Lecture 16 : Application of TIDPT: Fine structure in Hydrogen

Relativistic effects:

Recall characteristic units in Hydrogen

Given m_e, e, $\hbar$

$\Rightarrow$ Length: Bohr radius $a_0 = \frac{\hbar^2}{m_e e^2} \sim 0.5\,\mathring{A}$

Energy: Hartree $E_c = \frac{e^2}{a_0} = \frac{m_e e^4}{\hbar^2} \sim 27.2\text{ eV} = 2\,Ry$

$\Rightarrow$ time: $t_c = \frac{\hbar}{E_c} = \frac{\hbar a_0}{e^2}$

$\Rightarrow$ Velocity: $v_{ch} = \frac{a_0}{t} = \frac{e^2}{\hbar}$

Relativity $\Rightarrow$ New constant c

$\Rightarrow$ Dimensionless unit $\boxed{\alpha = \frac{v_{ch}}{c} = \frac{e^2}{\hbar c} \simeq \frac{1}{137}}$

Fine structure constant

$\Longrightarrow$ Relativistic effects small perturbation to energy levels given in nonrelativistic Schrödinger equation

Exact solution $\Rightarrow$ Dirac Equation

Relativistic perturbations

- Spin-orbit coupling

In the rest frame of the electron one sees a magnetic field due to the motion of the charged proton

$\Rightarrow$ In electron frame $\vec{B}_{eFrame} = -\frac{1}{c}\vec{v}\times\vec{E}$

$$\Rightarrow \vec{B}_{eFrame} = -\frac{1}{c}\vec{v}\times\left(\frac{e}{r^3}\vec{x}\right)$$

$$= \frac{e}{mc}\frac{(\vec{p}\times\vec{x})}{r^3}$$

$$= +\frac{e}{mc}\vec{L}\frac{1}{r^3} = \frac{e\hbar}{mc}\vec{\ell}\frac{1}{r^3}$$

$$= 2\mu_B\frac{\vec{\ell}}{r^3} \qquad \text{where } \mu_B = \frac{e\hbar}{2mc} = \text{Bohr magneton}$$

$$\vec{\ell} \equiv \vec{L}/\hbar$$

magnetic field of current loop, at position of electron (mag moment $\vec{\mu} = \mu_B\vec{\ell}$)

$\Rightarrow$ We would say

$$\hat{H}'_{SO} = -\vec{\mu}_{electron}\cdot\hat{\vec{B}}_{eframe} = -2\frac{\vec{\mu}_e\cdot\vec{\mu}_{current}}{r^3}$$

$$\vec{\mu}_{electron} = -g_s\mu_B\hat{\vec{S}}, \quad g_s = 2$$

Perturbation to Hydrogen due to spin-orbit

$$\hat{H}_{SO} = +4 \frac{\mu_B^2}{r^3} \hat{\vec{l}} \cdot \hat{\vec{s}}$$

In dimensionless units (take out Hartree)

$$\hat{H}_{SO} = \frac{\alpha^2}{\cancel{2}} \frac{\hat{\vec{l}} \cdot \hat{\vec{s}}}{r^3}$$

- Since ground state is $l=0 \Rightarrow$ no shift
- First excited state: 4 fold degenerate w/o spin
  $|2s\rangle$, $|2p, 1, 0, -1\rangle$

With spin: State space is tensor produce of orbital and spin degrees of freedom

$$|n, l, m_l\rangle \otimes |s, m_s\rangle \Rightarrow 8 \text{ fold degenerate}$$

Degenerate perturbation theory $\Rightarrow$ diagonalize $\hat{H}_{SO}$ in 8-dim subspace

However, in this case we note:

Recall $\hat{\vec{j}} \equiv \hat{\vec{l}} + \hat{\vec{s}}$ = Total electron angular momentum

$$\Rightarrow \hat{\vec{j}}^2 = \hat{\vec{l}}^2 + \hat{\vec{s}}^2 + 2 \hat{\vec{l}} \cdot \hat{\vec{s}}$$

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$$\Rightarrow \hat{H}'_{so} = 4(\mu_B)^2 (\hat{\vec{l}} \cdot \hat{\vec{s}}) \frac{1}{\hat{r}^3}$$

this is off by a factor of 2.

