Time-Independent Perturbation Theory

- Consider a time independent $\hat{H}$

Consider the <u>slight</u> modification of the eigenenergies and eigenstates under a perturbation $\hat{H}'$

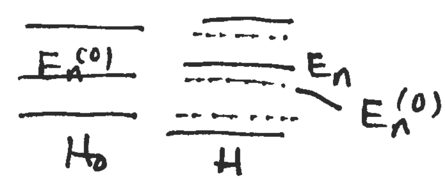
Thus: $\hat{H} = \hat{H}_0 + \underbrace{\lambda}_{\text{small parameter}} \hat{H}'$

For the unperturbed Hamiltonian; $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

$$\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij}$$

Need to solve $\hat{H} \psi_n = E_n \psi_n$

(• assume non-degenerate
• perturbation is small ~~enough~~ enough s.t.
E_n is closer to $E_n^{(0)}$ than any other unperturbed state)

g. 

- Expand E_n, ψ_n in powers of λ:

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \qquad \psi_n = \sum_{j=0}^{\infty} \lambda^j \psi_n^{(j)}$$

j: order of the perturbation

$$(H_0 + \lambda H')\left[\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots\right] =$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\right)\left[\psi_n^{(0)} + \lambda \psi_n^{(1)} + \dots\right]$$

Equate coefficients of equal powers of λ:

λ^0: $H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ (unperturbed)

λ^1: $H_0 \psi_n^{(1)} + H' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$ (leading 1st order)

λ^2: $H_0 \psi_n^{(2)} + H' \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$

$\vdots$

Consider the equation for λ' (leading order correction)

$\downarrow$

multiply both sides by $\psi_n^{(0)*}$ & integrate

$$\underbrace{\langle \psi_n^{(0)} | H_0 - E_n^{(0)} | \psi_n^{(1)} \rangle}_{\langle \psi_n^{(1)} | H_0 | \psi_n^{(0)} \rangle - E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle} + \underbrace{\langle \psi_n^{(0)} | H' - E_n^{(1)} | \psi_n^{(0)} \rangle}_{\langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle - E_n} = 0$$

$$\underbrace{\langle \psi_n^{(1)} | H_0 | \psi_n^{(0)} \rangle - E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{0 \text{ since } H_0 = H_0^*}$$

$$\Longrightarrow \boxed{E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle} \quad **$$

The first order correction to the energy is calculated by acting the <u>perturbing</u> Hamiltonian on the <u>original</u> eigenstates!

We can show:

$$\psi_n^{(1)} = \sum_{l \neq n} \frac{\langle \psi_l^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}} \psi_l^{(0)}$$

Note: For degenerate eigenstates, we need a more complex formula since we don't know which eigenfunctions are approached as $\lambda \to 0$.

Fine Structure of Hydrogen Atom

- Simple picture

$$E_n = \frac{-13.6\,eV}{n^2}$$ with no dependence on l or s

- Effects related to (i) relativistic corrections to the momentum + (ii) spin-orbit coupling break this degeneracy.

- Fine structure constant $\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137.036}$

Bohr energies: $\sim \alpha^2 m_e c^2$

Fine Structure: $\sim \alpha^4 m_e c^2$

Lamb shift: $\sim \alpha^5 m_e c^2$

Hyperfine structure: $\sim \left(\frac{m_e}{m_p}\right) \alpha^4 m_e c^2$

(i) Relativistic Corrections

$$KE = \frac{1}{2} m v^2 = \frac{p^2}{2m} \quad \text{(classically)}$$

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

$$KE = \underbrace{\frac{mc^2}{\sqrt{1-\gamma^2}}}_{\text{total energy}} - \underbrace{mc^2}_{\text{rest energy}} \qquad \gamma = v/c$$

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

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

$$= \left[(KE) + mc^2\right]^2$$

$$\rightarrow KE = \sqrt{p^2c^2+m^2c^4} - mc^2$$

$$= mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1+\frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots -1\right]$$

$$\approx \frac{p^2}{2m} + \frac{-p^4}{8m^3c^2}$$

(we have used $(1+x)^n \approx 1+nx+\ldots$ if $x \ll 1$)

Thus, the perturbing Hamiltonian due to lowest order is $\underbrace{H'_{\text{relativistic}}}_{H'_r} = \dfrac{-p^4}{8m^3c^2}$

