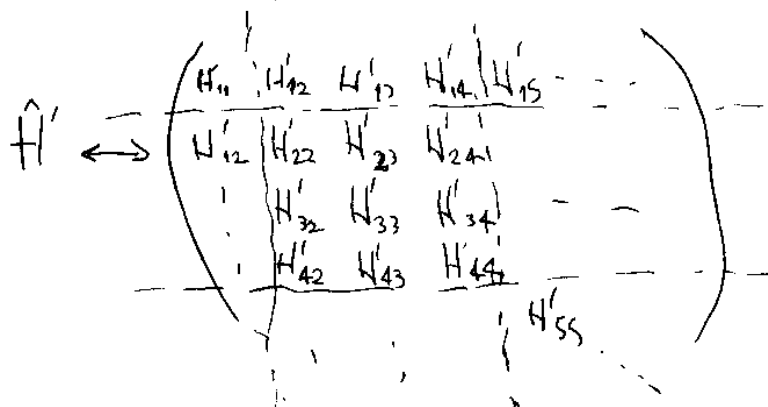
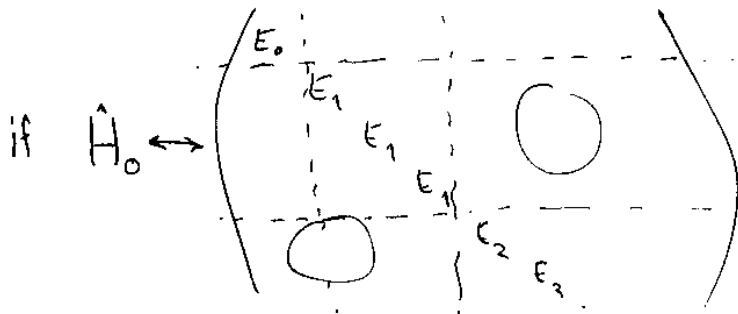


# PAAD LECTURE 27

Continuing degenerate perturbation theory:

~~Assumption~~ to clear up: in the degenerate subspace, only the "piece" of  $\hat{H}'$  defined in the subspace commutes with  $\hat{H}_0$ :



Can diagonalize the 3x3 sub-matrix of  $\hat{H}'_{sub}$  since  $\hat{H}_0 \approx E_1 \mathbb{1}$

~~So we are not claiming that there will be simultaneous eigenstates of the full  $\hat{H}$  and  $\hat{H}_0$ .~~

Suppose we've diagonalized  $\hat{H}'$  in the degenerate subspace of  $E_n^{(0)}$  so zeroth-order states  $|n_a^{(0)}\rangle$  are already eigenstates of  $\hat{H}'$  and  $\hat{H}_0$ . Now return to original pert. theory paradigm. Project pert. equation

$$\hat{H}_0 |n^{(k)}\rangle + \hat{H}' |n^{(k-1)}\rangle = E_n^{(k)} |n^{(k)}\rangle + E_n^{(k-1)} |n^{(k-1)}\rangle + \dots + E_n^{(0)} |n^{(0)}\rangle$$

with zeroth-order states in this diagonalized basis.

Be careful to use orthonormality relationships of degenerate states!

$$\langle n_a^{(0)} | n_b^{(0)} \rangle = \delta_{ab}, \quad \langle n_a^{(0)} | \hat{H}' | n_b^{(0)} \rangle = H'_{aa} \delta_{ab}$$

where  $a, b$  go from 1 to  $g$  for a  $g$ -fold degeneracy of  $\hat{H}_0$  eigenvalue  $E_n$ . (i.e.  $E_{n_a}^{(0)} = E_{n_b}^{(0)} = \langle n_a^{(0)} | \hat{H}_0 | n_a^{(0)} \rangle$  etc.) First-order energies are just  $\langle n_a^{(0)} | \hat{H}' | n_a^{(0)} \rangle = H'_{aa}$  eigenvalue of  $\hat{H}'$ .

For these degenerate states, first-order eigenstates and second-order eigenvalues are simply

$$|n_a\rangle \approx |n_a^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | \hat{H}' | n_a^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$E_{n_a} \approx E_n^{(0)} + \langle n_a^{(0)} | \hat{H}' | n_a^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle n_a^{(0)} | \hat{H}' | m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

where the sums are taken only over  $\hat{H}_0$  eigenstates of different energy than  $E_n$ . Note that:

- If there are other degenerate subspaces, we're OK because there's no divide-by-zero problem. Only have to diagonalize one degenerate subspace at a time. (i.e.  $E_m$  is degenerate)
- So not necessary to diagonalize full Hamiltonian (if that were simple, why use pert. theory at all?)

Summing up technique: for each degenerate subspace, we "pre-treat" by diagonalizing  $\hat{H}'$ . Once eigenvalues/states of  $\hat{H}'$  found, proceed with normal pert. theory, excluding terms that would have given divergent result.

An example: fine structure in H atom.

Improve on the hydrogen atom  $\hat{H}$  by including relativistic electron energy term:  $E = \sqrt{m^2c^4 + p^2c^2}$ . Since kinetic energy is small compared to rest mass, expand in a series:

$$E = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

Since the rest mass is constant it will just add a common phase factor  $e^{-imc^2t/\hbar}$  to every state  $\Rightarrow$  ignore it and say

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{r}, \quad \hat{H}' = -\frac{p^4}{8m^3c^2} = -\frac{1}{2mc^2} \left(\frac{\hat{p}^2}{2m}\right)^2$$

so ~~since~~ since  $\frac{\hat{p}^2}{2m} = \hat{H}_0 + \frac{Ze^2}{r}$ , this makes  $\hat{H}'$  matrix elements easy.

Zeroth order eigenstates are  $|n l m_l m_s^{(0)}\rangle$ , and for the degenerate states (everything with a given  $n$ ),  $\hat{H}'$  is already diagonal:

$$\begin{aligned} H'_{n l m_l m_s, n l m_l m_s} &= \frac{-1}{2mc^2} \langle n l m_l m_s | \left( \hat{H}_0 + \frac{Ze^2}{r} \right)^2 | n l m_l m_s \rangle \\ &= \frac{-1}{2mc^2} \langle n l m_l m_s | \left( E_n^{(0)} + \frac{2E_n^{(0)} Ze^2}{r} + \frac{Z^2 e^4}{r^2} \right) | n l m_l m_s \rangle \end{aligned}$$

Now - you should convince yourself that matrix elements of  $\frac{1}{r}$  and  $\frac{1}{r^2}$  do not couple states of different  $m_l, m_s, l$ . This means in the degenerate subspace  $\hat{H}'$  is already diagonal. Just need to evaluate  $\langle \frac{1}{r} \rangle$  and  $\langle \frac{1}{r^2} \rangle$  for the  $|n l m_l m_s\rangle$  eigenstates.

Liboff problem 10.48 gives result:

$$E_{nl}^{(1)} = -\frac{1}{2}(Z\alpha)^4 mc^2 \left[ \frac{-3}{4n^4} + \frac{1}{n^3(l+\frac{1}{2})} \right]$$

where  $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$  is the fine structure constant.

In terms of  $\alpha$ ,  $E_n^{(0)} = \frac{-(Z\alpha)^2 mc^2}{2n^2}$  so  $E_{nl}^{(1)} \ll E_n^{(0)}$ .