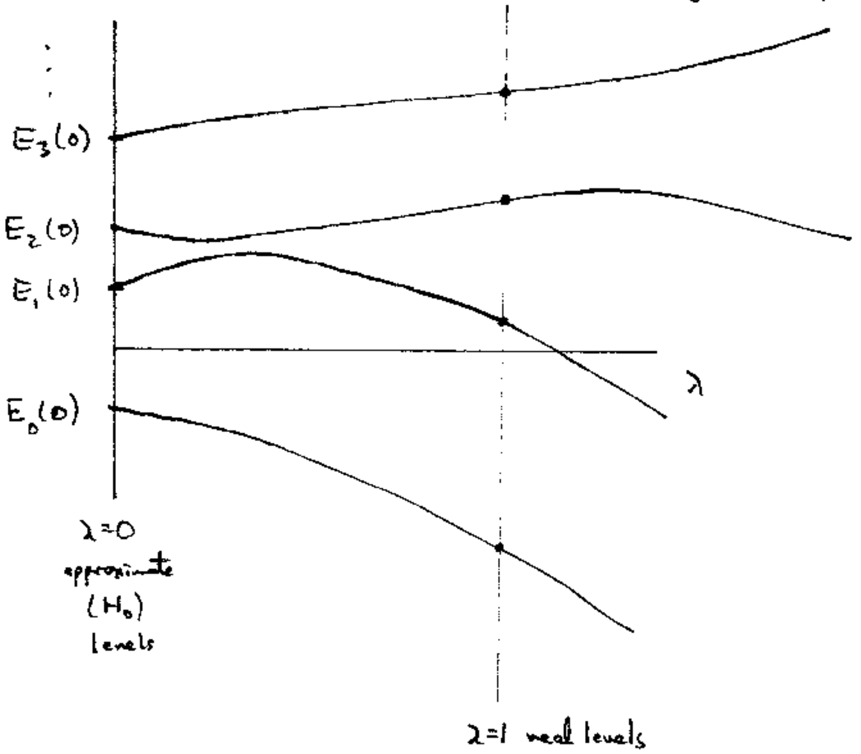
Degenerate perturbation theory

Thus far we have assumed that H_0 in $H = H_0 + \lambda H_I$ has a complete set of levels $\{|n\rangle\} \to \{E_n(0)\}$ which are nondegenerate,

e.g.



& this leads to a result for a level (e.g. ground state)

$$E_0 = E_0(0) + \overbrace{\langle \phi_0 | H_I | \phi_0 \rangle}^{E_0(1)} + \overbrace{\sum_{n \neq \phi_0} \frac{|\langle n | H_I | \phi_0 \rangle|^2}{E_0(0) - E_n(0)}}^{E_0(2)} + \mathcal{O}(H_I^3)$$

$$|\psi_0\rangle = |\phi_0\rangle + \underbrace{\sum_{n \neq \phi_0} \frac{\langle n | H_I | \phi_0 \rangle}{E_0(0) - E_n(0)} |n\rangle}_{|\phi_1\rangle} + \mathcal{O}(H_I^2)$$

Clearly this formalism is incorrect if e.g. unperturbed $|\phi_0\rangle$ is a degenerate level, because $\dfrac{1}{E_0(0) - E_n(0)} = \infty$ for $n =$ another level degenerate with $|\phi_0\rangle$.

Correct perturbation theory about an H_0 with degenerate levels is known as degenerate perturbation theory. For an illustration of how this works, consider a simple 3 level system with a degenerate H_0 ground state,

$$H_0 = \begin{bmatrix} E_1(0) & & \\ & E_0(0) & \\ & & E_0(0) \end{bmatrix} \quad \text{on} \begin{bmatrix} |3\rangle \\ |2\rangle \\ |1\rangle \end{bmatrix} ; \quad H_I = \begin{bmatrix} 0 & g & g \\ g & 0 & g \\ g & g & 0 \end{bmatrix}$$