- Evaluate using unperturbed eigenstates:

$$E_r^{(1)} = \langle H'_r \rangle = -\frac{1}{8m^3c^2}\langle \psi | p^4 | \psi \rangle = -\frac{1}{8m^3c^2}\langle p^2\psi | p^2\psi \rangle$$

From the Schrödinger equation

$$\hat{p}^2|\psi\rangle = 2m(E-V)|\psi\rangle$$

$$E_r^{(1)} = -\frac{1}{2mc^2}\langle (E-V)^2 \rangle = -\frac{1}{2mc^2}\left[E^2 - 2E\langle V\rangle + \langle V^2\rangle\right]$$

For the Hydrogen atom $V(r) = \dfrac{-e^2}{(4\pi\epsilon_0)r}$

Can calculate $\left\langle \dfrac{1}{r} \right\rangle = \dfrac{1}{n^2 a_\mu}$ ~ Bohr radius

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(\ell + 1/2) n^3 a_\mu^2}$$

$$\longrightarrow \quad E_r^{(1)} = -\frac{1}{2mc^2}\left[E_n^{(0)^2} + 2E_n^{(0)}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2 a_\mu} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{(\ell+1/2)n^3 a_\mu^2} \right.$$

$$= \underbrace{\frac{-E_n^{(0)^2}}{2mc^2}}_{\sim 10^{-5} \text{ smaller than } E_n^{(0)}} \left[\frac{4n}{\ell + 1/2} - 3 \right]$$

(ii) <u>Spin-Orbit Correction</u>

Basic idea: From the rest frame of the e^{-1}, the nucleus appears to be moving around it, generating a <u>magnetic field</u>. This magnetic field interacts with the spin of the electron.

$$H = -\underset{\substack{\downarrow \\ \text{magnetic moment of } e^{-1}}}{\vec{\mu}} \cdot \vec{B}$$

~ field of nucleus (i.e. proton)

For a current loop with current I, $B = \frac{\mu_0 I}{2r}$

Here, $I = \frac{e}{T}$ ~ period of orbit.

The orbital angular of the electron is $L = mvr = \frac{2\pi m r^2}{T}$

$\vec{B}$ and $\vec{L}$ point in the same direction, thus

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L} \quad \left(c = 1/\sqrt{\epsilon_0 \mu_0} \right)$$

Magnetic moment of electron: (classical approx)

- Classically $\mu = \underset{\downarrow q/T}{I} \times \underbrace{\text{Area of loop}}_{\pi r^2}$

$$\mu = \frac{q\pi r^2}{T}$$

$$\vec{S} = \underset{mr^2}{\text{moment of inertia}} \times \underset{2\pi/T}{\text{angular velocity}} = \frac{2\pi m_e r^2}{T}$$

gyromagnetic ratio $g = \frac{\mu}{S} = \frac{q}{2m}$ for ring

Dirac relativistic derivation shows $g = 2$

$$\Rightarrow \vec{\mu}_e = -\frac{e}{m} \vec{S}$$

$$\underset{\text{spin-orbit}}{H'_{s\text{-}o}} = -\vec{\mu}\cdot\vec{B} = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\,\vec{S}\cdot\vec{L}$$

<u>Thomas Precession</u> to account for Lorentz transformation multiplies by $\frac{1}{2}$

$$H'_{SO} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\,\vec{S}\cdot\vec{L}$$

- H no longer commutes with $\vec{L}$ and $\vec{S}$

  H does commute with L^2, S^2 and $\vec{J} = \vec{L}+\vec{S}$.

  The eigenstates of S_z and L_z are not <u>good</u> ones to use in our perturbation calculation.

