Today:

Examples of nondegenerate & degenerate pert. theory: the hydrogen atom

Full treatment of fine structure etc clearest from relativistic point of view (Dirac eqn) - next semester.

Today: heuristically motivate various corrections or perturbations on nonrelativistic Hamiltonian

Review of hydrogen atom:

$$H = \frac{p^2}{2m} - \frac{e^2}{r}$$

m really is reduced mass $m = \frac{m_e m_p}{m_e + m_p}$.

Use sep. of vars (HW)

$$\psi_{n,l,m}(\vec{r}) = \underset{\overset{\downarrow}{\frac{1}{r} u_{k,l}(r)}}{R_{n,l}(r)} \, Y_{lm}(\theta, \phi) \qquad \text{(denote } |n,l,m\rangle\text{)}$$

$n = k + l$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{r} \right] u_{k,l}(r) = E_{k,l}\, u_{k,l}(r)$$

Solutions: solve for large r, e^{-r/na_0},
get polynomial $\cdot\, e^{-r/na_0}$, solve recursion relations

$$R_{nl}(r) \sim (\text{degree } n-1 \text{ poly in } r) \cdot e^{-r/na_0}$$

[rel. to assoc. Laguerre polys]

$$E_n = -\frac{1}{2n^2} mc^2 \alpha^2 = -\frac{e^2}{2n^2 a_0} \approx \frac{-13.6 \text{ eV}}{n^2}$$

$$\alpha = \frac{e^2}{\hbar c} \cong \frac{1}{137} \qquad a_0 = \frac{\hbar^2}{me^2} \cong 0.52\ \text{Å} \quad \textit{(Bohr radius)}$$

Degeneracy of E_n : n^2 $(\ell = 0, 1, \dots, n-1)$
($2n^2$ if include e^- spin)

(1s) $$R_{n=1,\ell=0} = 2(a_0)^{-3/2} e^{-r/a_0}$$

(2s) $$R_{2,0} = 2(2a_0)^{-3/2}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

(2p) $$R_{2,1} = (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$$

$\vdots$

Examples of perturbation theory:

Nondegen pert theory : $n=1$

1) Relativistic correction (part of fine structure)

$$E = \sqrt{m^2c^4 + p^2c^2}$$
$$= mc^2 + \frac{p^2}{2m} - \frac{1}{8}\frac{(p^2)^2}{m^3c^2}$$

So consider

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}, \qquad \lambda V = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2$$

$$E^{(1)}_{n=0} = -\frac{1}{2mc^2}\langle 1,0,0|\left(\frac{p^2}{2m}\right)|1,0,0\rangle$$

$$= -\frac{1}{2mc^2}\underbrace{\overset{(n,\ell,m)}{\langle 1,0,0|}\left(H_0 + \frac{e^2}{r}\right)^2|1,0,0\rangle}_{E_1^2 + 2E_1e^2\langle\frac{1}{r}\rangle + e^4\langle\frac{1}{r^2}\rangle}$$

$$\downarrow$$

$E_n^2 + 2E_n e^2\langle 1/r\rangle + e^4\langle 1/r^2\rangle$ general n

$$= -\frac{5}{8\cancel{4}} mc^2\alpha^4$$

[note: down by $\alpha^2 \sim 5\times10^{-5}$ from E_1]

$\frac{1}{r}\rangle = \frac{1}{a_0 n^2}$

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

Generally:
$$\boxed{E^{(1)}_{\substack{n,\ell,m\\(\text{rel.})}} = -\frac{1}{2}mc^2\alpha^4\left[\frac{1}{n^3(\ell+1/2)} - \frac{3}{4n^4}\right]}$$

2) Quadratic Stark effect – external E field (n=1)

Imposing field $\vec{E} = E\hat{z}$,

$$V = -eEz.$$

- actually, no bound states, but lifetime ($\propto$ Im ΔE from nonzero) long

- V transforms under rotation as $T^{(1)}_{0}$ component of vector operator

For $n=1$,

$$E^{(1)}_{n=1} = -eE\langle 1,0,0|z|1,0,0\rangle$$

$$= 0$$ by Wigner-Eckart selection rules. (& by parity symmetry)