Take $E_0(0) = 0 \qquad E_1(0) = \varepsilon$

Exact soln for eigenvalues

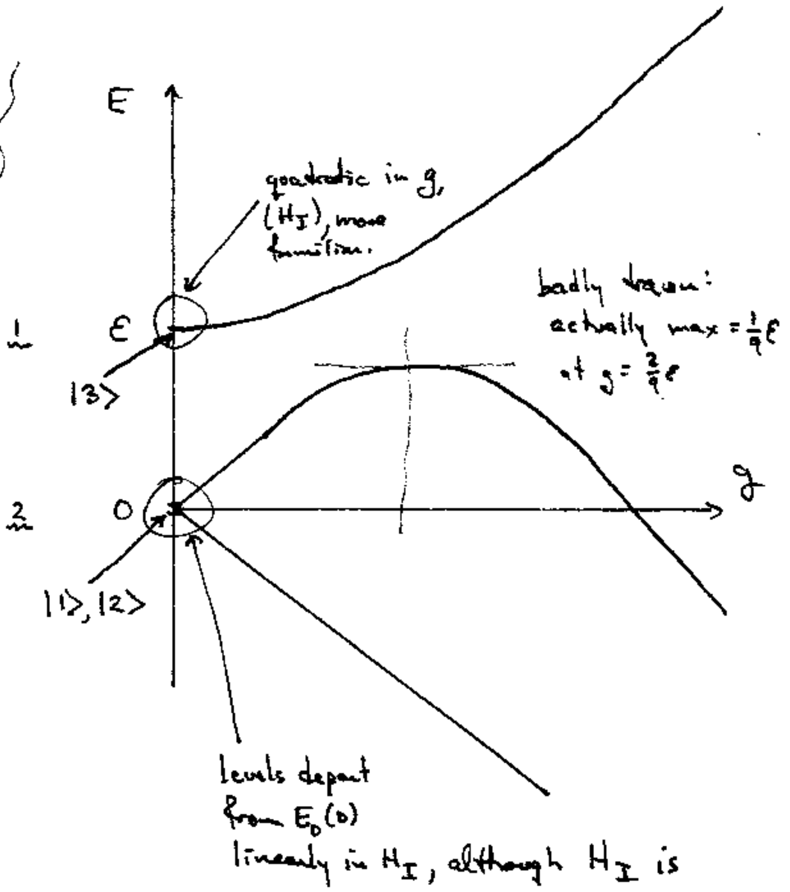
$$\| H - \lambda I \| = 0 \qquad \begin{vmatrix} (\varepsilon-\lambda) & g & g \\ g & -\lambda & g \\ g & g & -\lambda \end{vmatrix} = 0$$

$$\lambda = -g, \ \underbrace{\frac{g+\varepsilon}{2} \pm \sqrt{\left(\frac{\varepsilon}{2}\right)^2 - \frac{g\varepsilon}{2} + \frac{9g^2}{4}}}_{}$$

for small g/ε,

$$\varepsilon + \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3/\varepsilon^2)$$

