QM II
Phys 652

Lecture #22

Applications of time-independent perturbation theory: closer look at the hydrogen atom

So far: $H_0 = \frac{\vec{p}^{\,2}}{2\mu} - \frac{e^2}{r}$ $\Leftarrow$ (H)-atom: take into account only Coulomb interaction between (e⁻) and (p)

For a full description
$\Downarrow$
need relativistic Schrödinger equation

$$\left[\left(p^\mu - \frac{e}{c}A^\mu\right)^2 - m^2c^2\right]\Psi = 0,$$

$p^\mu = i\hbar\left(c\frac{\partial}{\partial t}, -\nabla\right)$
$\uparrow$
four-vector momentum

$A^\mu = (\varphi, \vec{A})$
$\uparrow$
four-vector potential

Or, for a spin-1/2 charged particle $\Rightarrow$ Dirac equation
$\Downarrow$

$$\left[\gamma_\mu\left(p^\mu - \frac{e}{c}A^\mu\right) - mc\right]\Psi = 0$$

$\Rightarrow$ for (H)-atom can be solved exactly

$$\gamma^0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \; ; \quad \vec{\gamma} = \begin{pmatrix} 0 & \hat{\vec{\sigma}} \\ -\hat{\vec{\sigma}} & 0 \end{pmatrix}$$

$\uparrow$ 4×4 matrix

$\hat{\vec{\sigma}} \leftarrow$ Pauli matrices

Fortunately, a (H)-atom is a weakly relativistic system $\Rightarrow$ Dirac equation can be simplified

How do we know that it's weakly relativistic? $\Rightarrow$ let's estimate velocity of the electron using the (primitive) Bohr model (semi-classical model, which is based on the hypothesis that the electron rotates around the proton following the circular orbit of radius r, so that $\underbrace{\frac{\mu v^2}{r}}_{\text{"centrifugal force"}} = \underbrace{\frac{e^2}{r^2}}_{\text{electrostatic force}}$, $\underbrace{\mu v r = n\hbar}_{\text{quantisation condition}}$) $\Rightarrow$

Then, for $n=1 \Rightarrow \mu v r = \hbar$, $r \sim a_0 \Rightarrow$

$$v = \frac{\hbar}{\mu a_0} = \frac{\hbar \mu e^2}{\mu \hbar^2} = \frac{e^2}{\hbar}; \quad \frac{v}{c} = \underbrace{\frac{e^2}{\hbar c}}_{=\alpha} = \underbrace{\frac{1}{137} \ll 1}_{\text{weakly relativistic}}$$

α — fine-structure constant

$\Downarrow$

Expand the (exact) Dirac Hamiltonian in powers of $\frac{v}{c}$

$\Downarrow$

$$H = \underbrace{\frac{\vec{p}^{\,2}}{2m_e} \overbrace{-\frac{e^2}{r}}^{=V(r)}}_{H_0} + \underbrace{V_{fine} + V_{hf}}_{\text{perturbation}}$$

next lecture

$$V_{fine} = \underbrace{-\frac{\vec{p}^{\,4}}{8m_e^3c^2}}_{①\ W''_{mv}} + \underbrace{\frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}\cdot\vec{S}}_{②\ W''_{SO}} + \underbrace{\frac{\hbar^2}{8m_e^2c^2}\Delta V(r)}_{③\ V_D} \qquad (23.1)$$

① variation of the mass with velocity

② spin-orbit coupling

③ Darwin term (non-locality of the interaction between the nucleus and Coulomb field)

<u>Example</u> where does $\underline{V_{mv}}$ come from?

