P423

Lecture 6 : Fine Structure of Hydrogen

Relativistic correction : a) Kinetic energy
b) Spin-orbit coupling

a) Kinetic energy :

In classical mechanics)

$$T = \frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m}\nabla^2$$

But we know that this expression is just the classical limit of

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

We need to express p in terms of relativistic momentum

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

Notice:

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

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

$$= mc^2\left\{\left(1+\frac{p^2}{m^2c^2}\right)^{\frac{1}{2}} - 1\right\} = mc^2\left\{\cancel{1} + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\frac{p^4}{m^4c^4} + O(p^6) - \cancel{1}\right\}$$

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + O(p^6)$$

The relativistic correction is evidently

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

But is p kinetic or canonical momentum? Actually it has to be kinetic momentum here.

Why? For Schrödinger eqn to be gauge invariant (i.e. $\psi \to \psi' = e^{i\frac{q}{\hbar}\Lambda}\psi$) we must have

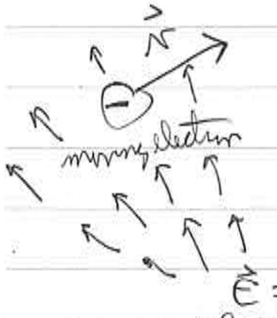
$$\boxed{H'_r = -\frac{1}{8m^3c^2}\underbrace{\left(\vec{p} - q\vec{A}\right)}_{\text{kinetic momentum!}}{}^4}$$

otherwise we won't have

$$\Big(\underbrace{\vec{p} - q\vec{A} - q\vec{\nabla}\Lambda}_{-q\vec{A}'}\Big)\underbrace{e^{\frac{iq\Lambda}{\hbar}}\psi}_{\psi'} = \left(\vec{p} - q\vec{A}\right)\psi \; !$$

b) Spin-orbit coupling

Another relativistic effect is that moving electric fields get converted to magnetic fields, and vice-versa.



$$\vec{E} = -\vec{\nabla}\Phi - \frac{\partial\vec{A}}{\partial t}$$

Electric field

If we are sitting at the top of the electron, the charges producing the $\vec{E}$ appear to move with $-\vec{v}$.
Hence the electron feels a field

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E} = \frac{1}{c^2}\vec{v}\times\left(\vec{\nabla}\Phi + \frac{\partial\vec{A}}{\partial t}\right)$$

This leads to a coupling energy of

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

For the electron $q = -e_0$ and $\vec{\mu}_e = -\frac{g_0 e_0}{2m} \vec{S}$ with $g_0 = 2.002 \ldots$.

Hence we get

$$H''_r = \frac{g_0 e_0}{2mc^2} \vec{S} \cdot \vec{v} \times \left(\vec{\nabla} \Phi + \frac{\partial \vec{A}}{\partial t} \right)$$

But $\vec{v} = \frac{1}{m} (\vec{p} + e_0 \vec{A})$ so

$$H''_r = \frac{g_0 e_0}{2m^2c^2} \vec{S} \cdot \left(\vec{p} + e_0 \vec{A} \right) \times \left(\vec{\nabla} \Phi + \frac{\partial \vec{A}}{\partial t} \right)$$

Actually this result is not quite correct because we used a non-inertial ref. frame — Correcting for that ("Thomas precession") we get

$$\boxed{H''_r = \frac{g_0 e_0}{4m^2c^2} \vec{S} \cdot \left(\hat{\vec{p}} + e_0 \vec{A} \right) \times \left(\vec{\nabla} \Phi + \frac{\partial \vec{A}}{\partial t} \right)}$$

We can derive the same result using relativistic QM — From Dirac's eqn, we get Schrödinger's eqn plus H'_1 and H''_r. Also Dirac's eqn leads to electron spin-$\frac{1}{2}$ with $g_0 = 2$ (the 0.002... correction comes from coupling with photons).