Reason: The electron rest frame is not an inertial frame. In the rotating frame the affect is like a fictitious magnetic field (recall Larmor's theorem) This is a purely kinematic effect, not due to E&M! The appropriate fictitious field leads to Thomas Precession (see, e.g. J.D. Jackson, Electrodynamics)

With Thomas precession

$$\hat{H}_{so} = -\frac{1}{2} \vec{\mu}_{electron} \cdot \vec{B}_{eframe}$$

$$\boxed{\hat{H}_{so} = +2\frac{\mu_B^2}{\hat{r}^3} (\hat{\vec{l}} \cdot \hat{\vec{s}})}$$

spin-orbit coupling also known as L-S coupling

estimate size of effect $\frac{\mu_B^2}{a_0^3} = \Delta E_{so}$

$$\mu_B \cong \frac{e\hbar}{mc} = \left(\frac{e^2}{\hbar c}\right)\left(e\frac{\hbar^2}{me^2}\right) = \alpha(ea_0)$$

$$\Delta E_{so} \sim \alpha^2 \frac{e^2}{a_0} = \alpha^2 (\text{Hartree})$$

Thus, $\hat{\vec{l}}\cdot\hat{\vec{s}} = \frac{1}{2}\left(\hat{\vec{j}}^2 - \hat{\vec{l}}^2 - \hat{\vec{s}}^2\right)$

$\Rightarrow$ $\hat{H}_{SO}$ is diagonalized in the coupled basis of angular momentum $|j\,l\,s\,m_j\rangle$

$$|n\,l\,s\,j\,m_j\rangle = \underbrace{|n\,l\rangle}_{\text{radial}} \otimes \underbrace{|j\,l\,s\,m_j\rangle}_{\text{angular + spin}}$$

$\Rightarrow$ In this basis:

$$\hat{H}_{SO} = \frac{\alpha^2}{2r^3}\left[\frac{j(j+1) - l(l+1) - s(s+1)}{2}\right]$$

For electron $s = \frac{1}{2}$ $\Rightarrow$ $s(s+1) = \frac{3}{4}$

Also, we know from the "triangle inequality"

$$|l-s| < j < l+s$$

$$\Rightarrow \quad j = l-\tfrac{1}{2} \quad \text{or} \quad j = l+\tfrac{1}{2}$$

$$\Rightarrow \hat{H}_{SO} = \frac{\alpha^2}{4r^3}\begin{cases} l & j = l+\frac{1}{2} \\ -(l+1) & j = l-\frac{1}{2}\end{cases}$$

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Thus the eigenvalues of $\hat{H}_{SO}$ within a manifold defined by principle q-number n

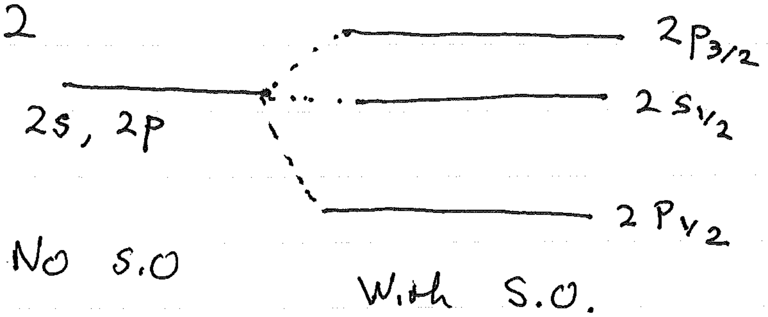
$$\Delta E^{S.O.}_{n,\ell,j} = +\frac{\alpha^2}{4}\left\langle\frac{1}{r^3}\right\rangle\begin{cases} \ell & j = \ell+\frac{1}{2} \\ -(\ell+1) & j = \ell-\frac{1}{2}\end{cases}$$

