4 Time-ind. Perturbation Theory II

We said we solved the Hydrogen atom exactly, but we lied. There are a number of physical effects our solution of the Hamiltonian $H = p^2/2m - e^2/r$ left out. We already said motion of proton can be accounted for by nearly trivial reduced mass correction—not important, since spectra of original problem unchanged except for tiny overall energy scaling.

In fact there are a hierarchy of other effects we left out, each of which can be treated in perturbation theory on top of the other. In the most complete theory, almost all degeneracies are split. Classify formally in powers of fine structure constant $\alpha \equiv e^2/\hbar c \simeq 1/137$.

1. Bohr levels: $E_n = -R/n^2 \quad \mathcal{O}(\alpha^2 mc^2)$
2. Fine structure: $-R^2\alpha^2 \left( \frac{n}{j+1/2} - \frac{3}{4} \right) \quad \mathcal{O}(\alpha^4 mc^2)$
   (relativistic effects–kinetic energy & spin-orbit coupling)
3. Hyperfine structure: $\mu_0 ge^2/3\pi m_p m_0 \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle \quad \mathcal{O}(m/m_p)(\alpha^4 mc^2)$
   (spin-spin coupling of $e^-$ & $p^+$ magnetic moments)
4. Lamb shift: $\frac{1}{3\pi} \frac{R}{n^2} \left( \frac{2\alpha}{n} \right)^3 \ln \frac{mc^2}{|E_p - E_n|_{\text{avg}}} \quad \mathcal{O}(\alpha^5 mc^2)$
   (quantization of photon field–really larger than hyperfine)

4.1 Fine Structure—spin-orbit coupling

1st effect of interest is coupling of i) spin of electron to ii) its motion, 2 things which we certainly treated independently before. Full derivation of proper $\hat{V}$ is hairy, give only hand-waving derivation here, misses factor of 2.

Force on electron is $-e\mathbf{E} = -e^2\mathbf{r}/(4\pi \epsilon_0 r^3)$. Recall that observer moving in electric field $\mathbf{E}$ sees magnetic field
\[ \mathbf{B} = \frac{\mathbf{v}}{c^2} \times \mathbf{E} \quad v \ll c \quad (1) \]

So electron with magnetic moment
\[ \vec{\mu} = -g \frac{e}{2m} \mathbf{S}, \quad g \simeq 2 \quad (2) \]

should have energy
\[ \hat{V} = -\mu \cdot \mathbf{B} \quad (3) \]
\[ = -g \frac{e}{2m} \mathbf{S} \cdot \frac{e}{4\pi \epsilon_0 r^3} \mathbf{r} \times \frac{\mathbf{v}}{c^2} \quad (4) \]

so with \( \mathbf{L} \simeq \mathbf{r} \times m\mathbf{v} \), get
\[ \hat{V} = \frac{ge^2}{2m^2 c^2} \left( \frac{1}{4\pi \epsilon_0 r^3} \right) \mathbf{L} \cdot \mathbf{S} \quad (5) \]

Off by factor of 2 from full relativistic calculation (neglected Thomas precession!):
\[ \hat{V} = \frac{ge^2}{4m^2 c^2} \frac{1}{4\pi \epsilon_0 r^3} \mathbf{L} \cdot \mathbf{S} \quad (6) \]
\[ = f(r) \mathbf{L} \cdot \mathbf{S} \quad (7) \]
\[ = f(r) \mathbf{L} \cdot \mathbf{S} \quad (8) \]

Now define total angular momentum
\[ \mathbf{J} = \mathbf{L} + \mathbf{S} \quad (9) \]

whose square is
\[ \hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\mathbf{L} \cdot \mathbf{S}, \quad (10) \]

so
\[ \hat{V} = \frac{f(r)}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \quad (11) \]

Verify: \( \hat{J}^2, \hat{L}^2, \hat{S}^2 \), and \( \hat{J}_z \) now commute with \( H = H_0 + \hat{V} \). \( \hat{L}_z \) and \( \hat{S}_z \) no longer do. We choose therefore to label states as
Thus we aren’t quite following prescription we set out, by looking at expectation value of $\hat{V}$ in original eigenstates of $H_0$. Why? Because we can find the new exact eigenstates with no work. So energy shift calculation is exact—except for higher order relativistic effects. In this basis we have

$$
(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)|n\ell sjm_j\rangle = \hbar^2 (j(j+1) - \ell(\ell+1) - \frac{3}{4})|n\ell sjm_j\rangle \quad (12)
$$

so energy shift due to spin-orbit coupling is

$$
\delta E_{so} = \langle n\ell sjm_j|\hat{V}|n\ell sjm_j\rangle = \hbar^2 (j(j+1) - \ell(\ell+1) - \frac{3}{4}) \langle f(r) \rangle \quad (13)
$$

