4. Perturbation theory

Previously discussed various approaches to solving eigenvalue problems:

- Exact solution (∞-dim: diff. eq's, operator methods; finite dim: explicit diagonalization)
- Shooting method (1D)
- Variational method (need good trial wf's in large D)
- Finite difference methods (small D)
- WKB
- Q. Monte Carlo

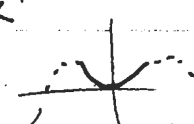
If H close to H_0 where answer known: use perturbation theory

Idea: write $H = H_0 + \lambda V$

solve $H|\psi\rangle = E|\psi\rangle$ as power series in λ.

Method often gives good approx — but must be careful, particularly when small pert $\to$ qualitative change

(e.g. $H_0 = \frac{p^2}{2m} + \frac{1}{2}x^2$, $V = -\lambda x^4$



unstable)

This semester: time-independent pert. theory
Next semester: time-dependent " ".

<u>Nondegenerate time-independent pert. theory</u> (Rayleigh - Schrödinger)

$H = H_0 + \lambda V$

unperturbed: $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$, $\langle n^{(0)} | m^{(0)}\rangle = \delta_{nm}$

exact: $H|n\rangle = E_n |n\rangle$, choose $\langle n^{(0)}|n\rangle = 1$ (convenient)

Assume $E_n^{(0)}$ are nondegenerate ($E_n^{(0)} \neq E_m^{(0)}$, $n \neq m$)

Expand

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

Normalization: $\langle n^{(0)}|n\rangle = 1$ for all λ

$\Rightarrow \langle n^{(0)}|n^{(k)}\rangle = 0 \quad \forall \; k \neq 0.$

- all corrections orthogonal to $|n^{(0)}\rangle$
Convenient, but $\langle n|n\rangle \neq 1$
so must normalize again @ end.

Setup: expand $H|n\rangle = E_n|n\rangle$,
collect terms @ each order in λ

$$(H_0 + \lambda V)[|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots]$$
$$= [E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots][|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots]$$

$\lambda^0: \quad H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle \quad \checkmark$

$\lambda^1: \quad H_0|n^{(1)}\rangle + V|n^{(0)}\rangle = E_n^{(1)}|n^{(0)}\rangle + E_n^{(0)}|n^{(1)}\rangle$

$\lambda^k: \quad H_0|n^{(k)}\rangle + V|n^{(k-1)}\rangle$
$\quad = E_n^{(0)}|n^{(k)}\rangle + E_n^{(1)}|n^{(k-1)}\rangle + \dots + E_n^{(k)}|n^{(0)}\rangle$

Take inner product with $\langle n^{(0)}|$ @ each order

$$\langle n^{(0)}|H_0|n^{(k)}\rangle + \langle n^{(0)}|V|n^{(k-1)}\rangle = E_n^{(k)}$$

$$\Rightarrow \quad \boxed{E_n^{(k)} = \langle n^{(0)}|V|n^{(k-1)}\rangle}$$

Take inner product with $\langle m^{(0)}|$, $m \neq n$ @ each order

$$\langle m^{(0)}|E_n^{(0)} - H_0|n^{(k)}\rangle = \langle m^{(0)}|\Big[(V - E_n^{(1)})|n^{(k-1)}\rangle - E_n^{(2)}|n^{(k-2)}\rangle \cdots - E_n^{(k-1)}|n^{(1)}\rangle\Big]$$

Define $\quad Q_n = 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{m\neq n} |m^{(0)}\rangle\langle m^{(0)}|$

(projects onto space orthog. to $|n^{(0)}\rangle$)

$\sum |m^{(0)}\rangle \cdot$ above, define $\frac{Q_n}{E_n^{(0)}-H_0} = \sum_{m\neq n} \frac{|m^{(0)}\rangle\langle m^{(0)}|}{E_n^{(0)} - E_m^{(0)}}$

$$\Downarrow$$

$$\boxed{|n^{(k)}\rangle = \frac{Q_n}{E_n^{(0)} - H_0}\Big[(V - E_n^{(1)})|n^{(k-1)}\rangle - E_n^{(2)}|n^{(k-2)}\rangle \cdots - E_n^{(k-1)}|n^{(1)}\rangle\Big]}$$

Low-order calculations:

$E^1)$ $\quad E_n^{(1)} = \langle n^{(0)}|V|n^{(1)}\rangle$

so $\quad E_n = E_n^{(0)} + \lambda\langle n^{(0)}|V|n^{(0)}\rangle + \mathcal{O}(\lambda^2)$