Aside: $\langle n\ell|\frac{1}{r^3}|n\ell\rangle = \dfrac{1}{n^3\ell(\ell+1)(\ell+\frac{1}{2})}$

$$\Rightarrow \boxed{\Delta E^{S.O.}_{n,\ell,j} = \frac{\alpha^2}{4}\,\frac{\begin{cases} \ell & j = \ell+\frac{1}{2} \\ -\ell-1 & j = \ell-\frac{1}{2}\end{cases}}{n^3\ell(\ell+1)(\ell+\frac{1}{2})}}$$

* $\ell = 0$ we have $\frac{0}{0}$ → indetermined. Work with Dirac eq!

e.g. $n = 2$



Spectroscopic notation: $|n\ell_j\rangle$

Spin orbit coupling partially breaks degeneracy. There is still axial symmetry $\Rightarrow$ $2j+1$ states for every $|n\ell_j\rangle$

Other relativistic effects

In the nonrelativistic case, in the center of mass frame, the kinetic energy

$$\hat{T} = \frac{\hat{p}^2}{2\mu} = \frac{\hat{p}^2}{2}\left(\frac{1}{m_e} + \frac{1}{M_p}\right)$$

μ ← reduced mass

where $\vec{p}$ = relative coordinate. In C.O.M. frame $\vec{P}_e = -\vec{P}_p = \vec{P}_{rel} = \vec{P}$

Relativistically, the ~~...~~ energy of the electron (excluding E&M potential energy) is $\sqrt{p_e^2 c^2 + (m_e c^2)^2}$. The proton is very massive so we neglect it's relativistic motion

$\Rightarrow$ To lowest order in $\frac{v_{ch}}{c}$

$$\sqrt{p_e^2 c^2 + (m_e c^2)^2} + \frac{P_{Proton}^2}{2M_p} \cong m_e c^2 + \frac{P_e^2}{2m_e} - \frac{(P_e^2)^2}{8 m_e^3 c^2} + \frac{P_{Proton}^2}{2M_p}$$

$$= \underset{\text{constant}}{m_e c^2} + \frac{P_{rel}^2}{2\mu} - \frac{1}{8}\frac{(P_{rel}^2)^2}{m_e^3 c^2}$$

$$\Rightarrow \hat{H}_{kin} = -\frac{1}{8}\frac{(P_{rel}^2)^2}{m_e^3 c^2}$$ another perturbation

$$\hat{H}_{kin} = -\frac{1}{8}\left(\frac{P_{rel}^2}{\mu^3 c^2}\right)\cancel{\left(\frac{m_e}{\mu}\right)^{-3}} \to \approx 1$$

$$\Rightarrow \quad \Delta E_{nlj}^{kin} = -\frac{\langle nl|\,\hat{p}^4\,|nl\rangle}{8\,m^3c^2}$$

$$= -\frac{\|\hat{p}^2\,|nl\rangle\|^2}{8\,m^3c^2}$$

Aside: $\left\{ \begin{array}{l} \hat{p}^2|nl\rangle = 2m\,(E_n - \hat{V})\,|nl\rangle \\ \Rightarrow \langle nl|\,\hat{p}^4|nl\rangle = 4m^2\left(E_n^2 - 2E_n\langle\hat{V}_{nl}\rangle + \langle\hat{V}^2\rangle_{nl}\right) \end{array}\right.$

$$\therefore \quad \Delta E_{nlj}^{kin} = -\frac{1}{2mc^2}\left(E_n^2 - 2E_n\langle\hat{V}\rangle_{nl} + \langle\hat{V}^2\rangle_{nl}\right)$$

with $E_n = -\frac{1}{2n^2}\frac{e^2}{a_0} = -\frac{1}{2n^2}\alpha^2 mc^2$

in atomic units

$$\frac{\Delta E_{nlj}^{kin}}{(e^2/a_0)} = -\frac{\alpha^2}{2}\left(\frac{1}{4n^4} - \frac{1}{n^2}\left\langle\frac{1}{r}\right\rangle_{nl} + \left\langle\frac{1}{r^2}\right\rangle_{nl}\right)$$

