Fine Structure + Lamb Shift

Lecture #2
PHYS 598 AQ
Fall 2017

Last time we treated the hydrogen atom with a non-relativistic Schrödinger Eqn. (and ignoring other things).

We'll find that a lot of the degeneracy that we found [i.e. E_n and not $E_{n\ell m}$] gets broken when we include these other considerations.

<u>Gross structure</u>: the E_n energies we found last time

$$E_n \sim \frac{Z^2 \alpha^2}{n^2} \underbrace{(RME)}_{mc^2}$$

<u>Fine structure</u>: corrections mostly due to relativistic effects

[so, should use Dirac Eqn relativistic QM

we'll look at approximations to this (in terms of expansions in order of $\frac{v}{c}$

Let's look @ how our KE term will change (i.e., $\frac{p^2}{2m}$)

$$KE = E - \text{rest mass energy}$$

$$KE = \sqrt{(mc^2)^2 + (pc)^2} - mc^2 = mc^2 \left[1 + \left(\frac{pc}{mc^2}\right)^2\right]^{\frac{1}{2}} - mc^2$$

↳ Let's rewrite expand this expression

②

$$KE \approx mc^2\left[1 + \frac{1}{2}\frac{p^2c^2}{m^2c^4} - \frac{1}{8}\frac{p^4c^4}{m^4c^8} + \dots\right] - mc^2$$

$$KE \approx \frac{p^2}{2m} \underbrace{- \frac{p^4}{8m^3c^2}}_{\text{let's include this next-highest order}} + \dots$$

Using 1^{st} order perturbation theory, we can estimate the energy shift due to this effect

$$\Delta E_{KE,nlm} = \frac{-1}{8m^3c^2}\langle \psi_{nlm} | p^4 | \psi_{nlm} \rangle$$

we can calculate this

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how about a cruder estimate? (from Foot p. 6)

$$E(v) = \gamma mc^2 \qquad w/ \quad \gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

$$KE = E(v) - E(0) = (\gamma - 1)mc^2 = \left[\left(1-\frac{v^2}{c^2}\right)^{-\frac{1}{2}} - 1\right]mc^2$$

what's the fractional change?

$$\frac{\Delta E}{E} \sim \frac{v^2}{c^2}$$

what's a typical velocity? estimate from Bohr model

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \qquad \text{centripetal vs. Coulomb}$$

$$mvr = n\hbar \qquad \text{quant. of angular momentum}$$

$$\boxed{v = \left(\frac{Z\alpha}{n}\right)c} \qquad \text{where} \quad \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$$

$$\boxed{\Delta KE \sim \left(\frac{Z\alpha}{n}\right)^2 E_{gross}}$$

alt., from virial thm $2\langle KE\rangle = -\langle PE\rangle \rightarrow E = \langle PE\rangle + \langle KE\rangle = -\langle KE\rangle$

$$\boxed{\frac{1}{2}mv^2 = \left(\frac{Z\alpha}{n}\right)^2 mc^2}$$

③ **Darwin term** – another relativistic effect, for charged particles

"Zitterbewegung", which is the fast undulatory motion of charged relativistic particles (due to the presence of negative energy solutions to the Dirac Eqn),

results in the electrons experiencing an effective, time-averaged potential.

The length scale of these wiggles is given by $\xi = \frac{\hbar c}{m} \sim 400$ fm $\approx \alpha a_0$

and the correction to the estimated energy only occurs for states with $\psi_{nlm}(r=0) \neq 0$, i.e. for states w/ $l=0$ (s-orbitals).

$$H_{Darwin} = \frac{\pi}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\xi^2\,\delta(\vec{r})$$