For $\langle f(r) \rangle$ we need

$$
\langle \frac{1}{r^3} \rangle = \frac{1}{\ell(\ell + 1/2)(\ell + 1)n^3a_0^3} \quad (\ell \neq 0) \quad (14)
$$

(see Griffiths Probs. 6.34, 6.35). Spin-orbit energy shift is therefore

$$
\delta E_{so} = \frac{E_n^2}{mc^2} \left( \frac{n(j(j+1) - \ell(\ell+1) - \frac{3}{4})}{\ell(\ell + \frac{1}{2})(\ell + 1)} \right) \quad (15)
$$

$$
= \frac{E_n^2}{mc^2} (\frac{2n}{j(j+1/2) - j(j+1/2)}) \quad \text{(check for } j = \ell \pm \frac{1}{2}!) \quad (16)
$$

Note although (15) looks singular at $\ell \to 0$, proper relativistic treatment
by Dirac shows nonsingular result (16) is correct for all \( \ell \)--not obvious though!

**Relativistic kinetic energy corrections.** Up to now we have neglected relativistic effects in kinetic energy term \( \hat{T} \). Properly we should probably write

\[
\hat{T} = \sqrt{\hat{p}^2 c^2 + m^2 c^4} - mc^2 \simeq \frac{\hat{p}^2}{2m} - \frac{\hat{p}^4}{8m^3c^2} + \ldots
\]  

(17)

Then we need to find the energy shift in \( |\psi\rangle \) to leading order in the perturbation \( \hat{V} \):

\[
\delta E_{\text{rel}} = -\frac{1}{8m^3c^2} \langle \psi | \hat{p}^4 | \psi \rangle = -\frac{1}{8m^3c^2} \langle \hat{p}^2 \psi | \hat{p}^2 \psi \rangle
\]

(18)

The rhs supposed to be evaluated using *unperturbed wave fctns*, so use \( (\hat{p}^2/2m - e^2/(4\pi\epsilon_0r))|\psi\rangle = E_n|\psi\rangle \) to find

\[
\delta E_{\text{rel}} = -\frac{1}{2mc^2} \left[ E_n^2 + 2E_n e^2 \left( \frac{1}{4\pi\epsilon_0 r} \right) + e^4 \left( \frac{1}{(4\pi\epsilon_0)^2 r^2} \right) \right]
\]

(19)

The expectation values depend only on \( a_0, n \) and \( \ell \) as usual:

\[
\langle \frac{1}{r} \rangle = \frac{1}{n^2a_0}; \quad \langle \frac{1}{r^2} \rangle = \frac{1}{(\ell + 1/2)n^3a_0^2}
\]

(20)

So full relativistic kinetic energy shift is

\[
\delta E_{\text{rel}} = -\frac{E_n^2}{2mc^2} \left( \frac{4n}{\ell + 1/2} - 3 \right)
\]

(21)

and full *fine structure* energy splitting is

\[
\delta E_{\text{fine}} = \delta E_{\text{so}} + \delta E_{\text{rel}}
\]

(22)

yielding an energy spectrum for hydrogen up to fine structure corrections of

\[
E = E_n + \delta E_{\text{fine}} = -\frac{R}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j + 1/2} - 3/4 \right) \right]
\]

(23)
4.2 Hyperfine Interaction

Hyperfine splitting of atomic spectral lines arises from interaction of electron & nuclear dipole moments. Whereas ground state in hydrogen not split by fine structure, it is split by hyperfine interaction, allowing for transition between two levels, producing radiation of wavelength 21 cm ($\sim 10^{-7}$Ryd, allows tracking of hydrogen by astronomers, measurements of proper motion of celestial objects (Doppler shifts of line), & construction of stable atomic clocks. Calculation is lengthy, but can be solved by elementary methods to high accuracy ("real" quantum mechanics problem!).