$$g - \frac{2g^2}{\varepsilon} + \mathcal{O}(g^3/\varepsilon^2)$$



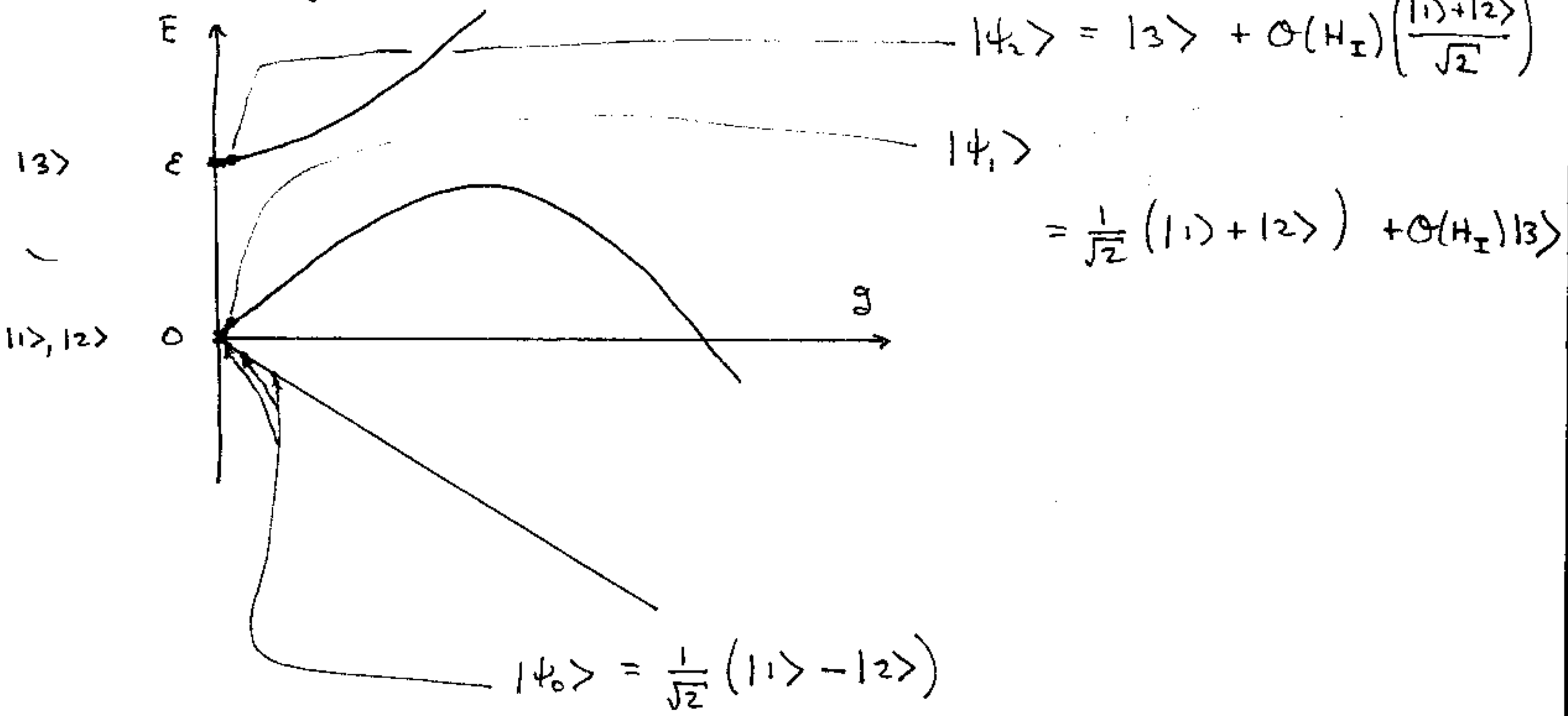
levels depart from $E_0(0)$ linearly in H_I, although H_I is purely off diagonal!

$\langle 1|H_I|1\rangle = 0 = \langle 2|H_I|2\rangle$

Look at eigenstates to see what has happened.
Suppose we were doing pert theory about ground state level $|1\rangle$,
nonpert theory suggests

$$|\psi\rangle = \underbrace{|\phi_0\rangle}_{|1\rangle} + \underbrace{|\phi_1\rangle}_{\substack{\mathcal{O}(H_I) = \mathcal{O}(g) \\ |2\rangle + |3\rangle \text{ l.c.}}} + \underbrace{|\phi_2\rangle}_{\substack{\mathcal{O}(H_I) = \mathcal{O}(g^2) \\ |2\rangle + |3\rangle \text{ l.c.}}}$$

Actual exact eigenstates are



That's the problem! As $g \to 0$, the true ground state $|\psi_0\rangle$ never approaches $|1\rangle$. Instead it approaches a special linear combination of the initial degenerate H_0 eigenstates, $(|1\rangle - |2\rangle)/\sqrt{2}$.

Assuming an energy eigenstate is almost $|1\rangle$ is never correct! For any $g > 0$ they are linear combinations of all the states in the degenerate multiplet. The selection of which linear combinations of degenerate basis states one approaches as $\langle H_I\rangle \to 0$ is determined by H_I.

For our e.g., we have to find l.c. of degenerate states $|1\rangle$ and $|2\rangle$, rather than just $|\phi_0\rangle = |1\rangle$ or $|\phi_0\rangle = |2\rangle$.
Try assuming a linear combination,

$$|\phi_0\rangle = c_1|1\rangle + c_2|2\rangle$$

now substitute this Ansatz into our $O(\lambda)$ eqn for $|\phi_1\rangle$,

$$[H_0 - E(0)]\,|\phi_1\rangle = -[H_I - E_0(1)]\,|\phi_0\rangle$$

$\langle 1|\cdot$ gives

$$\langle 1|\overleftarrow{[H_0 - E(0)]}|\phi_1\rangle = 0 = -\langle 1|H_I|\phi_0\rangle + E(1)c_1$$

$$\boxed{\begin{aligned} E(1)c_1 &= +c_1\langle 1|H_I|1\rangle + c_2\langle 1|H_I|2\rangle \\ E(1)c_2 &= c_1\langle 2|H_I|1\rangle + c_2\langle 2|H_I|2\rangle \end{aligned}}$$