$\langle H_D \rangle = 0$ for all orbitals w/ $l>0$ due to this delta function

plug in for $\psi_{n,l=0}(r=0)$ to estimate shift

$$\Delta E_{Darwin} = \langle H_D \rangle = \frac{\pi}{2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\xi^2\,|\psi(0)|^2$$

where $\psi_{n,l=0}(r=0) = \frac{1}{\sqrt{4\pi}}\,2\left(\frac{Z}{na_0}\right)^{3/2}$

$$\Delta E_{Darwin} = \frac{Z^4 e^2 \hbar^2}{4\pi\varepsilon_0 n^3 a_0^3 m^3 c^2} = \frac{2n\,E_n^2}{mc^2}$$

recall $E_n = \left(\frac{Z^2\alpha^2}{n^2}\right)mc^2$

$$= \underline{\frac{2Z^2\alpha^2}{n}E_n}$$

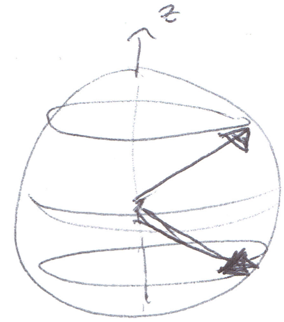
④ Spin-Orbit Coupling (this will be the main contribution for other atoms we'll be interested in)

We've so far ignored the spin of the electron (spin $\frac{1}{2}$), which can have measured angular momenta (z-axis projections) of $\pm\frac{1}{2}\hbar$. This intrinsic spin angular momentum relates to a magnetic moment of the electron

$$\vec{\mu} = -g_s \underbrace{\frac{e\hbar}{2m}}^{\mu_B} \vec{S}$$

taking value of ... w.r.t. fie... axis.

we can draw the spin of the electron as having a total length $S = \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$, where the z-axis projection can only be $\pm\frac{1}{2}\hbar$



$g_s \simeq 2$ (electron g-fa...

[$g_s - 2 = .0023193043718$ QED eff...

The electron's spin interacts with the magnetic field created by the electron's motion in the Coulomb potential

$$\vec{B} = -\frac{1}{c^2}\vec{v}\times\vec{E} = -\frac{1}{c^2}\vec{v}\times\left(\frac{1}{e}\frac{\partial V}{\partial r}\frac{\vec{r}}{r}\right)$$

$$\vec{B} = -\frac{\vec{v}}{c^2}\times\frac{\vec{r}}{r}\left[\frac{1}{e}\frac{\partial}{\partial r}\left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\right] = \frac{\vec{r}\times\vec{v}}{c^2}\left(\frac{Ze}{4\pi\varepsilon_0 r^3}\right)$$

Note: we're applying this to hydrogen-like atoms

$$\text{w/ } \hbar\vec{L} = m\vec{r}\times\vec{v}$$

$$\vec{B} = \frac{Ze\hbar}{mc^2 4\pi\varepsilon_0 r^3}\vec{L}$$

note: not quite right correction coming on next page

$$H_{S\text{-}O} = -\vec{\mu}\cdot\vec{B} = (g_s\mu_B)\vec{S}\cdot\vec{L}\left(\frac{Ze\hbar}{mc^2 4\pi\varepsilon_0 r^3}\right) = \frac{Z\hbar^2 e^2}{m^2c^2}\frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$

$\mu_B/\hbar = 2\pi \times 1.4$ MHz/G

⑤

Another relativistic effect – Thomas precession

the frame of reference rotates as the electron "orbits" the nucleus, and an appropriate, relativistic treatment of this problem reduces $\vec{B}$ by a factor of roughly 2. This is accounted for by taking $(g_s - 1) \simeq 1$

$$\underbrace{H_{s\text{-}o} = -\vec{\mu}\cdot\vec{B} = \frac{1}{4\pi\varepsilon_0}\,\frac{Ze^2\hbar^2}{m^2c^2r^3}\,\underbrace{\left(\frac{g_s-1}{2}\right)}_{\simeq\frac{1}{2}}\,\vec{L}\cdot\vec{S}}$$

← for hydrogen-like atoms

$V(r) \propto \frac{1}{r}$

for alkalis, or any atom w/ multiple electrons, where $V(r)$ is not $\propto \frac{1}{r}$, you'll use :