①

energy of a classical particle $\underset{\text{(kinetic) + rest}}{E} = c\sqrt{\vec{p}^{\,2} + m_e^2c^2}$

If $\frac{v}{c} \ll 1$ $\left(v = \frac{|\vec{p}|}{m_e}\right) \Rightarrow$

$$E = c \cdot m_e c\sqrt{1 + \frac{\vec{p}^{\,2}}{m_e^2c^2}} \approx m_e c^2\left(1 + \frac{\vec{p}^{\,2}}{2m_e^2c^2} - \frac{\vec{p}^{\,4}}{8m_e^4c^4} + \dots\right) =$$

$\sqrt{1+x} = 1 + \frac{x}{2} - \frac{x^2}{8} + \dots$

$$= \underbrace{m_e c^2}_{\text{rest mass energy}} + \underbrace{\frac{\vec{p}^{\,2}}{2m_e}}_{\text{non-relativistic kinetic energy}} - \frac{\vec{p}^{\,4}}{8m_e^3c^2} + \dots$$

first-order energy correction due to relativistic variation of the mass with velocity

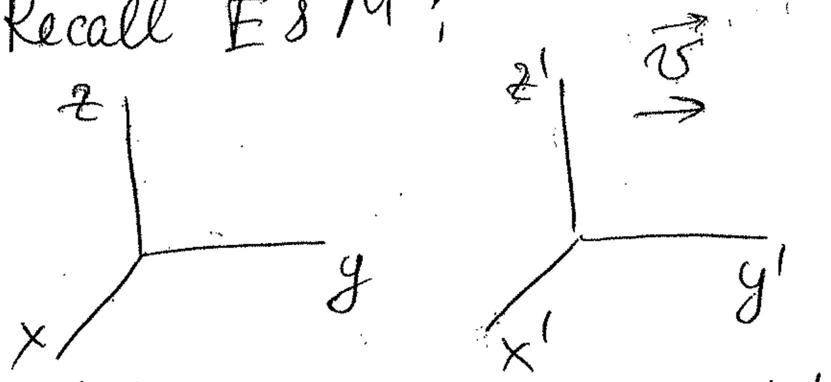
The size of the correction with respect to $\frac{\vec{p}^{\,2}}{2m_e}$:

$$\frac{\frac{\vec{p}^{\,4}}{8m_e^3c^2}}{\frac{\vec{p}^{\,2}}{2m_e}} = \frac{\vec{p}^{\,2}}{4m_e^2c^2} = \frac{1}{4}\left(\frac{v}{c}\right)^2 = \frac{1}{4}\alpha^2 \sim 1.3 \cdot 10^{-5}$$

very small

② V_{SO} term

Recall E & M;



stationary system K ⇓ proton

moving with velocity $\vec{v}$ system K' ⇓ electron

⇒ In the frame K', the magnetic field

$$\vec{B}' = -\frac{\vec{v}}{c}\times\vec{E} \leftarrow \text{electric field created by proton}$$

(to the 1st order in $\frac{v}{c}$)

The interaction between the electron's magnetic moment $\vec{M}_s = \frac{e}{m_e c}\vec{S}$ and $\vec{B}'$ is $V_{SO} = -\vec{M}_s\cdot\vec{B}' =$

$$= \frac{e}{m_e c^2}\vec{S}\cdot(\vec{v}\times\vec{E}) = -\frac{e^2}{m_e c^2 r^3}\vec{S}\cdot(\underbrace{\vec{v}}_{=\frac{\vec{p}}{m_e}}\times\vec{r}) =$$

force $\rightarrow \vec{F} = e\vec{E} = -\underbrace{\frac{dV(r)}{dr}}_{\frac{e^2}{r^2}}\cdot\frac{\vec{r}}{r} = -\frac{e^2}{r^3}\vec{r}$

$$= -\frac{e^2}{m_e c^2 r^3}\vec{S}\cdot(\underbrace{\vec{p}\times\vec{r}}_{=-\vec{L}}) = \frac{e^2}{m_e^2 c^2 r^3}\vec{L}\cdot\vec{S}$$

orbital angular momentum

compare with V_{SO} from Eq. (8.1)

a factor $\frac{1}{2}$ is missing since we only look into account translation of the ... and not rotation

Let's estimate the order of magnitude of this correction (5) with respect to non-relativistic $E \sim \frac{e^2}{r}$ $\Rightarrow$