Note: consistent with Feynman-Hellman

$$\frac{\partial E}{\partial \lambda} = \langle \psi|\frac{\partial H}{\partial \lambda}|\psi\rangle .$$

$$|1\rangle)\quad |n^{(1)}\rangle = \sum_{m\neq n} \frac{|m^{(0)}\rangle\langle m^{(0)}|}{E_n^{(0)} - E_m^{(0)}} \left(V - E_n^{(1)}\right) |n^{(0)}\rangle$$

$$= \sum_{m\neq n} |m^{(0)}\rangle \frac{\langle m^{(0)}|V|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} |m^{(0)}\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

(writing $V_{mn} = \langle m^{(0)}|V|n^{(0)}\rangle$).

so

$$|n\rangle = |n^{(0)}\rangle + \lambda \sum_{m\neq n} |m^{(0)}\rangle \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} + \mathcal{O}(\lambda^2)$$

$$E^2)\quad E_n^{(2)} = \sum_{m\neq n} \frac{V_{nm}V_{mn}}{E_n^{(0)} - E_m^{(0)}} \qquad \text{etc...}$$

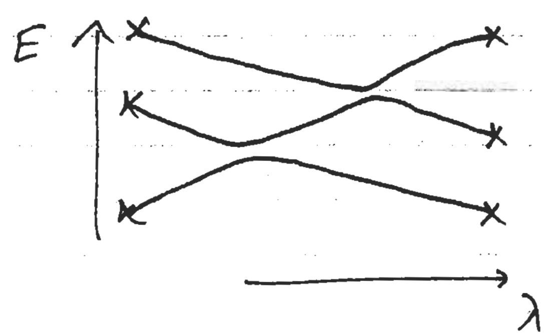
Notes: * 2nd order correction to ground state energy $E_0^{(2)}$ always negative (since $E_0^{(0)} < E_m^{(0)}$)

* More generally - levels repel <u>if coupled</u>.

If E_n, E_m are close, $E_n < E_m$ $(E_m - E_n \sim \varepsilon)$

$$E_n^{(2)} = -\frac{|V_{nm}|^2}{\varepsilon} \qquad E_m^{(2)} = \frac{|V_{nm}|^2}{\varepsilon}$$

General phenomenon : no level-crossing when states coupled



General structure of equations:

Abbreviate $E^k = \langle 0 | V | k-1 \rangle$

$$|k\rangle = \frac{Q}{\Delta}\left[(V-E^1)|k-1\rangle - E^2|k-2\rangle - \cdots - E^{k-1}|1\rangle\right]$$

$$E^1 = \langle 0|V|0\rangle = \langle V \rangle$$

$$|1\rangle = \frac{Q}{\Delta} V |0\rangle$$

$$E^2 = \langle 0|V|1\rangle = \langle V \frac{Q}{\Delta} V \rangle$$

$$|2\rangle = \frac{Q}{\Delta}(V - E^1)|1\rangle = \frac{Q}{\Delta}(V - \langle V\rangle)\frac{Q}{\Delta} V |0\rangle$$

$$E^3 = \langle 0|V|2\rangle = \langle V \frac{Q}{\Delta}(V - \langle V\rangle)\frac{Q}{\Delta} V |0\rangle$$

$$|3\rangle = \frac{Q}{\Delta}(V-E^1)|2\rangle - E^2|1\rangle$$

$$= \frac{Q}{\Delta}\left[(V - \langle V\rangle)\frac{Q}{\Delta}(V - \langle V\rangle) - \langle V \frac{Q}{\Delta} V\rangle\right]\frac{Q}{\Delta} V|0\rangle$$

$$E^4 = \langle V \frac{Q}{\Delta}\left[(V - \langle V\rangle)\frac{Q}{\Delta}(V - \langle V\rangle) - \langle V \frac{Q}{\Delta} V\rangle\right]\frac{Q}{\Delta} V|0\rangle$$

$$\vdots$$

systematic expansion, but complicated structure.

- recursion easy to implement, though.

Alternative approach: Brillouin - Wigner
→ simpler structure but nonlinear eqn for E_n.