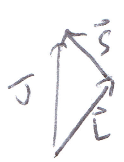
$$H_{so}^{\text{general}} = \frac{1}{2}\,\frac{\hbar^2}{m^2c^2}\,\vec{L}\cdot\vec{S}\left[\frac{1}{r}\frac{\partial V}{\partial r}\right]$$

let's find $\langle H_{s\text{-}o}\rangle$

need to know $\left\langle \frac{1}{r^3}\right\rangle = \dfrac{Z^3}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)}$

and $\langle \vec{L}\cdot\vec{S}\rangle$

We've put this off, but we'll now also work with the total angular momentum associated with this electron, $\vec{J} = \vec{L} + \vec{S}$



using → $\vec{J}^2 = \vec{L}^2 + 2\vec{L}\cdot\vec{S} + \vec{S}^2$

we find

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$$

and $\langle \vec{L}\cdot\vec{S}\rangle = \frac{1}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$

⑥ To finish up w/ spin-orbit coupling ...

let's throw it all together now

$$\Delta E_{s\text{-}o} = \langle H_{s\text{-}o} \rangle = \left[\frac{1}{4\pi\varepsilon_0}\frac{Ze^2h^2}{(2\pi)^2 m^2 c^2}\right]\left(\underbrace{\frac{1}{2}}_{}\right)^{\frac{g_s-1}{2}} \frac{Z^3}{a_0^3 n^3}\,\frac{1}{2}\left[\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

$$= \frac{Z^4\alpha^4}{4n^3}(mc^2)\left[\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

$$= \frac{Z^2\alpha^2}{2n}E_{gross}\left[\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

[all 3 terms are of $\alpha^2 \sim 10^{-4}$ smaller than the gross energy structure $\alpha^2 E_{n=1}^{Z=1} \sim 7.25\times10^{-4}$ eV $\approx \sim 100$ GHz

[also, importantly, all are diagonal in the $\vec{J}$ basis, such that states w/ the same n + j but different ℓ should be degenerate

^1H: $2P_{3/2} - 2P_{1/2} = [\,4.5\times10^{-}$ / 10.9 GH

[show energy shifts for hydrogen], Cs ^{133}Cs: $6P_{3/2} - 6P_{1/2} = [\,\sim 0.7$ / $16{,}600$ GHz

$$\Delta E_J^{so} = \frac{\alpha^2}{n\ell(\ell+1)}E_{gross}$$

$\downarrow$

$E_{n,\ell,j=\ell+\frac{1}{2}} - E_{n,\ell,j=\ell-\frac{1}{2}}$

[briefly on selection rules for electric dipole transitions

$\Delta n = 0, 1, 2, 3, \ldots$

$\Delta \ell = \pm 1$

$\Delta j = 0, \pm 1$

$\Delta m_j = 0, \pm 1$

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<u>Lamb shift</u> – the degeneracy between states w/ the same (n, j) gets broken in reality due to effects described by quantum electrodynamics (QED).
The measurement of these shifts in energy by Willis Lamb helped in the development of QED theory.

The electron is not really in <u>empty</u> space, but rather in the EM vacuum which has zero-point fluctuations.

Let's look @ a toy model by Welton (described in Sakurai), describing how fluctuations of the EM field smear out the electron in space.

for a vacuum field component of angular frequency ω, there will be a

<u>zero-point energy density</u> given by $\underbrace{\frac{1}{2}\hbar\omega}_{\text{ZPE for state } \omega}\underbrace{\rho(\omega)}_{\text{density of states}} = D_\omega$

we can also relate the energy density to the rms. field strength

in <u>cgs</u> $\rightarrow$ $$D_\omega = \frac{1}{8\pi}\left(\langle \vec{E}_\omega^2\rangle_t + \langle B_\omega^2\rangle_t\right) = \frac{E_\omega^2}{8\pi}$$ $\leftarrow$ <u>peak strength</u>

using $\rho(\omega)d\omega = \frac{1}{\pi^2}\frac{\omega^2}{c^3}d\omega$, we have

