Examples : Chapter 6 b

(1) Fine structure of hydrogen

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$H' \Rightarrow$ { relativistic correction; spin-orbit interaction; hyperfine interaction

(2) Hydrogen atom in an external field

$H' \longrightarrow$ in a weak magnetic field $\Rightarrow$ Zeeman effect

weak electric field $\Rightarrow$ Stark effect

Computational procedure:

Eigenfunctions of H_0, degenerate or not ?

perturbation theory — 1st order ?

2nd order ?

— degenerate theory

$H' = ?$

Nonzero matrix elements ?

key: computing matrix elements

parity: $\vec{r} \longrightarrow -\vec{r}$

$\psi(\vec{r}) = \pm \psi(-\vec{r})$ even or odd

$\vec{r} \longrightarrow -\vec{r}$

r does not change

Inversion in 3D $\begin{cases} \theta \longrightarrow \pi - \theta \\ \phi \longrightarrow \pi + \phi \end{cases}$

$$\boxed{Y_\ell^m(\pi-\theta, \pi+\phi) = (-1)^\ell Y_\ell^m(\theta,\phi)}$$

(1) Relativistic correction

In classical theory $T = \frac{p^2}{2m}$

In special relativity

$$T = \frac{mc^2}{\sqrt{1-\beta^2}} - mc^2 \qquad \beta = v/c$$

$$p = \frac{mv}{\sqrt{1-\beta^2}}$$

or the total energy $E = \sqrt{p^2c^2 + m^2c^4}$

$$T = E - mc^2$$

$$= \sqrt{p^2c^2 + m^2c^4} - mc^2$$

$$= mc^2 \left(\sqrt{1 + \left(\frac{p}{mc}\right)^2} - 1 \right)$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

Thus $$\boxed{H' = -\frac{p^4}{8m^3c^2}} \qquad (6.50)$$

The perturbation is spherical symmetrical, thus it commutes with L^2 and L_z. Even for excited states which are degenerate, there is no need to use degenerate perturbation theory

(2) spin-orbit interaction

The physics: e^- has spin, or dipole moment μ.

The e^- is moving, or orbiting around the proton

The proton exerts an electric field at the point where the electron is.

This electric field would appear as a magnetic field which will influence the $\vec{\mu}$.

or From the view point of a proton orbiting around the e^-

The B field at e^- is $B = \frac{\mu_0 I}{2r}$

$$H' = -\vec{\mu} \cdot \vec{B}$$

$$L = rmv = mr\frac{2\pi r}{T}$$

$$I = \frac{e}{T} \Rightarrow \vec{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\vec{L} \qquad c^2 = \frac{1}{\epsilon_0\mu_0}$$

$$\vec{\mu} = \left(-\frac{e}{m}\right)\vec{S} \qquad \text{for the electron}$$

$$H' = \frac{e^2}{4\pi\epsilon_0}\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}$$

↑ This derivation is not entirely correct

Since e^- is "orbiting", it is not an inertial frame

A correction, called Thomas precession (need special relativity), has to be included $\Rightarrow$ introduces a factor $(\frac{1}{2})$ to the expression above

$$\boxed{H'_{so} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}} \qquad (6.61)$$

Since we include the electron spin, the unperturbed wavefunctions should contain spin function, and the total angular momentum is $\vec{J} = \vec{L} + \vec{S}$

For example, if $\ell = 1$, $j = 1/2$ and $j = 3/2$

The eigenstates of H_0 is

$$|jm\rangle = |\tfrac{1}{2}m\rangle \text{ or } |\tfrac{3}{2}m\rangle$$

← only angular parts are shown

Note: If $H = H_0 + H'_{so}$

$$[H_0, L^2] = 0, \qquad [H, J^2] = 0$$

$$[H_0, J^2] \neq 0 \qquad [H, L^2] \neq 0$$

Note that H'_{so} is a scalar. It does not change the eigenstates of J^2 and J_z.

Use 1st-order perturbation theory, the zero-order w.f.'s

$$\psi = R_{ne}(r)|jm\rangle$$

$$E^{(1)}_{njl} = \langle\psi|H'_{so}|\psi\rangle$$

$$= \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^3}\langle R_{ne}|\frac{1}{r^3}|R_{ne}\rangle\langle jm|\vec{S}\cdot\vec{L}|jm\rangle$$

$$\vec{j} = \vec{S} + \vec{L} \qquad j^2 = S^2 + L^2 + 2\vec{S}\cdot\vec{L}$$

$$\langle jm|\vec{S}\cdot\vec{L}|jm\rangle = \langle jm|\frac{1}{2}(\vec{j}^2 - \vec{S}^2 - \vec{L}^2)|jm\rangle$$

$$= \frac{1}{2}\hbar^2\left(j(j+1) - s(s+1) - l(l+1)\right)$$

Thus the angular part can be calculated analytically.

$\langle\frac{1}{r^3}\rangle$ can be calculated or using Mathematica

Combine the relativistic effect and spin-orbit interaction, the energy of a hydrogen atom becomes

$$\boxed{E_{nj} = -\frac{13.6\,(eV)}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]} \qquad (6.67)$$

where $\alpha \equiv \frac{e^2}{\hbar c}\frac{1}{4\pi\epsilon_0} \simeq \frac{1}{137.04}$

is called the fine structure constant.

Note: $\alpha^2 \sim 10^{-4} \sim 10^{-5}$

$2P_{3/2}$

$2S_{1/2}, 2P_{1/2}$

$2S, 2P$ — H_0 — F.S. — $H_0 + H'$

(6.67) can be obtained directly from Dirac Eq.

(3) hyperfine interaction

The nucleus has spin also.

$$\vec{\mu}_p = \gamma\left(\frac{e}{2m_p c}\right)\vec{S}_p \qquad \text{or replace } \vec{S}_p \text{ by } \vec{I}$$

The spin-spin interaction between the electron and proton makes $\langle\vec{J}\rangle$ no longer a conserved quantity. Introduce

$$\vec{F} = \vec{J} + \vec{I}$$

($\vec{J}$: From e^-; $\vec{I}$: From proton)

F is a good quantum number

For hydrogenic 1S, $J = 1/2$, the spin of the p^+ is $1/2$, i.e., $I = 1/2$

Thus $I = 0,\ 1$

The hyperfine interaction