y + p_y[L_z, p_y]$$

where

$$[L_z, p_x] = [xp_y, p_x] - [yp_x, p_x], \quad \text{and} \quad [L_z, p_y] = 0$$

and

$$[xp_y, p_x] = x[p_y, p_x] + [x, p_x]p_y = \mathrm{i}\hbar p_y.$$

Thus,

$$[L_z, p^2] = 0$$

For p^4, L_x, L_y, L_z are equivalent. Similarly, $L^2 = L_x^2 + L_y^2 + L_z^2$, we have $[L^2, p^2] = 0$. Finally, Question 1 is answered!

Now, we evaluate $\langle \psi_{nlm} | H' | \psi_{nlm} \rangle$

[Trick:] $p^2 |\psi_{nlm}\rangle = 2m(E_n - \hat{V})|\psi_{nlm}\rangle \Longrightarrow$

$$\langle p^2 \psi_{nlm} | p^2 \psi_{nlm} \rangle = (2m)^2 \langle \psi_{nlm} | (E_n - \hat{V}) | \psi_{nlm} \rangle$$

which imples

$$E_r^{(1)} = -\frac{1}{8m^3c^2}(2m)^2(E_n^2 - 2E_n\langle V \rangle + \langle V^2 \rangle)$$

where

$$\langle V \rangle \equiv \langle \psi_{nlm} | \hat{V} | \psi_{nlm} \rangle$$

and

$$\langle V^2 \rangle \equiv \langle \psi_{nlm} | \hat{V}^2 | \psi_{nlm} \rangle.$$

For Hydrogen atom, $V = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ we evaluate $\langle V \rangle$ by using Eq. [3.97]: Stationary vivid theorem in 1D

$$2\langle T \rangle = \left\langle x \frac{\mathrm{d}V}{\mathrm{d}x} \right\rangle$$

In 3D:

$$2\langle T\rangle = \langle \vec{r}\cdot\nabla V\rangle. \quad \vec{r} \triangleq (x,y,z)$$

Because $V(\vec{r})$ has the spherical symmetry, so we use spherical coordinates

$$\nabla V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\right)\hat{r} + \hat{\theta}\ldots + \hat{\phi}\ldots$$

Thus,

$$2\langle T\rangle = \langle \vec{r}\cdot\nabla V\rangle = \frac{e^2}{4\pi\epsilon_0}\left\langle \frac{1}{r^2}\vec{r}\cdot\hat{r}\right\rangle = \left\langle \frac{1}{4\pi\epsilon_0}\frac{1}{r}\right\rangle = -\langle V\rangle.$$

Note that

$$\langle T\rangle + \langle V\rangle = E_n.$$

Therefore,

$$\begin{cases} \langle T\rangle = -E_n \\ \langle V\rangle = 2E_n \\ \langle V^2\rangle = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle = \frac{1}{\left(\ell+\frac{1}{2}\right)n^3a^2} \end{cases}.$$

Remark 1. For hydrogen atom, $2\langle T\rangle = -\langle V\rangle$. For Harmonic oscillator $\langle T\rangle = \langle V\rangle$. The result of the var vivid theorem is case by case, depend on $V(\vec{r})$.

Finally,

$$E_r^{(1)} = -\frac{1}{2mc^2}\left[E_n^2 - 2E_n(2E_n) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{\left(\ell+\frac{1}{2}\right)n^3a^2}\right].$$

Express Bohr energy E_n in terms of Bohr radius. Bohr radius

$$a \triangleq \frac{4\pi\epsilon_0\hbar^2}{m_e^2}$$

[4.72]

$$E_n = \frac{E_1}{n^2}, \quad E_1 \triangleq -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{a}\frac{1}{n^2} \Leftrightarrow \langle V\rangle = 2E_n = -\frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle$$

Therefore,

$$E_n = \underbrace{-\frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\frac{1}{a}\frac{1}{n^2}}_{\text{potential-like}} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{a^2}\frac{1}{n^2}}_{\text{kinetic-like}}.$$

$$\begin{aligned} E_r^{(1)} &= \frac{1}{2mc^2}\left[-3E_n^2 + E_n^2\frac{4n}{\ell+\frac{1}{2}}\right] \\ &= \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{\ell+\frac{1}{2}}\right) \underset{[6.57]}{\sim} 10^{-5}E_n. \end{aligned}$$

$$E_{n,\ell} = E_n + E_r^{(1)} = -\frac{13.6}{h^2}\mathrm{eV} + \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{\ell+\frac{1}{2}}\right)$$