$\langle 2|\cdot$ gives

This set of linear eqns for $|\phi_0\rangle = \sum_i c_i|i\rangle$ is called the secular equation.
[We are just trying to find eigenvectors of H_I within the degenerate subspace!]

$$\sum_j A_{ij}c_j = \underset{\substack{\uparrow \\ \text{source}}}{s_i} \quad \text{would have soln} \quad c_i = \sum_j (A^{-1})_{ij}s_j + \underbrace{c_i^{(0)}}_{\text{annih by } H_I}$$

$$A = H_I - E(1)I \qquad A^{-1} = \frac{1}{\det A}\,\mathrm{Minor}(A^T)$$

Nontrivial soln with $s_i = 0\ \forall i$ requires that $\det A = 0$ so can't invert.

This case

$$\underbrace{\begin{bmatrix} \langle 1|H_I|1\rangle - E(1) & \langle 1|H_I|2\rangle \\ \langle 2|H_I|1\rangle & \langle 2|H_I|2\rangle - E(1)\end{bmatrix}}_{\text{matrix } A} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

So nontrivial soln for c_1, c_2 requires $\det A = 0$

$$[\underbrace{\langle 1|H_I|1\rangle}_{\equiv h_{11}} - E(1)][\langle 2|H_I|2\rangle - E(1)] - |\underbrace{\langle 1|H_I|2\rangle}_{\equiv h_{12}}|^2 = 0$$

$$[h_{11}-E(1)][h_{22}-E(1)] - |h_{12}|^2 = 0$$

two solutions,

$$E(1) = \frac{h_{11}+h_{22}}{2} \pm \left| \left[\left(\frac{h_{11}-h_{22}}{2}\right)^2 + |h_{12}|^2\right]^{1/2}\right|$$

This is the 1st order pert energy for a twofold degenerate level. Note it doesn't involve other nondegenerate levels. In general $\det(H_I - E(1)I) = 0$ within degen subspace.

Note also if $|1\rangle$ and $|2\rangle$ don't communicate, $\langle 1|H_I|2\rangle \equiv h_{12} = 0$, we find

$$E(1) = \frac{h_{11}+h_{22}}{2} \pm \left|\frac{h_{11}-h_{22}}{2}\right| = \begin{cases} h_{11} = \langle 1|H_I|1\rangle = \langle\phi_0|H_I|\phi_0\rangle \text{ for } \phi_0 = 1 \\ h_{22} = \langle 2|H_I|2\rangle = \text{same},\ \phi_0 = 2 \end{cases}$$

so we recover ordinary 1st order nondegenerate pert theory for noncommunicating levels. The two general solutions for c_1 and c_2 are then found by solving the eigenvector eqn

$$\begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E(1) \begin{bmatrix} c_1 \\ c_2 \end{bmatrix},$$

solns are

$$\frac{c_2}{c_1} = \frac{E(1) - h_{11}}{h_{12}} = \frac{\frac{1}{2}\left(h_{22}-h_{11}\right) \pm \left| \sqrt{\left(\frac{h_{22}-h_{11}}{2}\right)^2 + |h_{12}|^2} \right|}{h_{12}}$$

For the specific problem we have considered,

$$H = \begin{bmatrix} E_1(0) & g & g \\ g & E_0(0) & g \\ g & g & E_0(0) \end{bmatrix} \quad H \text{ in degenerate subspace} \qquad \text{on} \begin{bmatrix} |3\rangle \\ |2\rangle \\ |1\rangle \end{bmatrix}$$

$$\underset{\langle 1|H_I|1\rangle}{h_{11}} = h_{22} = 0 \qquad h_{12} = \langle 1|H_I|2\rangle = g$$

so

$$\frac{c_2}{c_1} = \pm \frac{|g|}{g} = \pm 1 \ ,$$

i.e. normalized $|\phi_0^{(1)}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right) = |S\rangle$ symmetric

and $|\phi_0^{(2)}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right) = |A\rangle$ antisymmetric

are the 0^{th} order linear combinations chosen by an infinitesimal perturbation, with energy

$$E(1) = \frac{h_{11}+h_{22}}{2} \pm \left| \sqrt{\left(\frac{h_{11}-h_{22}}{2}\right)^2 + |h_{12}|^2} \right| = \pm g \quad \text{for} \begin{cases} |\phi_0^{(1)}\rangle \\ |\phi_0^{(2)}\rangle \end{cases}$$

Having found the l.c.'s $|S\rangle$ and $|A\rangle$ that are selected by an infinitesimal perturbation, we can rewrite the Hamiltonian matrix in this basis to do ordinary nondegenerate pert theory for higher orders.