Magnetic field due to dipole moment $\mu$:

$$\mathbf{B} = \frac{1}{4\pi\varepsilon_0} \left( \frac{3\mathbf{r}(\vec{\mu} \cdot \mathbf{r})}{r^5} - \frac{\vec{\mu}}{r^3} \right),$$

(24)

whereas the interaction of a magnetic moment with external field is

$$U = -\vec{\mu} \cdot \mathbf{B}$$

(25)
so interaction is

\[
\hat{V} = \frac{1}{4\pi\epsilon_0} \left( -\frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_p \cdot \vec{r})}{r^5} + \frac{(\vec{\mu}_e \cdot \vec{\mu}_p)}{r^3} \right)
\]  

(26)

where \( \vec{r} = \vec{r}_e - \vec{r}_p \)

Magnetic moment operators:

\[
\vec{\mu}_e = -g_e \frac{e}{2M_e} \vec{S}_e \quad ; \quad \vec{\mu}_p = g_p \frac{e}{2M_p} \vec{S}_p
\]  

(27)

with gyromagnetic ratios \( g_e \simeq 2.00, \ g_p \simeq 5.59 \).

Perturbation theory

Want to use \( \hat{V} \) in (25) as perturbation, write \( H = H_0 + H_{\text{fine}} + \hat{V} \), look for hyperfine energy shift \( \delta E_{hf} \) in ground state \( |\psi_0\rangle \).  

1 Can write ground state as

\[
|\psi_0\rangle = |\psi_{100}(r)\rangle |m_e \ m_p\rangle
\]  

(28)

where 1st factor is spatial part, old friend \( \psi_{100} = e^{-r/a_0}/\sqrt{\pi a_0^3} \), 2nd factor represents spin state of electron and now proton, too (before we ignored proton spin since it didn’t contribute to energy, now we must include it as

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1 Note we will focus exclusively on the ground state of the H-atom, where the spin-orbit coupling has already been accounted for. Although in general states of definite \( m_p, m_e \) are not eigenstates because of the \( \vec{L} \cdot \vec{S} \) coupling, for the \( S_{1/2} \) ground state, \( m_j \) (e’value of \( J_z/\hbar \)) is the same as \( m_s \) (e’value of \( S_z/\hbar \)) always since \( \ell = 0 \). We call \( m_s \) of electron \( m_e \) here, and \( m_s \) for proton \( m_p \).
dynamical variable). Note there are four degenerate states before taking $\hat{V}$ into account, since both $m_e$ and $m_p$ can be $\pm 1/2$. A priori we expect that since $\hat{V}$ commutes with $\hat{S}^2 = (\hat{S}_e + \hat{S}_p)^2$, eigenstates of new $H$ with hyperfine term should be eigenstates of $\hat{S}^2$, i.e. either $S = 1$ (triplet) or $S = 0$ (singlet).² 21cm spectral line we’re looking for will be difference in shifts of 3 degenerate triplet states $|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$, and singlet state $|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$.

So we want to evaluate

$$\delta E_{hf} = \langle \psi'_0 | \hat{V} | \psi'_0 \rangle = \frac{g_e g_p e^2}{16\pi\epsilon_0 M_e M_p} \int d^3r |\psi_{100}(r)|^2 \left( \frac{3(S_e \cdot r)(S_p \cdot r)}{r^3} - \frac{(S_e \cdot S_p)}{r^3} \right)$$

which the $|SM\rangle$ are e’states of total spin $\hat{S}^2$ and total $\hat{S}_z$, and

$$I^{\alpha\beta} = \int d^3r |\psi_{100}(r)|^2 \left( \frac{3r_\alpha r_\beta}{r^5} - \frac{\delta^{\alpha\beta}}{r^3} \right)$$

is a tensor we have to evaluate using the wave function $\psi_{100}$. Tedious but straightforward to show that $I^{\alpha\beta} = I^\delta_{\alpha\beta}$, with $I = 8\pi |\psi_{100}(0)|^2/3$ (see below!). $I$ diagonal $\implies$ only spin matrix elements we need are

$$\langle SM|S_e \cdot S_p|SM\rangle = \langle SM|\frac{1}{2}(\hat{S}^2 - \hat{S}_e^2 - \hat{S}_p^2)|SM\rangle$$

$$= \langle SM|\frac{\hbar^2}{2} \begin{cases} 0 & S = 1 \\
\frac{3}{8} - \frac{1}{8} & S = 0 \end{cases} \rangle$$

$$\delta E_{hf} = \langle \psi'_0 | \hat{V} | \psi'_0 \rangle = \frac{g_e g_p e^2}{16\pi\epsilon_0 M_e M_p} \int d^3r |\psi_{100}(r)|^2 \left( \frac{3(S_e \cdot r)(S_p \cdot r)}{r^3} - \frac{(S_e \cdot S_p)}{r^3} \right)$$

So energy shifts for singlet and triplet states are

²Check that $\hat{S}^2$ commutes with $\hat{V}$ by first writing $\hat{S}^2 = (\hat{S}_e + \hat{S}_p)^2 = \hat{S}_e^2 + \hat{S}_p^2 + S_e \cdot S_p$. First of all, $\hat{S}_e^2$ commutes with $\hat{V}$ since $[\hat{S}_e^2, S_{e,\alpha}] = 0$, similarly for $\hat{S}_p^2$. Now $S_e \cdot S_p$ obviously commutes with second term of $\hat{V}$ (see (25)), harder part is to see $[S_e \cdot S_p, (\hat{S}_e \cdot \hat{S}_e \cdot r)\hat{S}_p \cdot \hat{S}_p] = 0$. To see this, use relation $\sigma_i \sigma_j = \delta_{ij} + \epsilon_{ijk} \sigma_k$.