Wavefunction renormalization

define $|n\rangle_N = Z_n^{1/2}|n\rangle$, $\quad Z_n = \dfrac{1}{\langle n|n\rangle}$

so $\;{}_N\langle n|n\rangle_N = 1$

$$Z_n^{-1} = \langle n|n\rangle = 1 + \lambda^2\langle n^{(1)}|n^{(1)}\rangle + \dots$$

$$= 1 + \lambda^2 \sum_{m\neq n} \frac{V_{nm}V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} + \dots$$

Note: $Z_n = |\langle n^{(0)}|n\rangle_N|^2$ is prob. of finding perturbed state in original eigenstate.

$$Z_n \sim 1 - \lambda^2 \sum_{m\neq n} \frac{V_{nm}V_{mn}}{(E_n^{(0)} - E_m^{(0)})^2} + \dots$$

prob. for "leakage" into other states, to order $\mathcal{O}(\lambda^2)$.

Example: $\quad H = \dfrac{p^2}{2} + \dfrac{1}{2}x^2 + \lambda x. \qquad (m = \hbar = \omega = 1)$

Exact solution:

$$H = \frac{1}{2}p^2 + \frac{1}{2}(x+\lambda)^2 - \frac{\lambda^2}{2}$$

so all energies shift by $-\lambda^2/2$

Perturbation calculation

$$E_n^{(1)} = \langle n^{(0)} | x | n^{(0)} \rangle = 0 \quad \checkmark$$

$$\left\{ \langle n' | x | n \rangle = \frac{1}{\sqrt{2}} \left[\delta_{n,n'+1} \sqrt{n} + \delta_{n+1,n'} \sqrt{n'} \right] \right\}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\langle n^{(0)} | x | m^{(0)} \rangle \langle m^{(0)} | x | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

since $E_n^{(0)} = n + 1/2$,

$$E_n^{(2)} = -\frac{n+1}{2} + \frac{n}{2} = -\frac{1}{2} \quad \checkmark$$

Convergence of perturbation series:

In general, perturbation series do not converge for most useful problems — anharmonic oscillator, QED, etc...

BUT — for small perts, series usually converges near correct answer to some order, then diverges.

Example: anharmonic oscillator.

Real example of QM in HW.
Here: consider pert. expansion of integral

$$Z(\lambda) = \int_{-\infty}^{\infty} dx \, e^{-\frac{1}{2}x^2 - \frac{\lambda}{4}x^4}$$

Can do perturbative expansion of $Z(\lambda)$

$$Z(\lambda) = \sum_k \int_{-\infty}^{\infty} dx \; e^{-\frac{1}{2}x^2} \left[(-1)^k \frac{\lambda^k x^{4k}}{4^k k!} \right]$$

$$= \sum_k \lambda^k Z_k .$$

$$Z_k = \sqrt{2\pi} \; \frac{(-1)^k (4k-1)!!}{4^k \; k!} = \sqrt{2\pi} \; \frac{(-1)^k \; (4k)!}{k! \, 16^k \, (2k)!}$$

$$Z(\lambda) = \sqrt{2\pi} \left[1 - \frac{3}{4}\lambda + \frac{105}{32}\lambda^2 - \frac{3465}{128}\lambda^3 + \frac{675675}{2048}\lambda^4 - \dots \right]$$

note: power series non-analytic @ 0, since problematic for $\lambda < 0$

Stirling: $n! \sim \sqrt{2\pi}\, n^{n+1/2} e^{-n}$

$$Z_k \sim \sqrt{2} \left(-\frac{4\lambda k}{e} \right)^k \quad \text{diverges badly.}$$

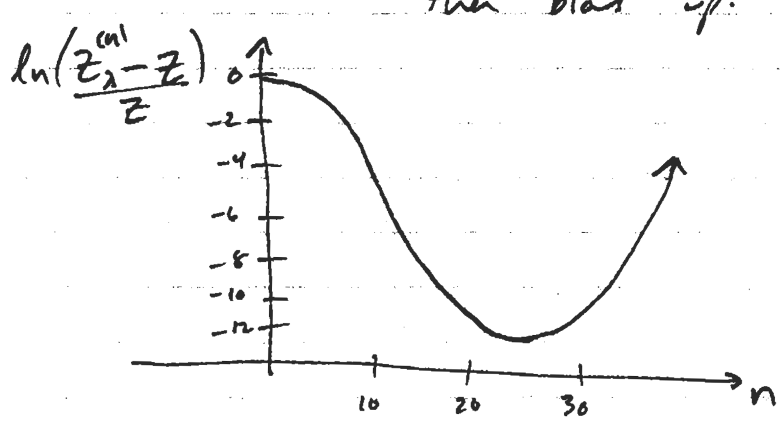
but convergent for small $k \ll \frac{e}{4\lambda}$.