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

  $\vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2) \Longrightarrow$ eigenvalues are $\frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)$

- $\left\langle \frac{1}{r^3} \right\rangle = \dfrac{1}{l(l+\frac{1}{2})(l+1)n^3 a_\mu^3}$

$\longrightarrow$ $$E^{(1)}_{SO} = \frac{E_n^{(0)2}}{mc^2}\left\{\frac{n\left[j(j+1) - l(l+1) - 3/4\right]}{l(l+1/2)(l+1)}\right\}$$

$\longrightarrow$ $$E^{(1)}_{fs} = E^{(1)}_{r} + E'_{(SO)} = \frac{E_n^{(0)}}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right)$$

The full formula for E with first order corrections,

$$E_{nj} = \frac{-13.6\,eV}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2}-3/4\right)\right]$$

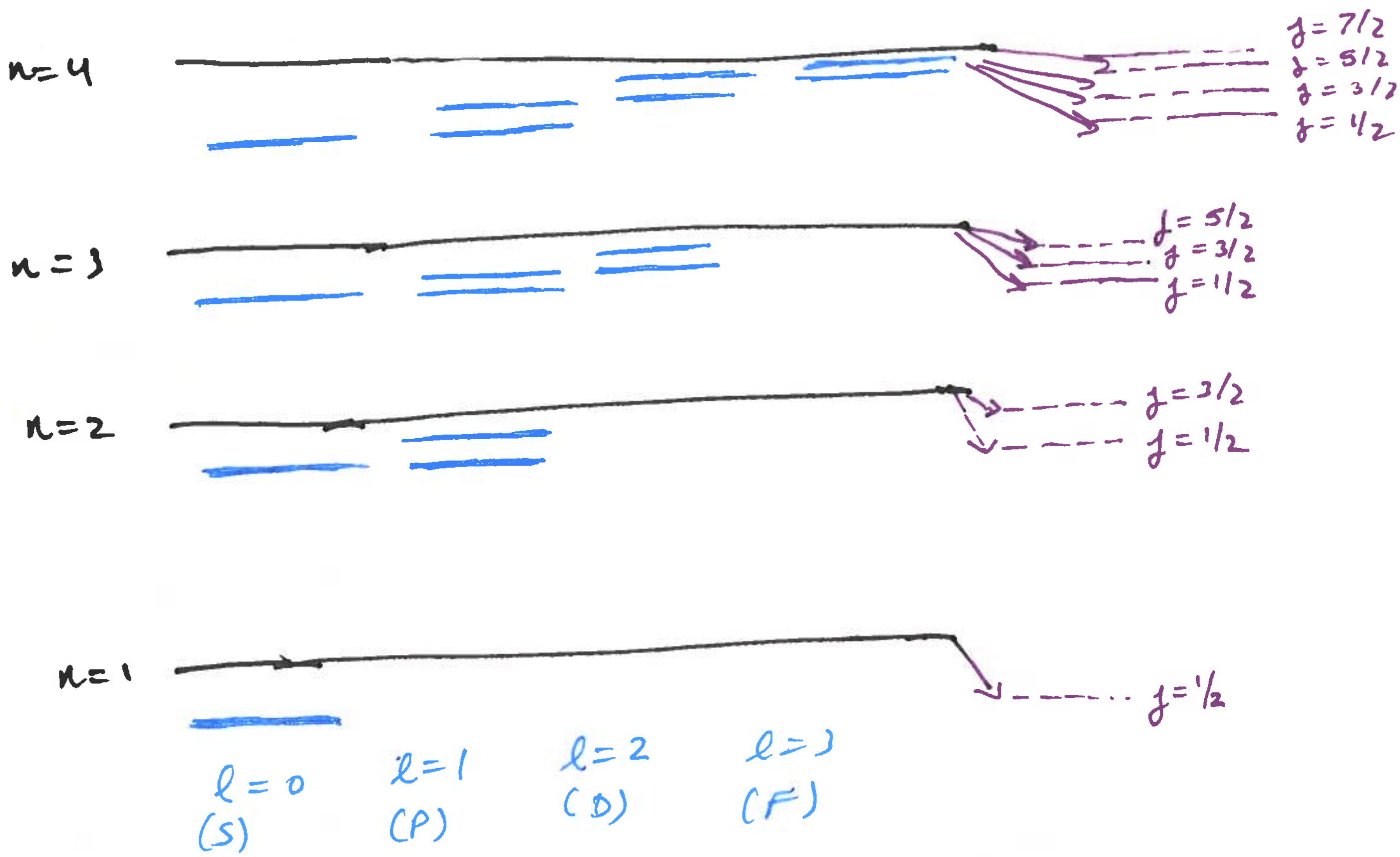
→ breaks degeneracy in l; energies determined by n, j

→ m_l, m_s no longer "good" quantum #s

↓ eigenstates have combinations of these quantities.