Having used $\hat{V} = -\frac{e^2}{r} = -\frac{e^2}{a_0}\frac{1}{r}$

Aside: $\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2}$ $\qquad \left\langle\frac{1}{r^2}\right\rangle = \frac{1}{n^3(l+\frac{1}{2})}$

$$\therefore \quad \Delta \bar{E}_{nlj}^{kin} = -\frac{\alpha^2}{2}\left(\frac{1}{n^3(l+\frac{1}{2})} - \frac{3}{4}\frac{1}{n^4}\right)$$

Now let us add together these two contributions to get the total "fine structure" for $l \neq 0$

• $j = l + \frac{1}{2}$

$$\Delta \bar{E}^{(+)}_{nlj} = \frac{\alpha^2}{2}\left(\frac{1}{2n^3(l+1)(l+\frac{1}{2})} - \frac{1}{n^3(l+\frac{1}{2})} + \frac{3}{4n^4}\right)$$

$$= \frac{\alpha^2}{2}\left(\frac{-1}{n^3(l+1)} + \frac{3}{4n^4}\right)$$

$$= -\frac{\alpha^2}{2n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)$$

• $j = l - \frac{1}{2}$

$$\Delta \bar{E}^{(-)}_{nlj} = \frac{\alpha^2}{2}\left(\frac{-1}{2n^3 l(l+\frac{1}{2})} - \frac{1}{n^3(l+\frac{1}{2})} + \frac{3}{4n^4}\right)$$

$$= \frac{\alpha^2}{2}\left(\frac{-1}{n^3 l} + \frac{3}{4n^4}\right)$$

$$= -\frac{\alpha^2}{2n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)$$

Thus, we see that the Fine structure in H (first relativistic correction) depends only and not the l total electron ang. mom. q-number j

$$\boxed{\Delta \bar{E}_{nlj} = -\frac{\alpha^2}{2n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)}$$

lowest in α correction

Note: the "exact solution" in the Dirac eq is

$$E_{nlj} = mc^2\left[1 + \alpha^2\left(n - j - \tfrac{1}{2} + \sqrt{(j+\tfrac{1}{2})^2 + \alpha^2}\right)\right]^{-1/2}$$

(includes rest mass and zeroth order)

S-states

For s-states ($l=0$), there is no spin-orbit coupling (since oribital angular momentum is zero). There is a kinetic perturbation

$$\Delta \bar{E}^{kin}_{n\, l=0} = -\frac{\alpha^2}{2}\left(\frac{2}{n^3} - \frac{3}{4}\frac{1}{n^4}\right)$$

There is one additional effect that is of order α^2 in atomic units that arises in the relativistic theory of the electron. The true relativistic theory is not a single-particle theory. Electrons and positrons can be created and annihilated. When one looks as the Dirac theory as a single electron theory in the non-relativistic limit one finds that the even for a free particle the position is rapidly fluctuating. Schrödinger referred to this as "Zitterbewegung" or "trembling motion". The end result is that the position of the electron is "smeared out" on the order of $\Delta r = \frac{\hbar}{mc}$ (the Compton wavelength)

The Coulomb energy is thus smeared out

$$V(r+\Delta\vec{r}) = V(r) + \Delta\vec{r}\cdot\vec{\nabla}V + \frac{1}{2}\sum_{ij}\Delta r_i\,\Delta r_j\,\frac{\partial^2}{\partial x_j\partial x_j}V$$

Averaging over the fluctuation

$$\langle\Delta\vec{r}\rangle = 0 \qquad \langle\Delta r_i\Delta r_j\rangle = \frac{1}{3}\langle\Delta r^2\rangle = \frac{\hbar^2}{3mc^2}$$

$$\Rightarrow V(\vec{r}+\Delta\vec{r}) \approx V(r) + \frac{\hbar^2}{6m^2c^2}\nabla^2 V(r)$$

For the Coulomb potential, $V(r) = \frac{e^2}{r}$, $\nabla^2 V = e^2 4\pi\delta^{(3)}(\vec{r})$

$$\Rightarrow \text{Perturbation } H_{Dar} = \frac{\hbar^2 e^2}{8m^2c^2}4\pi\delta(\vec{x}) = \frac{\hbar^2 e^2}{8mc^3 a_0^3}\,4\pi\delta^{(3)}(\vec{X}) \quad \text{Dimensionless}$$