Wigner – Eckart:

$$\langle\alpha';j',m'|T^{(k)}_{q}|\alpha,j,m\rangle$$

$$\langle j',m'|k,q;j,m\rangle\frac{\langle\alpha',j'\|T^{(k)}\|\alpha,j\rangle}{\sqrt{2j+1}}$$

$$E^{(2)}_{n=1} = e^2E^2\sum_{I\neq|1,0,0\rangle}\frac{\langle 1,0,0|z|I\rangle\langle I|z|1,0,0\rangle}{E^{(0)}_{n=1} - E^{(0)}_{I}}$$

Summation: simple upper bound

$$-\frac{1}{E^{(0)}_{n=1} - E^{(0)}_{I}} \leq \frac{4}{3}\cdot\frac{2a_0}{e^2}$$

$$\sum_{I\neq|1,0,0\rangle}\langle 1,0,0|z|I\rangle\langle I|z|1,0,0\rangle = \langle 1,0,0|z^2|1,0,0\rangle = a_0^2$$

$$\Rightarrow \quad E^{(2)}_{n=1} > -\frac{8}{3}a_0^3E^2 \qquad (-2.6667)$$

Exact calculation of sum: $E^{(2)}_{n=1} = -\frac{9}{4}a_0^3E^2$ (-2.25)

To go to $n > 1$, we need

Degenerate perturbation theory

Recall $$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{m\neq n}' |m^{(0)}\rangle \frac{\langle m^{(0)}|V|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}.$$

Problem if $V_{mn} \neq 0$, $E_n^{(0)} = E_m^{(0)}$!

Need to choose good basis for degenerate states $|n^{(0)}\rangle$.

Solution: diagonalize wrt V.
(only in degenerate subspace!)

Assume $E_l^{(0)}$ is same for all $l \in D$ $(E_D^{(0)})$

Choose basis $|l^{(0)}\rangle$ so that $\langle l^{(0)}|V|k^{(0)}\rangle = 0$, $k \neq l$, $k, l \in D$.

Note: $\langle l^{(0)}|V|n^{(0)}\rangle$ can be nonzero for $n \notin D$.

Note: If $H_0 = \text{const} \cdot \mathbb{1}$, just solving full eigenvalue problem!

Nondegenerate analysis goes through,
except, for $|l\rangle$ replace $$Q_n = \sum_{m\neq n} |m^{(0)}\rangle\langle m^{(0)}|$$
$$\downarrow$$
$$Q_D = \sum_{m\notin D} |m^{(0)}\rangle\langle m^{(0)}|$$

$\Rightarrow$ have $\langle l^{(0)}|k\rangle = 0$, $l \neq k$, $l, k \in D$.

Explicitly,

λ^1 : $$H_0|l^{(1)}\rangle + V|l^{(0)}\rangle = E_l^{(1)}|l^{(0)}\rangle + E_D^{(0)}|l^{(1)}\rangle$$

i.p. with $\langle l^{(0)}|$:

$$E_l^{(1)} = \langle l^{(0)}|V|l^{(0)}\rangle$$

i.p. with $\langle k^{(0)}|$, $k \in D$, $k \neq l$

$$\langle k^{(0)}|V|l^{(0)}\rangle = 0 \quad \checkmark$$

with $\sum_{m \notin D} |m^{(0)}\rangle\langle m^{(0)}|$

$$\Rightarrow \quad |l^{(1)}\rangle = \underset{\underset{\sum_{m\notin D} \frac{|m^{(0)}\rangle\langle m^{(0)}|}{E_D^{(0)} - E_m^{(0)}}}{\downarrow}}{\frac{Q_D}{E_D^{(0)} - H_0}} V|l^{(0)}\rangle$$

skip

λ^2 : $$E_l^{(2)} = \sum_{m \notin D} \frac{|V_{ml}|^2}{E_D^{(0)} - E_m^{(0)}}$$

etc.
⋮

Examples of degenerate perturbation theory:

3) Linear Stark effect (n = 2)

Again, $V = -eEz$.

