Lecture 13: Degenerate Perturbation Theory (I)

System with many degrees of freedom can possess ~~a~~ degenerate energy spectrum, usually associated with symmetries.

$$\hat{H}_0 |\phi_{n,i}^{(0)}\rangle = E_n^{(0)} |\phi_{n,i}^{(0)}\rangle$$ i labels other quantum #s in the complete set.

For given n $\{|\phi_{ni}^{(0)}\rangle, \ i = 1, 2, 3, \ldots, g_n\}$ g_n = degeneracy

Naive perturbation theory as we have presented it so far breaks down.

$$\Delta E_{n,i}^{(2)} = \sum_{(n'j) \neq ni} \frac{\langle \phi_{n'j}^{(0)} | \hat{H}_1 | \phi_{n,i}^{(0)} \rangle}{E_n^{(0)} - E_{n'}^{(0)}}$$ Blows up for degenerate states!

We need to be more careful here. The trick is to start with the "correct" zeroth order basis set.

Within a degenerate subspace of dimension g_n we can take any linear combination of states and still have energy eigenstates

$$|\tilde{\phi}_{n,\alpha}^{(0)}\rangle = \sum_{i=1}^{g_n} C_{ni}^{\alpha} |\phi_{n,i}^{(0)}\rangle$$

$$\hat{H}_0 |\tilde{\phi}_{n,\alpha}^{(0)}\rangle = E_n^{(0)} |\tilde{\phi}_{n,\alpha}^{(0)}\rangle$$

First order perturbation expansion

$$\left(\hat{H}_0 - E_n^{(0)}\right)|\tilde{\phi}^{(1)}_{n,\alpha}\rangle + \left(\hat{H}_1 - E^{(1)}_{n,\alpha}\right)|\tilde{\phi}^{(0)}_{n,\alpha}\rangle = 0$$

Require $\langle \tilde{\phi}^{(0)}_{n',\alpha'}|\tilde{\phi}^{(0)}_{n,\alpha}\rangle = \delta_{n'n}\,\delta_{\alpha'\alpha}$

$$\langle \tilde{\phi}^{(1)}_{n,\alpha}|\tilde{\phi}^{(0)}_{n,\alpha}\rangle = 0$$

Take inner product with $\langle \tilde{\phi}^{(0)}_{n,\alpha'}|$

$$\Rightarrow \cancel{\langle \tilde{\phi}^{(0)}_{n,\alpha'}|\hat{H}_0 - E_n^{(0)}|\tilde{\phi}^{(1)}_{n,\alpha}\rangle}_{\to 0} + \langle \tilde{\phi}^{(0)}_{n\alpha'}|\,\hat{H}_1 - E^{(1)}_{n,\alpha}\,|\tilde{\phi}^{(0)}_{n,\alpha}\rangle = 0$$

$$\Rightarrow \boxed{\langle \tilde{\phi}^{(0)}_{n,\alpha'}|\hat{H}_1|\tilde{\phi}^{(0)}_{n,\alpha}\rangle = E^{(1)}_{n,\alpha}\,\delta_{\alpha\alpha'}}$$

$\therefore$ The matrix representation of $\hat{H}_1$ is diagonal is the degenerate subspace

$\Rightarrow$ Choose $|\tilde{\phi}^{(0)}_{n,\alpha}\rangle$ to be simultaneous eigenstate of $\hat{H}_0$ and $\hat{H}_1$ in degenerate subspace $\Rightarrow$ Diagonalize $g_n \times g_n$ matrix

Given first order corrections, we can proceed to higher order in usual fashion. Note, the offending resonant denominators are now removed.

$$\Delta E^{(2)}_{n,\alpha} = \sum_{\substack{n' \neq n \\ \beta = 1}}^{g_{n'}} \frac{|\langle n', \beta|\hat{H}_1|n,\alpha\rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}}$$

<u>Example:</u> Stark effect for state in Hydr.

("Linear" Stark effect)

$n=2$ state in Hydrogen (ignoring spin)

2s: $|2s, \underbrace{0}_{m_\ell}\rangle$

2p: $|2p,-1\rangle$, $|2p,0\rangle$, $|2p,1\rangle$

Hamiltonian: $\hat{H} = \hat{H}_0 + \hat{H}_{int}$, $\hat{H}_1 = \hat{H}_{int} = +e\mathcal{E}_z \hat{z}$

(Electric field in z-direction)

Selection rule for matrix element

$$\langle n'\ell' m_\ell' | \hat{z} | n\ell m_\ell \rangle \quad \begin{cases} |\ell' - \ell| \text{ odd (parity)} \\ \Delta m_\ell = 0 \text{ (rotation)} \end{cases}$$