→ good #s are n, l, s, j, and m_j

<u>Energy levels.</u>



Additional Corrections to Hydrogen — Lecture #30

• **Zeeman Effect**

$$H_Z' = -(\vec{\mu}_l + \vec{\mu}_s)\cdot \vec{B}_{ext}$$

orbital motion

$$\vec{\mu}_l = -\frac{e}{2m}\vec{L}$$

spin

$$\vec{\mu}_s = -\frac{e}{m}\vec{S}$$

$$H_Z' = \frac{e}{2m}(\vec{L} + 2\vec{S})\cdot \vec{B}_{ext}$$

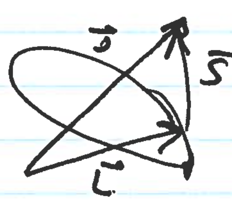
proton

• If $B_{ext} \ll B_{int}$ → Zeeman is a perturbation to fine structure

If $B_{ext} \gg B_{in}$ → Fine structure is a perturbation to Zeeman

A. Weak-field

$$E_Z' = \langle n\, l\, j\, m_j | H_Z' | n\, l\, j\, m_j \rangle = \frac{e}{2m} \vec{B}_{ext} \cdot \langle \vec{L} + 2\vec{S} \rangle$$



$$\langle S \rangle = \frac{(\vec{S}\cdot\vec{J})}{J^2}\vec{J} \leftarrow \text{projection}$$

$$\langle \vec{L} + 2\vec{S} \rangle = \langle \vec{J} + \vec{S} \rangle = \left\langle \left(1 + \frac{\vec{S}\cdot\vec{J}}{J^2}\right)\vec{J} \right\rangle =$$

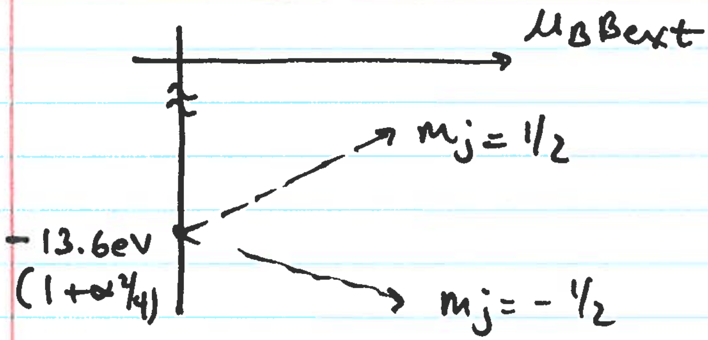
$$\overbrace{= \left[1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right]}^{\text{Landé g-factor } g_J} \qquad ②$$

since $\vec{S}\cdot\vec{J} = \frac{1}{2}(J^2+S^2-L^2)$

Thus $E_Z^1 = \mu_B g_J B_{ext} m_j$

$\mu_B \equiv$ Bohr magneton $= \dfrac{e\hbar}{2m}$

Total energy $= -13.6\,eV(1+\alpha^2/4) \pm \mu_B B_{ext}$



B. <u>Strong field</u>

Unperturbed energies are now $E_{n m_l m_s} = \dfrac{-13.6\,eV}{n^2} + \mu_B B_{ext}(m_l + 2m_s)$

Fine structure perturbation

$$E^{(1)}_{fs} = \langle n\, l\, m_l\, m_s | (H_r' + H_{so}') | n\, l\, m_l\, m_s \rangle$$

$$\langle \vec{S}\cdot\vec{L} \rangle = \langle S_x\rangle\langle L_x\rangle + \langle S_y\rangle\langle L_y\rangle + \langle S_z\rangle\langle L_z\rangle$$

$= \hbar^2 m_\ell m_s$ since $\langle S_x \rangle = \langle S_y \rangle = \langle L_x \rangle = \langle L_y \rangle$ 3
$= 0$ for z eigenstates

$$E_{fs}^{(1)} = \frac{13.6\,\text{eV}}{n^3}\alpha^2 \left\{ \frac{3}{4n} - \left[\frac{\ell(\ell+1) - m_\ell m_s}{\ell(\ell+\frac{1}{2})(\ell+1)} \right] \right\}$$

$$E^{(1)} = E_{n m_\ell m_s} + E_{fs}^{(1)}$$

Hyperfine Splitting

Spin of the proton interacts with spin of the electron!