In this new $\begin{bmatrix} |3\rangle \\ |S\rangle \\ |A\rangle \end{bmatrix}$ basis.

(Could do this by

$$\begin{bmatrix} |3\rangle \\ |s\rangle \\ |A\rangle \end{bmatrix} = \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix}}_{\mathcal{Y}} \begin{bmatrix} |3\rangle \\ |2\rangle \\ |1\rangle \end{bmatrix}$$

or $\qquad |e'\rangle = \mathcal{Y}|e\rangle$

so

$$H' = \mathcal{Y}^{-1} H \mathcal{Y}.$$

It's easier just to note $\quad H|A\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} \varepsilon & g & g \\ g & & g \\ g & g & 0 \end{bmatrix}\begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ (g)/\sqrt{2} \\ (-g)/\sqrt{2} \end{bmatrix}$

$= -g|A\rangle$

|A> is already a full H eigenstate

$$H|3\rangle = \begin{bmatrix} \varepsilon & g & g \\ g & 0 & g \\ g & g & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} \varepsilon \\ g \\ g \end{bmatrix} = \varepsilon|3\rangle + \sqrt{2}g|s\rangle$$

$$H|s\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} \varepsilon & g & g \\ g & 0 & g \\ g & g & 0 \end{bmatrix}\begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} \sqrt{2}g \\ g/\sqrt{2} \\ g/\sqrt{2} \end{bmatrix} = \sqrt{2}g|3\rangle + g|s\rangle$$

So

$$H\begin{bmatrix} |3\rangle \\ |s\rangle \\ |A\rangle \end{bmatrix} = \left[\begin{array}{cc|c} \varepsilon & \sqrt{2}g & 0 \\ \sqrt{2}g & g & 0 \\ \hline 0 & 0 & -g \end{array}\right]$$

So $E_A = -g$ exactly

$E_s(g)$ and $E_3(g)$ can solve exactly as a 2×2 problem,

$$E_s(g) = \tfrac{1}{2}(g+\varepsilon) - \sqrt{\left(\tfrac{g-\varepsilon}{2}\right)^2 + 2g^2}\ , \quad E_3(g) = \tfrac{1}{2}(g+\varepsilon) + \sqrt{}.$$

However could proceed with e.g. $E_s(g)$ in ordinary nondegen pert theory,

$$E_s = E_0(0) + \langle s|H_I|s\rangle + \sum_{n\neq s} \frac{|\langle n|H_I|s\rangle|^2}{E_s(0)-E_n(0)}$$

($|s\rangle$ by construction is an eigenvector of H_I in the $|1\rangle, |2\rangle$ subspace as is $|A\rangle$, these are orthogonal since they have different eigenvalues.)

so $\quad \langle A|H_I|s\rangle = 0$, need only $\langle 3|H_I|S\rangle = \sqrt{2}\,g$,

$$E_s = 0 + g + \frac{(\sqrt{2}\,g)^2}{-\varepsilon} = g - \frac{2g^2}{\varepsilon} + O(g^3)$$

exact result

$$E_s = \tfrac{1}{2}g + \tfrac{1}{2}\varepsilon - \tfrac{1}{2}\varepsilon\sqrt{1 - \frac{2g}{\varepsilon} + \frac{9g^2}{\varepsilon^2}}$$