$\Rightarrow$ Only one non-zero matrix element

$$\langle 2s, 0 | \underset{\Downarrow\ \sqrt{\frac{4\pi}{3}}\, r Y_{1,0}(\theta)}{\hat{z}} | 2p, 0\rangle = \frac{a_0}{\sqrt{3}} \underbrace{\int d\bar{r}\, \bar{r}\, u_{21}(\bar{r})\, u_{20}(\bar{r})}_{=-3\sqrt{3}} \underbrace{\int d\Omega\, Y_{10}^* Y_{00}}_{=1}$$

$$\Rightarrow \quad \langle 2s, 0 | \hat{z} | 2p, 0\rangle = -3a_0$$

$\therefore$ In $n=2$ manifold

$$\hat{H} = \hat{H}_0 + \hat{H}_{int} = \begin{array}{c} \begin{array}{cccc} |2s\rangle & |2p,0\rangle & |2p,1\rangle & |2p,-1\rangle \end{array} \\ \left[\begin{array}{cc|cc} E_2^{(0)} & \epsilon & 0 & 0 \\ \epsilon & E_2^{(0)} & 0 & 0 \\ \hline 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{array}\right] \end{array}$$

Thus we must diagonalize only the ~~4~~2X2 matrix

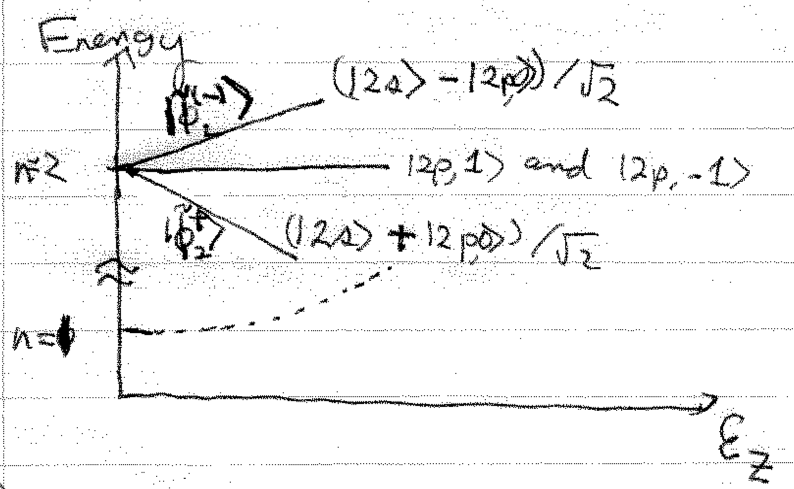
$$\hat{H} \doteq \begin{array}{cc} \begin{bmatrix} E_2^{(0)} & \epsilon \\ \epsilon & E_2^{(0)} \end{bmatrix} \\ |2s\rangle \quad |2p,0\rangle \end{array} \qquad \text{where} \quad \epsilon = -3e\mathcal{E}_z a_0 \quad \text{(real)}$$

$$\hat{H} = E_2^{(0)}\hat{\mathbb{1}} + \epsilon\,\hat{\sigma}_x \qquad \text{(pseudo-spin)} \quad \begin{array}{l} |\uparrow\rangle = |2s\rangle \\ |\downarrow\rangle = |2p,0\rangle \end{array}$$

Eigenvalues of $\hat{\sigma}_x = \pm 1$, eigenvectors $\dfrac{|\uparrow\rangle \pm |\downarrow\rangle}{\sqrt{2}}$

$\Rightarrow$ Energy levels to first order

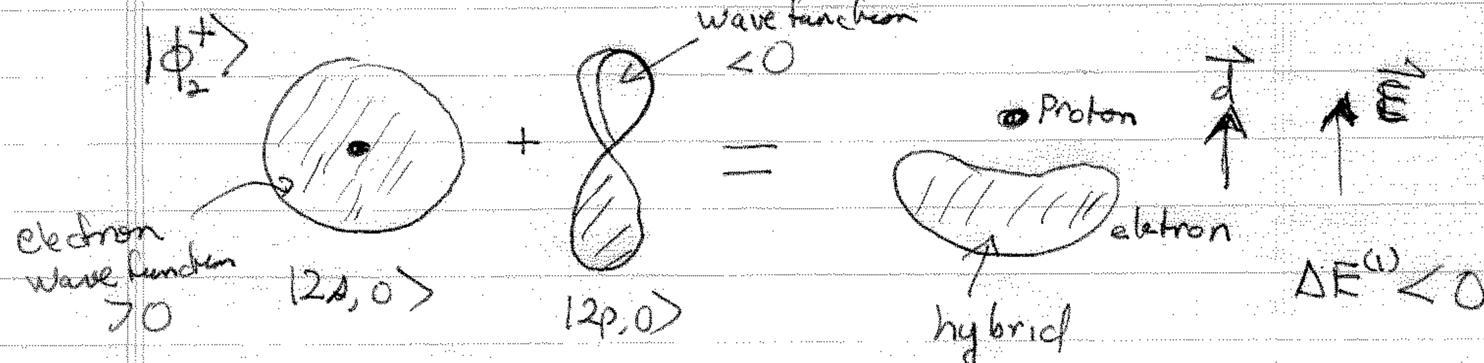
$$\boxed{\begin{aligned} E_2^{(\pm)} &= E_2^{(0)} \pm \epsilon = \frac{-e^2}{8a_0} \mp 3a_0 e\mathcal{E}_z \quad \text{linear in } \mathcal{E}_z \\ |\tilde{\phi}_2^{(\pm)}\rangle &= \frac{1}{\sqrt{2}}\left(|2s\rangle \pm |2p,0\rangle\right) \end{aligned}}$$