(Known as "Darwin term")

$$= \left(\frac{e^2}{a_0}\right)\frac{\alpha}{2}\pi\delta^{(3)}(\vec{X})$$

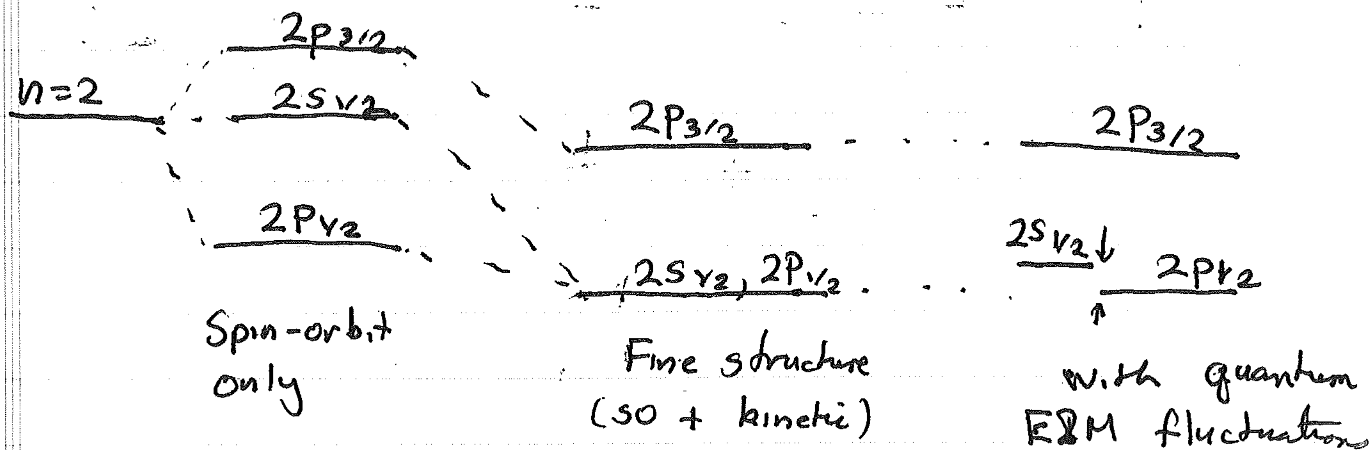
<u>This perturbation only contributes for s-states</u> since $R_{nl}\propto r^l$

$$\Rightarrow \Delta\bar{E}^{Darwin}_{n0} = \frac{\alpha^2}{2}\pi|R_{n0}(0)|^2 = \frac{\alpha^2}{2n^3}$$

⇒ Total perturbation Energy for S-states

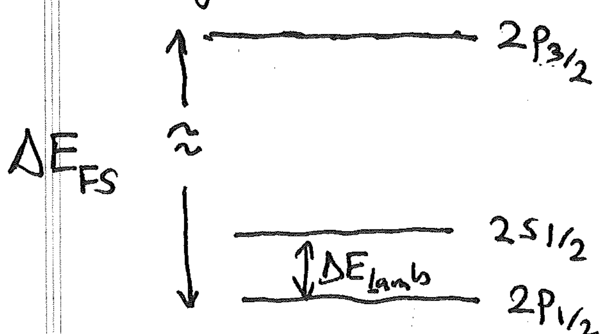
$$\Delta E_{n\,l=0\,j=1/2} = -\frac{\alpha^2}{2n^3}\left(1 - \frac{3}{4n}\right) = -\frac{\alpha^2}{2n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) \checkmark$$

The relativistic corrections to the $n=2$ state of H are sketched ~~below~~ below:



Here we have shown in the last diagram an effect not included in the Dirac equation — coupling to the electromagnetic vacuum. These fluctuation yield a shift of the $2S_{1/2}$ known as the "Lamb shift". It comes from QED and is of order (in atomic units) $\alpha^3 \log\alpha$

Thus the true spectrum of Hydrogen (neglecting the hyperfine splitting to be discussed next lecture)



$$\frac{\Delta E_{FS}}{h} = 10.969 \text{ GHz}$$

$$\frac{\Delta E_{Lamb}}{h} = 1.0578 \text{ GHz}$$