Consider effect on degenerate n=2 states:

$$|n,l,m\rangle : \underbrace{|2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle}_{l=1}, \underbrace{|2,0,0\rangle}_{l=0}$$

By Wigner-Eckart,

$$\langle n, l, m \,|\, z \,|\, n, l', m' \rangle \neq 0$$

only when $m = m'$

$$(\text{just } [J_z, z] = 0)$$

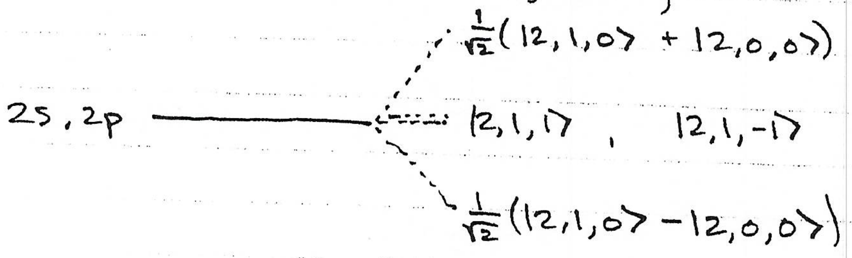
Parity: z is odd, so diagonal terms vanish.

Matrix of V:

$$V = \begin{array}{cccc} 2s & 2p\ m=0 & 2p\ m=1 & 2p\ m=-1 \\ \left(\begin{matrix} 0 \\ 3ea_0E \\ 0 \\ 0 \end{matrix}\right. & \begin{matrix} 3ea_0E \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \end{matrix} & \left.\begin{matrix} 0 \\ 0 \\ 0 \\ 0 \end{matrix}\right) \end{array}$$

Eigenvalues: $0^{(2)}$, $\pm 3 e a_0 E$.

Breaks 4-fold $n=2$ degeneracy



Note: 2s, 2p levels not really degenerate (fine structure)

Is degen. pert. theory still valid?

Yes: as long as perturbation effect is > effect removing degeneracy

(can think of doing pert theory in either order.)

4) Spin-orbit splitting

- really 2 degenerate states for each electron.

Qualitatively: $\vec{E} = \frac{e}{r^3}\vec{r}$

$$\vec{B}_{(\text{on } e^-)} = -\frac{\vec{v}}{c} \times \vec{E}$$ (relativistic effect)

magnetic moment $\mu = \frac{e}{mc}\vec{S}$

$\Rightarrow$ spin-orbit term

$$H_{LS} = -\mu \cdot \vec{B} = \mu \cdot \left(\frac{\vec{v}}{c} \times \vec{E}\right)$$

$$\Rightarrow \boxed{\frac{1}{2}} \frac{e^2}{m^2c^2r^3} \vec{L}\cdot\vec{S}$$

extra correction factor (Thomas precession) – clearest in relativistic treatment.

Apply pert. theory to $n=2$ states.

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

so use J^2, J_z basis.

spectroscopic notation: $n^{2s+1} l_j$

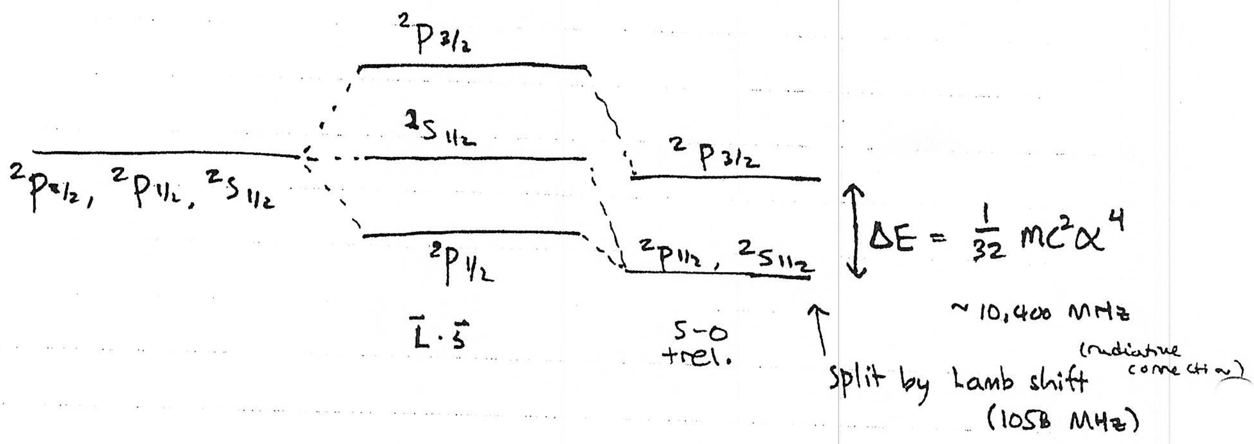
6 states $|n=2, l=1, m, m_s\rangle \Rightarrow \underset{(2^2p_{3/2})}{|n=2, j=3/2, m\rangle}, \underset{(2^2p_{1/2})}{|n=2, j=1/2, m\rangle}$