Note: eventually, for $\mathcal{E}_z$ huge $\sim 10^8\, V/cm$ $n=1$ and $n=2$ manifolds become degenerate

This result is generic. The original degeneracy was due to symmetry (rotational). The perturbation breaks the symmetry (partially) and thus breaks degeneracy (partially). We still have axial symmetry $\Rightarrow$ $\hat{L}_z$ commutes

Perturbed eigenstates: "Hybrid orbital"



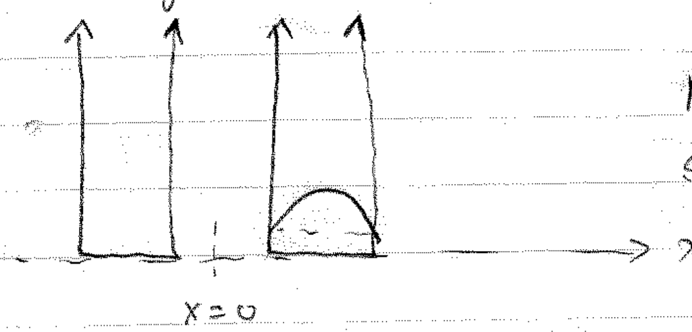
Even in the absence of a perturbing electric field the hybrid orbitals $\frac{|2s\rangle \pm |2p, 0\rangle}{\sqrt{2}}$ are eigenstates of $\hat{H}_0$. This is an example of "spontaneous symmetry breaking". The states $|\phi_2^\pm\rangle$ do not respect the spherical symmetry of $\hat{H}_0$ yet are eigenstates of $\hat{H}_0$. This is only possible when there is degeneracy.

Note: The states $|\phi_2^\pm\rangle$ have a permanent electric dipole moment. Thus the perturbation $\hat{H}_{Stark}$ has effect to first order in $\vec{E}$

$\Rightarrow$ Linear Stark effect

Other examples of "Broken Symmetry"

Two infinite square wells:



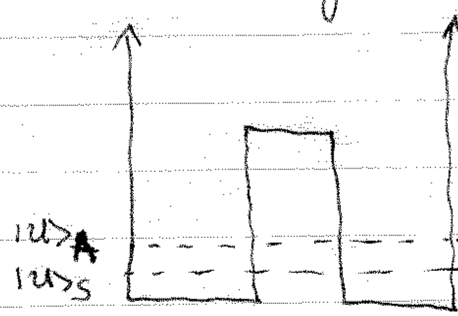
Parity is a symmetry

Degenerate states $|u_n\rangle_L$ and $|u_n\rangle_R$

$\Uparrow$ Left localized, $\Uparrow$ Right localized

do not respect parity

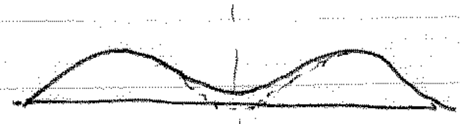
Break degeneracy by coupling $|u_n\rangle_L$ and $|u_n\rangle_R$



$\updownarrow \Delta E \sim {}_L\langle u_n | u_n \rangle_R$ (overlap)

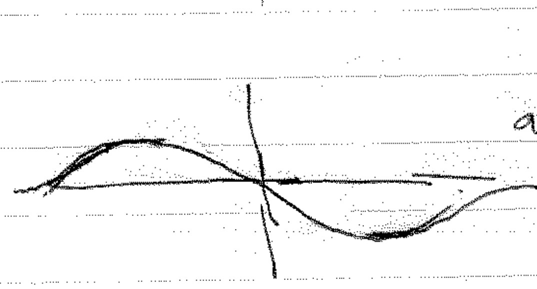
respect Parity

$$|u_S\rangle = \frac{|u_n\rangle_L + |u_n\rangle_R}{\sqrt{2}}$$



Symmetric combo

$$|u_A\rangle = \frac{|u_n\rangle_L - |u_n\rangle_R}{\sqrt{2}}$$



anti-symmetric combo

Tunneling couples right and left localized states