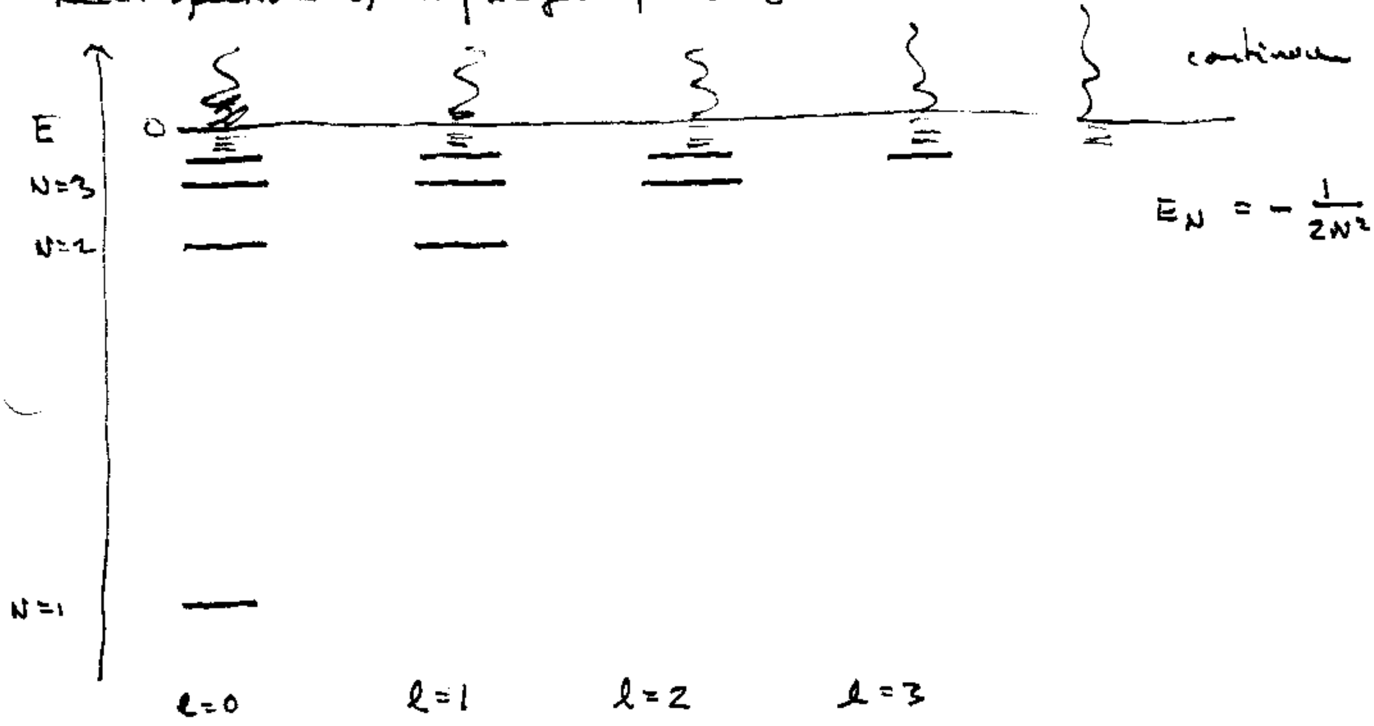
$$= \tfrac{1}{2}g + \cancel{\tfrac{1}{2}\varepsilon} - \tfrac{1}{2}\varepsilon\left(\cancel{1} - \frac{g}{\varepsilon} + \underbrace{\frac{9}{2}\left(\frac{g}{\varepsilon}\right)^2 - \frac{1}{8}4\left(\frac{g}{\varepsilon}\right)^2}_{4g^2/\varepsilon^2}\right) + O(g^3)$$

$$E_s = g - 2g^2/\varepsilon + O(g^3) \checkmark$$

Application: First order Stark effect in $N=2$ Hydrogen levels

$$H = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{\alpha\hbar c}{r}}_{H_0} \; \underbrace{+\, e\mathbb{E}z}_{H_I}$$

Recall spectrum of hydrogen from H_0:



$$E_N = -\frac{1}{2N^2} mc^2\alpha^2$$

At $N=2$ we have degenerate $l=0$ and $l=1$ levels.
Since $H_I = e\mathbb{E}r\cos\theta$, H_I will have a matrix element between the $l=0$ and $l=1$ states. Recall in degen pert theory the problem is to find l.c.'s of states within the degenerate subspace that are eigenvectors of H_I.

