Physics 472 Lecture 12

Degenerate perturbation theory

Recall the results of nondegenerate pert. thy:

$$H = H_0 + \lambda H_1$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \cdots$$

with $$H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle,$$

$$E_n^{(1)} = \langle n| H_1 |n\rangle ,$$

$$|\psi_n^{(1)}\rangle = \sum_{n' \neq n} \frac{|n'\rangle\langle n'| H_1 |n\rangle}{E_n^{(0)} - E_{n'}^{(0)}} ,$$

$$E_n^{(2)} = \sum_{n' \neq n} \frac{|\langle n'| H_1 |n\rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}} .$$

Obviously, a problem arises if

$E_{n'}^{(0)} = E_n^{(0)}$ for some $n' \neq n$!

Last time, we saw how to treat the case where just two levels are degenerate.

Let us generalize to the case of m degenerate states:

$$H_0 |\psi_i^{(0)}\rangle = E_1^{(0)} |\psi_i^{(0)}\rangle, \quad i = 1, 2, \ldots, m.$$

Any linear combination

$$|\tilde{\psi}_j^{(0)}\rangle = \sum_{k=1}^{m} C_{jk}^{(0)} |\psi_k^{(0)}\rangle$$

also satisfies $H_0 |\tilde{\psi}_j^{(0)}\rangle = E_1^{(0)} |\tilde{\psi}_j^{(0)}\rangle$.

If we change to a basis $|\tilde{\Psi}_j^{(0)}\rangle$, $j=1,\dots,m$ such that

$$\langle \tilde{\Psi}_i^{(0)} | H_1 | \tilde{\Psi}_j^{(0)} \rangle = 0 \quad \text{for } i \neq j,$$

then whenever the denominators vanish in the perturbation expressions, the numerator will vanish too. Then we can use ordinary perturbation theory to find

$$E_i^{(1)} = \langle \tilde{\Psi}_i^{(0)} | H_1 | \tilde{\Psi}_i^{(0)} \rangle .$$

In general, then

$$\langle \tilde{\Psi}_i^{(0)} | H_1 | \tilde{\Psi}_j^{(0)} \rangle = E_i^{(1)} \delta_{ij}$$

This condition is obviously satisfied if $|\tilde{\varphi}_j^{(0)}\rangle$ are eigenvectors of H_1. However, they need not be eigenvectors of the full operator H_1, only of H_1 restricted to the m-dimensional subspace spanned by $|\psi_i^{(0)}\rangle$, $i = 1, 2, \ldots, m$.

Define $\tilde{H}_1 = \mathbb{1}_m H_1 \mathbb{1}_m$,

where $\mathbb{1}_m = \sum_{k=1}^{m} |\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|$

is the projection operator onto the subspace.

$\tilde{H}_1$ is equivalent to the $m \times m$ matrix

$$\begin{pmatrix} \langle 1|H_1|1\rangle & \langle 1|H_1|2\rangle & \cdots & \langle 1|H_1|m\rangle \\ \langle 2|H_1|1\rangle & \langle 2|H_1|2\rangle & \cdots & \\ \vdots & & & \\ \langle m|H_1|1\rangle & & \cdots & \langle m|H_1|m\rangle \end{pmatrix}$$

since $H_1 = H_1^{+}$, $\tilde{H}_1 = \tilde{H}_1^{+}$.
Thus the eigenvectors of $\tilde{H}_1$ corresponding to distinct eigenvalues are orthogonal, and we may write

$$\tilde{H}_1 |\Psi_i^{(0)}\rangle = E_i^{(1)} |\Psi_i^{(0)}\rangle$$

or $\tilde{H}_1 \sum_{k=1}^{m} c_{ik}^{(0)} |k\rangle = E_i^{(1)} \sum_{k=1}^{m} c_{ik}^{(0)} |k\rangle$ (6

$$\sum_{k=1}^{m} \langle k' | \tilde{H}_1 | k \rangle c_{ik}^{(0)} = E_i^{(1)} c_{ik'}^{(0)}$$

$$\left(\tilde{H}_1 \right) \begin{pmatrix} c_{i1}^{(0)} \\ \vdots \\ c_{im}^{(0)} \end{pmatrix} = E_i^{(1)} \begin{pmatrix} c_{i1}^{(0)} \\ \vdots \\ c_{im}^{(0)} \end{pmatrix}$$

Thus, the prescription for degenerate perturbation theory is simply to diagonalize the $m \times m$ matrix $\tilde{H}_1$ for every set of m degenerate eigenstates of H_0. Once the basis that diagonalizes $\tilde{H}_1$ has been found, all of the formulas of ordinary nondegenerate perturbation theory can be used.