dipole moments $\vec{\mu}_p = \frac{ge}{2m_p}\vec{S}_p \quad \vec{\mu}_e = \frac{-e}{m_e}\vec{S}_e$

The magnetic field of a dipole $\vec{\mu}$ is (classically):

$$\vec{B} = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}\cdot\hat{r})\hat{r} - \vec{\mu}\right] + \frac{2}{3}\mu_0\vec{\mu}\,\delta^3(\vec{r})$$

$$\hat{H} = -\mu\cdot\vec{B}$$

$$H'_{hf} = \frac{\mu_0 g e^2}{8\pi m_p m_e}\frac{\left[3(\vec{S}_p\cdot\hat{r})(\vec{S}_e\cdot\hat{r}) - \vec{S}_p\vec{S}_e\right]}{r^3} + \frac{\mu_0 g e^2}{3 m_p m_e}\vec{S}_p\cdot\vec{S}_e\,\delta^3(\vec{r})$$

- For the ground state, $l = 0$ (4)
and the first term vanishes due to symmetry.

- $$|\psi_{100}(0)|^2 = \frac{1}{\pi a_\mu^3}$$

$$\longrightarrow E'_{hf} = \frac{\mu_0 g e^2}{3\pi m_p m_e a_\mu^3} \underbrace{\langle \vec{S}_p \cdot \vec{S}_e \rangle}_{\frac{1}{2}(S^2 - S_e^2 - S_p^2)}$$

$S_e^2 \to \frac{3}{4}\hbar^2$, $S_p^2 \to \frac{3}{4}\hbar^2$

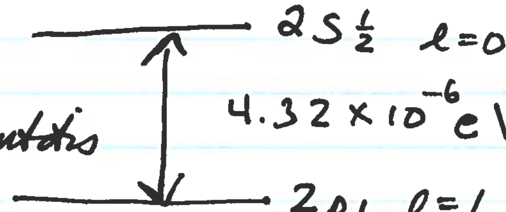
$S^2 = 0$ singlet
$S^2 = 2\hbar^2$ triplet

$$\longrightarrow E'_{hf} = \frac{4g\hbar^4}{3m_p m_e^2 c^2 a_\mu^4} \cdot \begin{Bmatrix} +1/4 \\ -3/4 \end{Bmatrix} \begin{matrix} \text{triplet} \\ \text{singlet} \end{matrix}$$

$$\Delta E = \frac{4g\hbar^4}{3m_p m_e^2 c^2 a_\mu^4} = 5.88 \times 10^{-6}\,\text{eV} \leftrightarrow 1420\ \text{MHz}$$

$\sim$21cm line.

Lamb Shift → Radiative corrections! ⑤

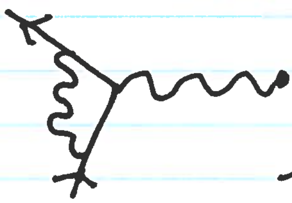


Quantum effect due to vacuum fluctuations

↓

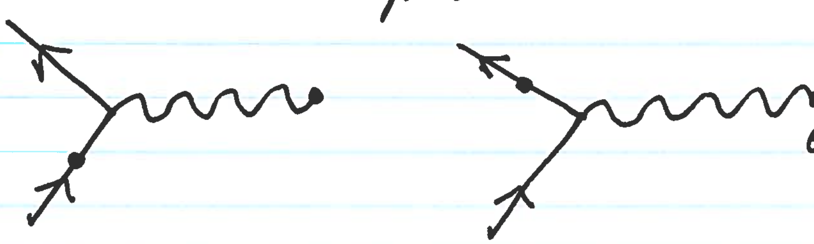
pushes on the electron

self energies

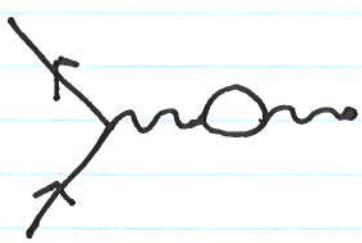


vertex correction

e^{-1} emits a virtual photon then interacts with background $\vec{E}$ and re-absorbs photon



e^{-1} mass counterterm



photon self-energy