For example, @ $\lambda = 0.01$,

12 terms gives $\sim 10^{-10}$ accuracy.

25 terms " $\sim 10^{-12}$ " (best approx)

then blows up.



$\sum \lambda^k Z_k$ poorly behaved for large λ.

$Z(1) \cong 1.93525$

Successive approx's give

$\sqrt{2\pi}\,(1) \cong 2.5$
$\sqrt{2\pi}\,(1/4) \cong 0.627$
$\sqrt{2\pi}\,(113/32) \cong 8.851$
$\sqrt{2\pi}\,(-3013/64) \cong -59.004$
$\vdots$

worse & worse.

Can we use Z_k's to get an accurate estimate of $Z(\lambda)$ for large λ?

Yes: Padé approximants

$$P_n^n = \frac{a_0 + a_1\lambda + \dots + a_n\lambda^n}{b_0 + b_1\lambda + \dots + b_n\lambda^n}$$

defined uniquely by cond $= Z_0 + \lambda Z_1 + \dots + \lambda^{2n} Z_{2n} + O(\lambda^{2n+1})$.

$$P_1^1(\lambda) = \frac{1 + \frac{29}{8}\lambda}{1 + \frac{35}{8}\lambda} = 1 - \frac{3}{4}\lambda + \frac{105}{32}\lambda^2 + \dots$$

$$P_1^1(1) = 2.1569$$

$$P_2^2(\lambda) = \frac{1 + \frac{3939}{248}z + \frac{54525}{1984}z^2}{1 + \frac{4125}{248}z + \frac{72765}{1984}z^2} \Rightarrow P_2^2(1) = 2.04768$$

... gives systematic approx scheme for any λ.

Padé's may not always work, but often very effective.

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 as 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)

$$\psi_{n,l,m}(\vec{r}) = R_{n,l}(r)\, Y_{lm}(\theta, \phi) \qquad (\text{denote } |n,l,m\rangle)$$

$$R_{n,l}(r) \to \frac{1}{r} u_{k,l}(r) \qquad n = k + l$$

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

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]

$$E_n = -\frac{1}{2n^2} mc^2 \alpha^2 = -\frac{e^2}{na_0} \approx \frac{-13.6 \text{ eV}}{n^2}$$

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

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

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

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

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

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

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

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 $\overset{\text{from nonzero}}{(\mathrm{Im}\,\Delta E)}$ 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)

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

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

To go to $n > 1$, we need

Degenerate perturbation theory

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

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 $E_\ell^{(0)}$ is same for all $\ell \in D$ $\quad (E_D^{(0)})$

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

Note: $\langle \ell^{(0)}|V|n^{(0)}\rangle$ 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 $|\ell\rangle$ 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 $\langle \ell^{(0)}|k\rangle = 0$, $\ell \neq k$, $\ell, k \in D$.

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

$$\Rightarrow \quad |l^{(1)}\rangle = \frac{Q_D}{E_D^{(0)} - H_0} V|l^{(0)}\rangle$$

$$\downarrow$$

$$\sum_{m \notin D} \frac{|m^{(0)}\rangle\langle m^{(0)}|}{E_D^{(0)} - E_m^{(0)}}$$

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

etc.
⋮

skip

Examples of degenerate perturbation theory:

3) Linear Stark effect $(n=2)$

Again, $V = -eEz$.

Consider effect on degenerate $n=2$ states:

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

By Wigner-Eckart,

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

only when $m = m'$

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

Parity: z is odd, so diagonal terms vanish.

Matrix of V:

$$V = \begin{array}{c} \begin{array}{cccc} 2s & 2p\ m=0 & 2p\ m=1 & 2p\ m=-1 \end{array} \\ \begin{pmatrix} 0 & 3ea_0E & 0 & 0 \\ 3ea_0E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array}$$

Eigenvalues: $0^{(2)}$, $\pm 3ea_0E$.