³Need to use states $\psi'_0 >$ in which $\hat{V}$ is diagonal—these are precisely the $|SM\rangle$! 

7
\[
\delta E_{hf} = \frac{g_e g_p e^2}{16\pi \epsilon_0 M_e M_p} \left(\frac{8\pi |\psi_{100}(0)|^2}{3}\right) \begin{cases} 
\hbar^2/4 & S = 1 \\
-3\hbar^2/4 & S = 0 
\end{cases}
\] \\
= \frac{g_e g_p e^8 M_e^2}{24\pi \epsilon_0 M_p \hbar^4} \begin{cases} 
1 & S = 1 \\
-3 & S = 0 
\end{cases}
\]

(33)

So splitting between triplet and singlet (energy of photon emitted in triplet decay) is

\[
\hbar \omega = \delta E_{hf}(S = 1) - \delta E_{hf}(S = 0)
\]

\[
= \frac{g_e g_p e^8 M_e^2}{6\pi \epsilon_0 M_p \hbar^4}
\]

(34)

and frequency of transition is

\[
\nu = \omega/2\pi = \frac{g_e g_p e^8 M_e^2}{12\pi^2 \epsilon_0 M_p \hbar^3}
\]

\[
= 1420405751.800 \pm 0.028 \text{ Hz}
\]

(35)

(36)

or \(\lambda = c/\nu = 21.1 \text{ cm}\). Value given is current measurement!

Pf. of \(I^{\alpha\beta} = 8\pi |\psi_{100}(0)|^2 \delta_{\alpha\beta}/3\)

Recall definition

\[
I^{\alpha\beta} = \int d^3r |\psi_{100}(r)|^2 \left(\frac{3r_\alpha r_\beta}{r^5} - \frac{\delta_{\alpha\beta}}{r^3}\right)
\]

(37)

Quantity \(I^{\alpha\beta}\) is singular integral and must be handled carefully. Note
1. Off-diagonal terms vanish because in $\ell = 0$ state answer must be invariant under rotation of coordinate system, so $I^{\alpha\beta} = I^\delta_{\alpha\beta}$.

2. Diagonal terms funky, since angular part of, e.g. $I^{zz}$ gives

$$\int d\Omega \ (3z^2 - r^2) = 2\pi r^2 \int_{-1}^1 d\cos \theta (3 \cos^2 \theta - 1) = 0$$  \hspace{1cm} (38)

but radial integral is proportional to

$$\int dr \frac{e^{-r/r_0}}{r} = \infty$$  \hspace{1cm} (39)

So we have to find way to take limit $0 \cdot \infty$ sensibly. Note singularity in (38) comes entirely from $r = 0$; if we were to exclude $r = 0$ from range of integration integral would vanish!. So consider very small sphere around $r = 0$, of radius $r_0$ so small we can approximate smoothly varying fctn. $\psi_{100}(r)$ by $\psi_{100}(0)$. Consider diagonal elt. $I^{zz}$ (others must be same by rotation symmetry), express in cylindrical coords:

$$I^{zz} = |\psi_{100}(0)|^2 \int_0^{r_0} d\rho^2 \sqrt{\rho^2 + z^2} \pi \left[ \frac{3z^2}{(\rho^2 + z^2)^{3/2}} - \frac{1}{(\rho^2 + z^2)^{3/2}} \right]_{\rho^2=r_0^2}$$

$$= |\psi_{100}(0)|^2 \int_{-r_0}^{r_0} dz \pi \left[ \frac{-2z^2}{(\rho^2 + z^2)^{3/2}} + \frac{2}{(\rho^2 + z^2)^{1/2}} \right]_{\rho^2=0}$$

$$= |\psi_{100}(0)|^2 \int_{-r_0}^{r_0} dz \ 2\pi \left( \frac{1}{r_0} - \frac{z^2}{r_0} \right)$$

$$= \frac{8\pi}{3} |\psi_{100}(0)|^2$$  \hspace{1cm} (40)