$|\vec{L}|, |\vec{S}| \sim \hbar \Rightarrow V_{SO} \sim \frac{e^2\hbar^2}{m_e^2 c^2 r^3} \Rightarrow$

$$\frac{V_{SO}}{\frac{e^2}{r}} = \frac{\cancel{e^2}\hbar^2}{m_e^2 c^2 r^3 \cancel{\frac{e^2}{r}}} = \underset{\substack{\uparrow \\ r \sim a_0 = \frac{\hbar^2}{m_e e^2}}}{\frac{\hbar^2}{m_e^2 c^2 r^2}} \sim \frac{\cancel{\hbar^2} \cancel{m_e^2} e^4}{\cancel{m_e^2} c^2 \hbar^{\cancel{4}\,2}} \sim \frac{e^4}{\hbar^2 c^2} = \alpha^2$$

③ V_D (Darwin term)

$$V_D = \frac{\hbar^2}{8m_e^2c^2}\Delta\left(-\frac{e^2}{r}\right) = -\frac{\hbar^2 e^2}{8m_e^2c^2}\underbrace{\Delta\left(\frac{1}{r}\right)}_{-4\pi\delta(\vec{r})} = \frac{\pi e^2\hbar^2}{2m_e^2c^2}\delta(\vec{r})$$

check: $\Delta_{\vec{r}}\varphi = \int \Delta_{\vec{r}} G \rho(\vec{r}\,')\,d\vec{r}\,' = -4\pi\rho(\vec{r})$ $\Leftarrow \varphi = \int G(\vec{r}-\vec{r}\,')\rho(\vec{r}\,')\,d^3r'$ $\quad G(\vec{r}-\vec{r}\,') = \frac{1}{|\vec{r}-\vec{r}\,'|}$ recall Green's functions! E&M: $\Delta\varphi = -4\pi\rho$

$$\langle\psi|V_D|\psi\rangle \sim \frac{\pi e^2\hbar^2}{2m_e^2c^2}\int|\psi|^2\delta(\vec{r})\,d\vec{r} = \frac{\pi e^2\hbar^2}{2m_e^2c^2}|\underset{\substack{\uparrow \\ \text{at } \vec{r}=0}}{\psi(0)}|^2$$

Recall wavefunctions of the (H)-atom $\Rightarrow \psi \sim C r^l e^{-r/na_0} Y_l^m(\theta,\varphi)$

$\psi(0) \neq 0$ only for $l=0$, i.e. S-states $\Rightarrow$

Darwin term matters only for S-states!

To estimate an order of magnitude of $V_D \Rightarrow$

$|\psi(0)|^2 \simeq ?$ $\Rightarrow \int|\psi(r)|^2 dV = 1 \Rightarrow |\psi(0)|^2 \cdot \frac{4\pi a_0^3}{3} \sim 1$

S-states are localised around 0

$$|\psi(0)|^2 \sim \frac{3}{4\pi a_0^3} \Rightarrow$$

$$\langle\psi|V_D|\psi\rangle \sim \frac{\pi e^2\hbar^2}{2m_e^2c^2}\cdot\frac{3}{4\pi a_0^3} = \frac{3}{8}\, m_e c^2\alpha^4$$

$$\frac{\langle\psi|V_D|\psi\rangle}{\frac{p^2}{2m_e} \text{ or } \frac{e^2}{r}} = \frac{3}{8}\,\frac{\cancel{m_e} c^2\alpha^4\hbar^2}{e^2 \cancel{m_e} e^2} = \frac{3}{8}\,\underbrace{\frac{\hbar^2c^2}{e^4}}_{\frac{1}{\alpha^2}}\,\alpha^4 = \frac{3}{8}\alpha^2$$

So, all terms $\Rightarrow V_{mv}$, V_{so}, V_D are of the order of α^2 compared to unperturbed (Coulomb only interaction) Hamiltonian.

<u>Homework</u>: How do V_{mv}, V_{so}, V_D affect the energy level of the ground state of the H atom?

<u>Note</u>: The exact solution of the Dirac equation is

$$E_{n,j} = m_ec^2\left[1+\alpha^2\left(n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^2-\alpha^2}\right)^{-2}\right]^{-1/2} = \quad (23.2)$$

show!

$$= \underbrace{m_ec^2}_{\text{rest mass}} - \underbrace{\frac{E_I}{n^2}}_{\text{Coulomb}} - \underbrace{\frac{m_ec^2\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)}_{\text{due to } V_{fine}} + \ldots \quad (23.3)$$

expansion in powers of α

$\Downarrow$

fine structure correction introduces j-dependence in energy