2 states $|n=2, l=0, m, m_s\rangle \Rightarrow |n=2, j=1/2, m\rangle \quad (2^2s_{1/2})$

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

changes relativistic corrections to

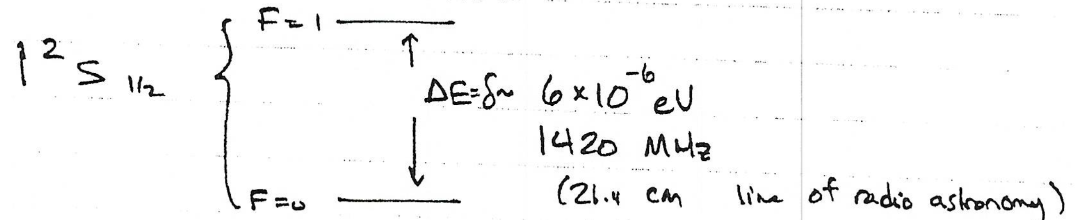
$$\Delta E^{(1)}_{so+rel.} = -\frac{1}{2} mc^2 \alpha^4 \left[\frac{1}{n^3 (j+1/2)} - \frac{3}{4n^4} \right]$$



5) Hyperfine splitting: include nuclear spin I

$$F = I + S$$

H_{HF} [illegible] $S \cdot I \ \delta^3(r)$ for s states



δ very accurately measured experimentally better than 1 part in 10^6.

6) Zeeman (external B field)

$\vec{B} = B\hat{z}$ couples to $\vec{S}, \vec{L}$

$$\circlearrowleft \quad \mu_L = \frac{IA}{c} = \frac{\left(\frac{ev}{2\pi r}\right)(\pi r^2)}{c} = \frac{eL}{2mc}$$

so take

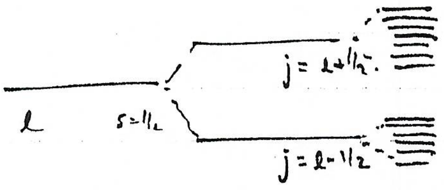
$$\lambda V = -\frac{e\vec{B}}{2mc}\cdot(\vec{L}+2\vec{S})$$

$$= -\frac{eB}{2mc}(J_z + S_z)$$

$$\Delta E_B^{(1)} = -\frac{e\hbar B}{2mc} m\left[1 \pm \frac{1}{2l+1}\right] \qquad (j = l \pm 1/2)$$

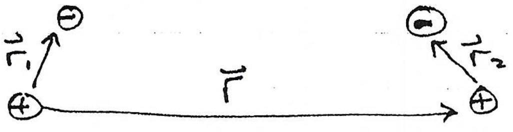
from $\langle J_z \rangle = m\hbar$
$\langle S_z \rangle = \pm \dfrac{m\hbar}{2l+1}$ (from explicit rep. of $j = l \pm 1/2$ stat or proj. theorem)

splits $j = l \pm 1/2$ multiplets, & removes degeneracy.
combine with fine structure



7) Van der Waals interactions

Consider 2 hydrogen atoms in ground states



$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

$$V = \frac{e^2}{r} + \frac{e^2}{|\vec{r}+\vec{r}_2-\vec{r}_1|} - \frac{e^2}{|\vec{r}+\vec{r}_2|} - \frac{e^2}{|\vec{r}-\vec{r}_1|} = \underset{\text{(dipole)}}{\frac{e^2}{r^3}(x_1x_2+y_1y_2-2z_1z}$$

$\Delta E^{(1)} = 0$, $\Rightarrow$ force order $1/r^6$ – Van der Waals potential.