Breaks 4-fold $n=2$ degeneracy

$\frac{1}{\sqrt{2}}(|2,1,0\rangle + |2,0,0\rangle)$

2s, 2p ——— $|2,1,1\rangle$, $|2,1,-1\rangle$

$\frac{1}{\sqrt{2}}(|2,1,0\rangle - |2,0,0\rangle)$

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

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

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

$\Rightarrow$ spin-orbit term

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

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

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: $n\,^{2s+1}l_j$

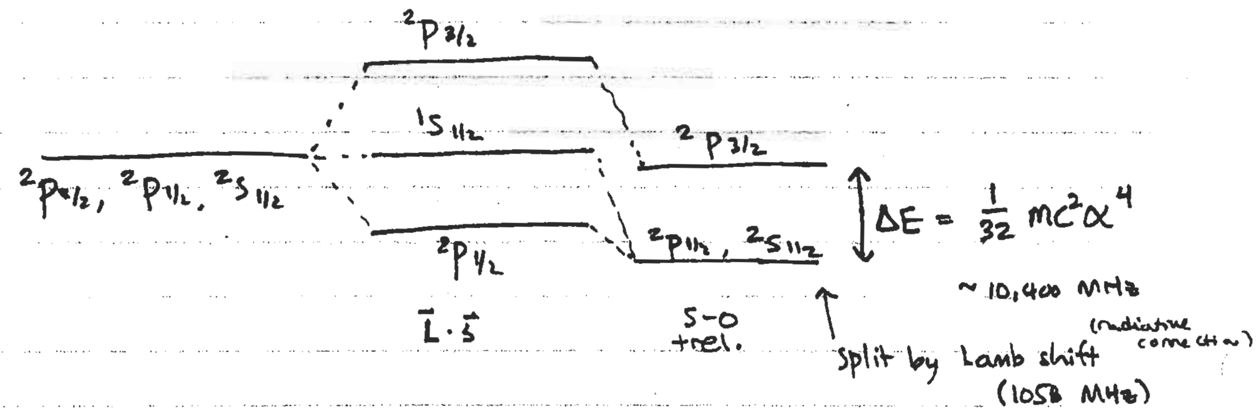
6 states $|n=2, l=1, m, m_s\rangle \Rightarrow |n=2, j=3/2, m\rangle$, $|n=2, j=1/2, m\rangle$
($2^2p_{3/2}$) ($2^2p_{1/2}$)

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

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

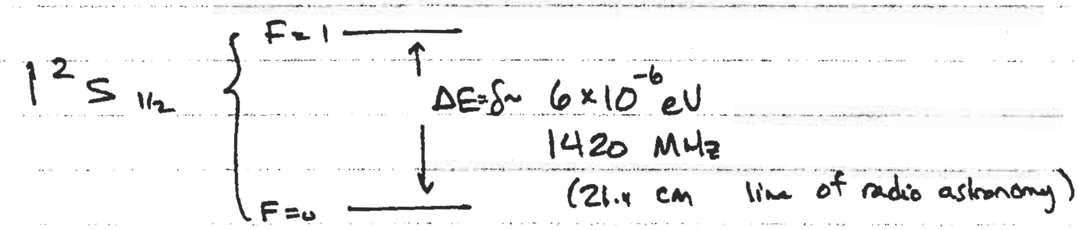
$$\Delta E^{(1)}_{so+rel.} = -\frac{1}{2} mc^2 \alpha^4 \left[\frac{1}{n^3 (j+1/2)} - \frac{3}{4n^4} \right]$$



5) Hyperfine splitting : include nuclear spin I

$F = I + S$

$H_{HF} \propto S\cdot I \; \delta^3(r)$ 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

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

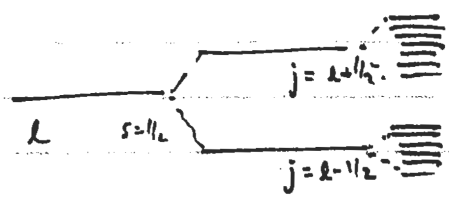
$$= -\frac{eB}{2mc}(J_z + S_z)$$

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

from $\langle J_z \rangle = m\hbar$

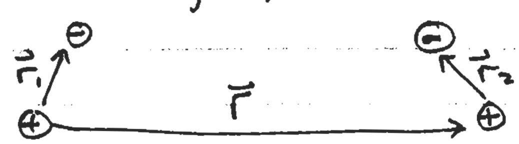
$\langle S_z \rangle = \pm \dfrac{m\hbar}{2l+1}$ (from explicit rep. of $j = l \pm 1/2$ states or proj. theorem)

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



7) Van der Waals interaction

Consider 2 hydrogen atoms in ground states



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

$$V = \frac{e^2}{r} + \frac{e^2}{|\vec{r} + \vec{r}_2 - \vec{r}_1|} - \frac{e^2}{|\vec{r} + \vec{r}_2|} - \frac{e^2}{|\vec{r} - \vec{r}_1|} = \frac{e^2}{r^3}(x_1x_2 + y_1y_2 - 2z_1z_2)$$

(dipole)

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