$$E_\omega^2 = \frac{4}{\pi}\hbar\left(\frac{\omega}{c}\right)^3$$

we can imagine that the oscillating E-field for the angular freq. ω leads to acceleration of the charged electron. Let's model this in 1D

$$m\ddot{x}_\omega = e E_\omega \cos(\omega t)$$

$$\hookrightarrow x_\omega(t) = \frac{-eE_\omega}{m\omega^2}\cos(\omega t) \longrightarrow \langle x_\omega\rangle_t = 0, \text{ but } \langle x^2\rangle \neq 0$$

$$\langle x_\omega^2\rangle_t = \longrightarrow \frac{1}{2}\frac{e^2E_\omega^2}{m^2\omega^4} = \frac{hc\ e^2}{\pi^2(mc^2)^2\omega}$$

This result for $\langle x_\omega^2 \rangle_t$ is for one freq.

- Need to integrate of all <u>relevant</u> frequencies, and consider how this <u>smearing</u> out of the electron changes its energy in the Coulomb potential

$$\Delta V_\omega = \overline{V(\vec{r}+\vec{x}_\omega)} - V(\vec{r})$$

$i,j \in (x,y,z)$

expand as

$$V(\vec{r}+\vec{x}_\omega) = V(\vec{r}) + \underbrace{\vec{\nabla} V \cdot \vec{x}_\omega} + \frac{1}{2}\sum_{i,j} \frac{\partial^2 V}{\partial x_{\omega,i}\,\partial x_{\omega,j}} x_{\omega,i}\, x_{\omega,j}$$

$\vec{x}_\omega$ are random, this averages to zero

$\langle x_x \, x_y \rangle = 0$ for random fluctu

$$V(\vec{r}+\vec{x}_\omega) \approx V(\vec{r}) + \frac{1}{2}\sum_i \frac{\partial^2 V}{\partial x_{\omega,i}^2}\langle x_{\omega,i}^2 \rangle$$

$$\langle x_{\omega,x}^2 \rangle = \langle x_{\omega,y}^2 \rangle = \langle x_{\omega,z}^2 \rangle = \frac{1}{3}\langle x_\omega^2 \rangle$$

$$\Delta V_\omega = V(\vec{r}+\vec{x}_\omega) - V(\vec{r}) \approx \frac{1}{6}\left(\vec{\nabla}^2 V(r)\right)\langle x_\omega^2 \rangle$$

$\frac{1}{r}$ Coulomb potential $\longrightarrow$ $\vec{\nabla}^2 V = 4\pi Z e \,\delta(\vec{r})$

$$\Delta E_\omega = e\,\Delta V_\omega = \frac{4\pi Z e^2}{6}\langle x_\omega^2 \rangle \langle \delta(\vec{r}) \rangle$$

$|\psi(r=0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}$

$$\Delta E_\omega = \frac{2}{3\pi^2}\frac{Z^4 e^4\, hc}{(mc^2)^2\,\omega\, n^3 a_0^3}$$

$\longrightarrow$ this again is one ω, integrate this over relevant ω

diverges 8then

let's say

$$\hbar \omega_{max} \sim mc^2$$ ← biggest scale

$$\hbar \omega_{min} \sim E_{gross} = \left(\frac{Z\alpha}{n}\right)^2 mc^2$$ ← smallest scale

cgs

$$\int_{\omega_{min}}^{\omega_{max}} \Delta E_\omega \, d\omega = \frac{2}{3\pi^2} \frac{Z^4 e^4}{(mc^2)^2} \frac{\hbar c}{n^3 a_0^3} \underbrace{\ln\left(\frac{\omega_{max}}{\omega_{min}}\right)}$$

$$\sim \frac{Z^2 \alpha^3}{n} E_n \left(\frac{4}{3\pi^2}\right) \ln\left(\frac{n^2}{Z^2 \alpha^2}\right)$$

plug in and get $\overbrace{\frac{\Delta E}{h} \sim 1.6 \text{ GHz}}^{\text{less bound}}$ for hydrogen 2s, close to experiment

↳ precise measurement is a sensitive probe for new physics, refining theory