At $N=2$ the 4 states are

$|N=2, l=0, l_z=0\rangle \qquad \langle \vec{r}\,|N=2, l=0, l_z=0\rangle = \psi_0^{(2s)}(r)\, Y_{00}(\Omega)$

$|N=2, \ell=1, \ell_z=+1,0,-1\rangle \qquad \langle \vec{r}\,|\overset{2}{\overset{"}{N}},\overset{1}{\overset{"}{\ell}},m\rangle = \psi_0^{(2P)}(r)\,Y_{1m}(\Omega)$

What are the matrix elements of H_I in this subspace?

$$\langle 2S|H_I|2P,m\rangle = \int d\vec{x}\;\psi_0^{(2S)*}(r)\,Y_{00}^{*}(\Omega)\;e\mathbb{E}r\cos\theta\;\psi_0^{(2P)}(r)\,Y_{1m}(\Omega)$$

$$= \begin{cases} 0 & m\neq 0 \\ \underbrace{\frac{1}{\sqrt{3}}\,e\mathbb{E}\int_0^\infty r^3\,\psi_0^{(2S)}(r)^*\,\psi_0^{(2P)}(r)\,dr}_{\equiv e\mathbb{E}d} & m=0 \end{cases}$$

$\longrightarrow d = 3a_0$ (from explicit overlap $\int$s)

$$\langle 2S|H_I|2S\rangle \propto \int d\Omega\,\cos\theta = 0$$

$$\langle 2P,m=0|H_I|2P,m=0\rangle = \int d\vec{x}\,|\psi_0^{(2P)}(r)|^2|Y_{10}(\Omega)|^2\,e\mathbb{E}r\cos\theta$$

$$\propto \int d\Omega\,\cos^3\theta = 0$$

$$\langle 2P,m=\pm1|H_I|2P,m=\pm1\rangle = \int \;.\;\;.\;.\;|Y_{11}(\Omega)|^2\ldots \propto \int d\Omega\,\sin^2\theta\cos\theta = 0$$

So the subspace H_I we have to diagonalize is

$$\begin{bmatrix} 0 & e\mathbb{E}d & & \\ e\mathbb{E}d & 0 & & \\ & & 0 & \\ & & & 0 \end{bmatrix} \quad \text{on basis} \quad \begin{bmatrix} |2S\rangle \\ |2P,m=0\rangle \\ |2P,m=+1\rangle \\ |2P,m=-1\rangle \end{bmatrix}$$

Recall what we are trying to find is

$$|\phi_0\rangle = \sum_i \underbrace{c_i}\, |i\rangle$$

↳ states in degenerate subspace

& these satisfy the secular equation

$$E(1)\, c_i = \sum_j \langle i | H_I | j \rangle c_j$$

$$\begin{bmatrix} E(1)\, c_{2s} \\ E(1)\, c_{2P,0} \\ E(1)\, c_{2P,1} \\ E(1)\, c_{2P,-1} \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & e\mathbb{E}d & & \\ e\mathbb{E}d & 0 & & \\ & & 0 & \\ & & & 0 \end{bmatrix}}_{\langle i | H_I | j \rangle} \begin{bmatrix} c_{2s} \\ c_{2P,0} \\ c_{2P,1} \\ c_{2P,-1} \end{bmatrix}$$

The 4 solutions (normalized to $\langle \phi_0 | \phi_0 \rangle = 1$) are

$\frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\\0\\0\end{bmatrix}$ $\quad |\phi_0^{(1)}\rangle = \frac{1}{\sqrt{2}}\left(|2s\rangle + |2P,0\rangle \right)$ $\quad E(1) = e\mathbb{E}d$

$\frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\\0\\0\end{bmatrix}$ $\quad |\phi_0^{(2)}\rangle = \frac{1}{\sqrt{2}}\left(|2s\rangle - |2P,0\rangle \right)$ $\quad E(1) = -e\mathbb{E}d$

$\begin{bmatrix}0\\0\\1\\0\end{bmatrix}$ $\quad |\phi_0^{(3)}\rangle = |2P, m=1\rangle$ $\quad E(1) = 0$

$\begin{bmatrix}0\\0\\0\\1\end{bmatrix}$ $\quad |\phi_0^{(4)}\rangle = |2P, -1\rangle$ $\quad E(1) = 0$

And, doing the overlap integral, the actual value of the energy shift is (using $d = 3a_0$),

$$E(1) = \pm\, 3 e\mathbb{E} a_0,\ 0,\ 0$$