Let's write H''_r for a central potential $V(\vec{r}) = -e_0 \Phi(\vec{r})$ and $\vec{A} = 0$.
In this case

$$\vec{\nabla} \Phi = -\frac{1}{e_0} \vec{\nabla} V = -\frac{1}{e_0} \frac{\vec{r}}{r} \frac{dV}{dr}$$

$$\Rightarrow H''_r = \frac{g_0 \cancel{e_0}}{4m^2c^2} \vec{S} \cdot \hat{\vec{p}} \times \left(-\frac{1}{\cancel{e_0}} \frac{\vec{r}}{r} \frac{dV}{dr} \right) = -\frac{g_0}{4m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{S} \cdot \underbrace{(\vec{p} \times \vec{r})}_{= -\vec{L}} = \boxed{\frac{g_0}{4m^2c^2} \frac{1}{r} \left(\frac{dV}{dr} \right) \vec{S} \cdot \vec{L}}$$

Central potential only!

Relativistic correction to energy levels of Hydrogen (Fine structure)

For Hydrogen,

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e_0^2}{4\pi\varepsilon_0}\frac{1}{r}$$

3 coordinate x, y, z → Need 3 commuting operators to describe the problem. Choose

$$(\vec{L})^2 = (\vec{r}\times\vec{p})^2, \quad \hat{L}_z, \quad \text{and } \mathcal{H}.$$

They all commute with each other! The eigenstates are $|n\,l\,m\rangle$ with

$$\mathcal{H}\,|n\,l\,m\rangle = E_n\,|n\,l\,m\rangle, \quad E_n = \frac{E_1}{n^2} \quad (n=1,2,3,\ldots)$$

where $E_1 = -\frac{\hbar^2}{2m}\frac{1}{a_B^2} = -13.6\,eV$ = "Rydberg", $a_B = \frac{4\pi\varepsilon_0\hbar^2}{m e_0^2} = 0.529\,\text{Å}$ = "Bohr radius".

or $E_1 = -\frac{\hbar^2}{2m}\Big(\underbrace{\frac{m e_0^2}{4\pi\varepsilon_0\hbar^2}}_{=\frac{mc\alpha}{\hbar}}\Big)^2 = -\frac{\hbar^2}{2m}\left(\frac{mc\alpha}{\hbar}\right)^2 = -\frac{1}{2}\underbrace{mc^2}_{\substack{\text{rest mass of electron}\\ = 0.5110\,MeV}}\alpha^2$ // $\left(\alpha = \frac{e_0^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137.036} \text{ is fine structure constant.}\right)$

Also

$$(\hat{\vec{L}})^2\,|n\,l\,m\rangle = l(l+1)\hbar^2\,|n\,l\,m\rangle \quad \text{with } l = 0,1,2,\ldots,n-1 \quad (n \text{ values of } l)$$

$$\hat{L}_z\,|n\,l\,m\rangle = m\hbar\,|n\,l\,m\rangle, \quad \text{with } m = -l, -l+1, \ldots, l \quad (2l+1 \text{ values of } m)$$

degeneracce of $E_n \Rightarrow \sum_{l=0}^{n-1}(2l+1) = 2\frac{(n-1)(n-1+1)}{2} + n = n^2$ //

Also

$$\langle\vec{r}\,|n\,l\,m\rangle = \sqrt{\left(\frac{2}{na_B}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}\; e^{-\frac{r}{na_B}}\left(\frac{2r}{na_B}\right)^l \Big[\underbrace{L^{2l+1}_{n-l-1}\left(\frac{2r}{na_B}\right)}_{\text{"associated Laguerre polynomials"}}\Big]\underbrace{Y_{lm}(\theta,\varphi)}_{\text{"Spherical Harmonics"}}$$

For example, ground state

$$\langle \vec{r} | 100 \rangle = \psi_{100}(\vec{r}) = \frac{1}{\sqrt{\pi a_B^3}} e^{-\frac{r}{a_B}}$$ with energy $E_1 = -Ry = -13.6\,eV$.

1st order relativistic corrections to H-atom

$$E_r^1 = \langle nlm | H_r^1 | nlm \rangle = -\frac{1}{8m^3c^2} \langle nlm | p^4 | nlm \rangle$$

$$= -\frac{1}{8m^3c^2} \left(\langle nlm | \hat{\vec{p}}^2 \right) \left(\hat{\vec{p}}^2 | nlm \rangle \right)$$

But

$$p^2 | nlm \rangle = 2m (E_n - V) | nlm \rangle$$

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

$$= -\frac{1}{2} \frac{1}{mc^2} \langle nlm | \left[E_n^2 - 2E_n V + V^2 \right] | nlm \rangle$$

$$= -\frac{1}{2} \frac{1}{mc^2} \left\{ E_n^2 - 2E_n \underbrace{\left(\frac{-e_0^2}{4\pi\varepsilon_0} \right) \left\langle \frac{1}{r} \right\rangle_{nlm}} + \left(\frac{-e_0^2}{4\pi\varepsilon_0} \right)^2 \underbrace{\left\langle \frac{1}{r^2} \right\rangle_{nlm}} \right\}$$

use Virial theorem for H:

$\langle V \rangle = 2E_n$

or $\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_B}$

$$= \frac{1}{(l+\frac{1}{2}) n^3 a_B^2}$$ (need to use Feynman-Hellman trick, see A3).

$$\boxed{E_r^1 = -\frac{1}{2} \frac{1}{mc^2} \left\{ -3E_n^2 + \underbrace{\left(\frac{e_0^2}{4\pi\varepsilon_0} \right)^2 \frac{1}{(l+\frac{1}{2}) n^3 a_B^2}}_{\frac{E_n^2\, 4n}{(l+1/2)}} \right\} = -\frac{E_n^2}{mc^2} \left[\frac{4n}{(l+\frac{1}{2})} - 3 \right]}$$

Note: H-levels now depend on l!

⑥

Spin-orbit correction:

$$H''_r = \frac{g_0}{4m^2c^2}\frac{1}{r}\underbrace{\frac{dV}{dr}}_{\frac{e_0^2}{4\pi\varepsilon_0}\frac{1}{r^2}}\vec{S}\cdot\vec{L} = \left(\frac{e_0^2}{8\pi\varepsilon_0}\right)\left(\frac{1}{m^2c^2}\frac{1}{r^3}\right)\vec{S}\cdot\vec{L}$$

$g_0 = 2$

Because of H''_r, the H does not commute with $\hat{L}_z$ and $\hat{S}_z$ anymore. However, consider the total ang. momentum $\vec{J}$:

$(\vec{J})^2 = (\vec{L}+\vec{S})^2 = (\vec{L})^2 + 2\vec{L}\cdot\vec{S} + (\vec{S})^2 \Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}\left[(\vec{J})^2 - (\vec{L})^2 - (\vec{S})^2\right]$ so the H will commute with $(\vec{J})^2, (\vec{L})^2, (\vec{S})^2$, and $\vec{J}_z$ (rotates both $\vec{L}$ and $\vec{S}$ together!).

$\Rightarrow$ Choose $\{H, (\vec{J})^2, \hat{J}_z\}$ as the set of commuting operators! Our wavefns become $|n\,j\,m_j\rangle$ with:

$$\begin{cases} (\vec{J})^2|n\,j\,m_j\rangle = j(j+1)\hbar^2|n\,j\,m_j\rangle, \\ \hat{J}_z|n\,j\,m_j\rangle = m_j\hbar|n\,j\,m_j\rangle, \\ (\vec{L})^2|n\,j\,m_j\rangle = l(l+1)\hbar^2|n\,j\,m_j\rangle, \\ (\vec{S})^2|n\,j\,m_j\rangle = \underbrace{S(S+1)}_{=\frac{1}{2}(\frac{1}{2}+1)=\frac{3}{4}}\hbar^2|n\,j\,m_j\rangle = \frac{3}{4}\hbar^2|n\,j\,m_j\rangle. \end{cases}$$

So $(\vec{L}\cdot\vec{S})|n\,j\,m_j\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]$

Moreover, $\left\langle\frac{1}{r^3}\right\rangle = \dfrac{1}{l(l+\frac{1}{2})(l+1)n^3a_B^3}$, hence

$$E^1_{SO} = \langle H''_r\rangle_{n j m_j} = \underbrace{\frac{e_0^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2}\frac{\hbar^2}{2}}_{=\frac{E_n^2}{mc^2}n^4a_B^3}\frac{\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{l(l+\frac{1}{2})(l+1)\,n^3\,a_B^3} = \frac{E_n^2}{mc^2}\left\{\frac{n\left[j(j+1)-l(l+1)-\frac{3}{4}\right]}{l(l+\frac{1}{2})(l+1)}\right\}$$

This correction is of the same order as the E^1_r! $\left(\sim\frac{E_n^2}{mc^2}\right)$. Add both with $j = l\pm\frac{1}{2}$ to get a result independent of $\pm$:

$$E^1_{\text{fine structure}} = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+\frac{1}{2}}\right].$$