<u>Example</u> Orbital Zeeman effect for the 2p states of a Hydrogen atom.

$$H_0 = \frac{\vec{p}^{\,2}}{2\mu} - \frac{e^2}{|\vec{r}|}$$

Consider the three states with $n=2$, $l=1$, $m=-1,0,1$

$$E^{(0)} = E^{(0)}_{n=2} = -\frac{13.6\,\text{eV}}{4}$$

Let $H_1 = -\vec{\mu}\cdot\vec{B}$ with $\vec{B} = B\hat{x}$.

$$\vec{\mu} = -\frac{e}{2m_e c}\vec{L}, \text{ so}$$

$$H_1 = \frac{eB}{2m_e c} L_x .$$

Try blindly applying nondeg. pert. thy:

$$E^{(1)}_{n\ell m} = \langle n\ell m | H_1 | n\ell m \rangle$$

$$= \frac{eB}{2m_e c} \langle n\ell m | \frac{L_+ + L_-}{2} | n\ell m \rangle = 0$$

→ No first-order shift ?

$$E^{(2)}_{21m} = \sum_{m' \neq m} \frac{|\langle 21m' | H_1 | 21m \rangle|^2}{E^{(0)}_{n=2} - E^{(0)}_{n=2}} = \infty$$

→ undefined!

Need degenerate pert. thy!

Find eigenstates of H_1 in the subspace spanned by

$|n=2, \ell=1, m=-1\rangle$, $|2\,1\,0\rangle$, $|2\,1\,1\rangle$.

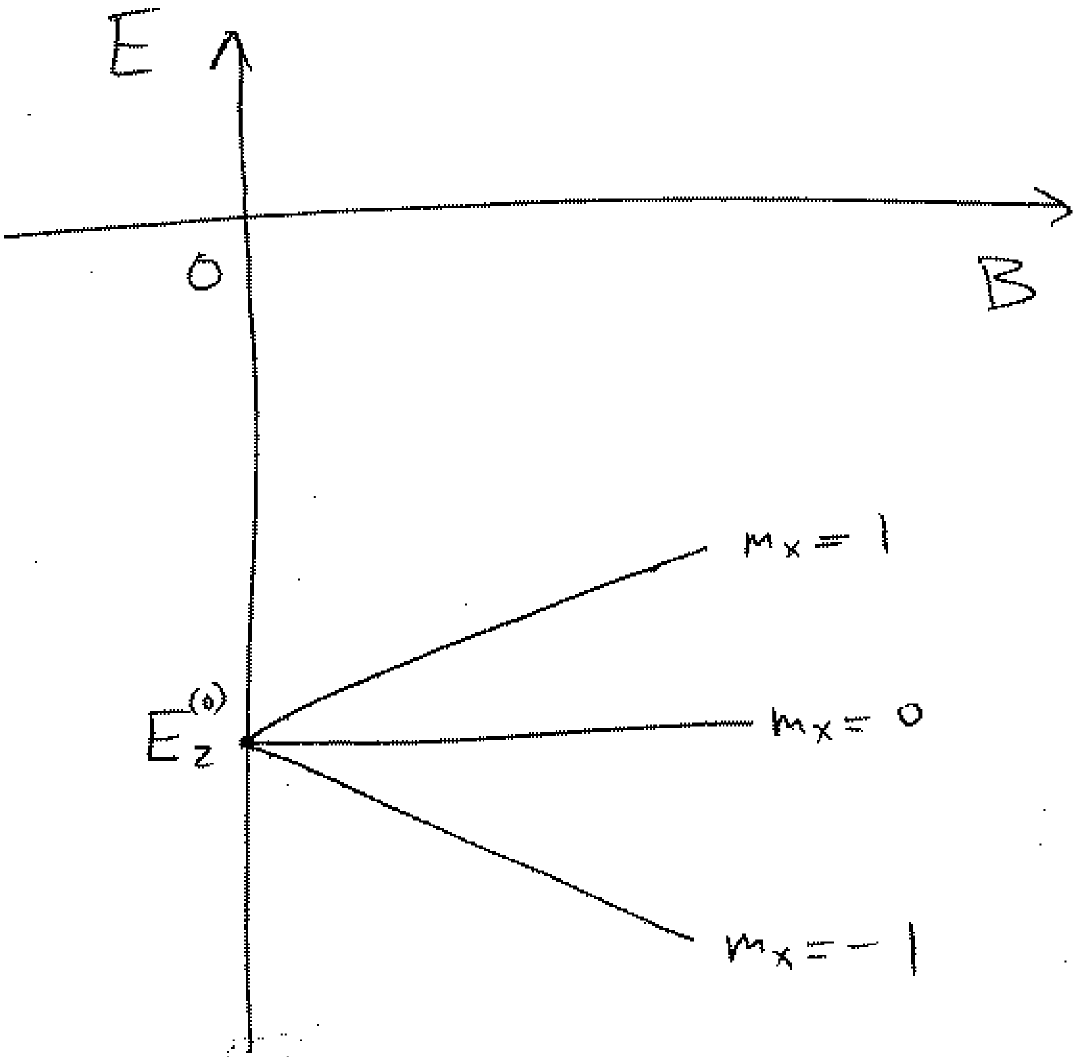
We already did this in 371; they are the eigenstates of $\vec{L}^2$, L_x:

$$\vec{L}^2 \, |n \ell m_x\rangle = \hbar^2 \ell(\ell+1) \, |n \ell m_x\rangle$$

$$L_x |n \ell m_x\rangle = \hbar m_x \, |n \ell m_x\rangle$$

In this basis,

$$E^{(1)}_{n \ell m_x} = \frac{e \hbar B}{2 m_e c} m_x$$



→ degeneracy lifted by Zeeman effect.

Q: Actually, the state with $n=2$, $\ell=0$ is also degenerate with these three states. Why don't we have to worry about it?

Q: What about higher-order terms?

<u>Theorem</u> If there is a hermitian operator $\hat{A}$ that commutes with H_0 and H_1, and if $|\tilde{\Psi}_i^{(0)}\rangle$ and $|\tilde{\Psi}_j^{(0)}\rangle$ are degenerate eigenfunctions of H_0 that are also eigenfunctions of $\hat{A}$ with distinct eigenvalues,

$$\hat{A}\,|\tilde{\Psi}_i^{(0)}\rangle = a_i\,|\tilde{\Psi}_i^{(0)}\rangle,$$

$$\hat{A}\,|\tilde{\Psi}_j^{(0)}\rangle = a_j\,|\tilde{\Psi}_j^{(0)}\rangle,$$

with $a_i \neq a_j$, then

$\langle\tilde{\Psi}_i^{(0)}|H_1|\tilde{\Psi}_j^{(0)}\rangle = 0$, and hence these are the desired basis states for degenerate pert. thy.

Proof: $[\hat{A}, H_1] = 0$, so

$$\langle \tilde{\Psi}_i^{(0)} | [A, H_1] | \tilde{\Psi}_j^{(0)} \rangle = 0$$

$$= \langle \tilde{\Psi}_i^{(0)} | A H_1 | \tilde{\Psi}_j^{(0)} \rangle - \langle \tilde{\Psi}_i^{(0)} | H_1 A | \tilde{\Psi}_j^{(0)} \rangle$$

$$= (a_i - a_j) \langle \tilde{\Psi}_i^{(0)} | H_1 | \tilde{\Psi}_j^{(0)} \rangle$$

$\Rightarrow \langle \tilde{\Psi}_i^{(0)} | H_1 | \tilde{\Psi}_j^{(0)} \rangle = 0$ since $a_i - a_j \neq 0$. Q.E.D.

Remark: For the Zeeman effect, let $A = L^2 \Rightarrow$ states with different l automatically uncoupled by H_1.