Lecture 22: Degenerate Perturbation theory

We have seen that our perturbation series converges when

$$\left| \langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle \right| \ll \left| E_m^{(0)} - E_n^{(0)} \right|$$

The "mixing matrix element" must be small compared to the energy gap between unperturbed energy levels.

What happens when there are <u>degeneracies</u> in the spectrum of $\hat{H}_0$? These typically occur because of symmetries; there are other degrees of freedom and conserved quantities.

$$\hat{H}_0 | \phi_{n,i}^{(0)} \rangle = E_n^{(0)} | \phi_{n,i}^{(0)} \rangle$$

i labels other quantum numbers in the complete set.

For a given n

$$\{ | \phi_{n,i}^{(0)} \rangle \mid i = 1, 2, 3, \cdots g_n \}$$

Degenerate manifold of dim g_n

of state with energy $E_n^{(0)}$

In the degenerate manifold, the mixing matrix element cannot possibly be small, and in principle couples states to <u>all</u> ~~other~~ <u>orders</u> in ϵ.

All hope is not lost. Recall that within a degenerate subspace, any linear combination of states is another eigenstate of $\hat{H}_0$ with the same eigenvalue

$$\text{Let} \quad |\tilde{\phi}^{(0)}_{n,\alpha}\rangle = \sum_{i=1}^{g_n} C^{\alpha}_{n,i} \, |\phi^{(0)}_{n,i}\rangle$$

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

We choose new set to be orthonormal

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

$$\text{and} \quad \langle \delta\phi_{n,\alpha} | \tilde{\phi}_{n,\alpha}\rangle = 0$$

perturbation orthogonal to zeroth order

First order perturbation expansions

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

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

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

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

$\therefore$ to have a consistent perturbation series, we must choose states with diagonalize $\hat{H}_1$ in the subspace of the degenerate manifold.

Because off-diagonal matrix elements of $\hat{H}_1$ vanish in this basis, so the offending terms in second order do not blew up.

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

Loosely, the perturbation mixes the degenerate subspace to all orders. These new states can then be used to higher order perturbations with other manifolds.

Example: Stark effect for $n=2$ in Hydrogen
("Linear" Stark effect)

$n=2$ state in Hydrogen (ignoring spin) $|n, \ell, m_\ell\rangle$

2s: $|2,0,0\rangle$

2p: $\{|2,1,+1\rangle, |2,1,0\rangle, |2,1,-1\rangle\}$

4-fold degenerate manifold.

Hamiltonian: $\hat{H} = \hat{H}_0 + \hat{H}_{int}$, $\hat{H}_{int} = \hat{H}_1 = e\underset{\substack{\text{applied } \vec{E} \\ \text{in } z\text{-direction}}}{\mathcal{E}}\hat{z}$

Lowest order correction diagonalize 4×4 matrix representation of $\hat{H}_1$ in degenerate manifold

Need matrix elements:

$$\langle 2\ell' m_\ell' | \hat{H}_1 | 2\ell m_\ell\rangle = e\mathcal{E}\langle 2\ell' m_\ell' | \hat{z} | 2\ell m_\ell\rangle$$

$$= e\mathcal{E}\int r^2 dr\, d\Omega\, \underbrace{(r\cos\theta)}_{=z}\, R_{2\ell'}(r)\, R_{2\ell}(r)\, Y^*_{\ell' m_\ell'}\, Y_{\ell,m}(\theta,\phi)$$

aside: $\cos\theta = \sqrt{\frac{4\pi}{3}}\, Y_{1,0}(\theta,\phi)$ $\quad R_{n\ell}(r) = \frac{u_{n\ell}(r)}{r}$

$$= e\mathcal{E}a_0 \underbrace{\left[\int_0^\infty d\bar{r}\, \bar{r}\, u_{2\ell'}(\bar{r})\, u_{2\ell}(\bar{r})\right]}_{\text{radial integral}} \underbrace{\left[\sqrt{\frac{4\pi}{3}}\int d\Omega\, Y^*_{\ell' m_\ell'}\, Y_{1,0}\, Y_{\ell m_\ell}\right]}_{\text{angular integral}}$$

The angular integral determines selection rules

$l' = l \pm 1$ (inversion symmetry)

$m_{l'} = m_l$ (rotation symmetry)

$\Rightarrow$ Only one nonvanishing matrix element (and its conjugate)

$$e\mathcal{E}\langle 2p,0|\hat{z}|2s,0\rangle = e\mathcal{E}\langle 2,1,0|\hat{z}|2,0,0\rangle$$

$$= e\mathcal{E}a_0 \underbrace{\left[\int_0^\infty d\bar{r}\; \bar{r}\; u_{21}(\bar{r})\, u_{20}\right]}_{-3\sqrt{3}} \underbrace{\left[\sqrt{\frac{4\pi}{3}}\frac{1}{\sqrt{4\pi}}\int d\Omega\, Y^*_{1,0}\, Y_{1,0}\right]}_{\frac{1}{3}}$$

(need to do integral over functions)

(Having used $Y_{00} = \frac{1}{\sqrt{4\pi}}$)

$$\therefore \langle 2p,0|\hat{H}_1|2s\rangle = -3e\mathcal{E}a_0 \equiv \Delta E$$

$\Rightarrow$ In the $n=2$ manifold (order appropriately)

$$\hat{H}_1 \doteq \begin{array}{cccc} |2s\rangle & |2p\,0\rangle & |2p,1\rangle & |2p,-1\rangle \end{array}$$
$$\left[\begin{array}{cc|cc} 0 & \Delta E & 0 & 0 \\ \Delta E & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right]$$

With the basis appropriately ordered we must diagonalized the 2×2 matrix

$$\hat{H}_1 \doteq \begin{array}{c} \begin{bmatrix} 0 & \Delta E \\ \Delta E & 0 \end{bmatrix} \end{array} \begin{array}{l} \langle 2s| \\ \langle 2p,0| \end{array} = \Delta E \, \hat{\sigma}_x$$

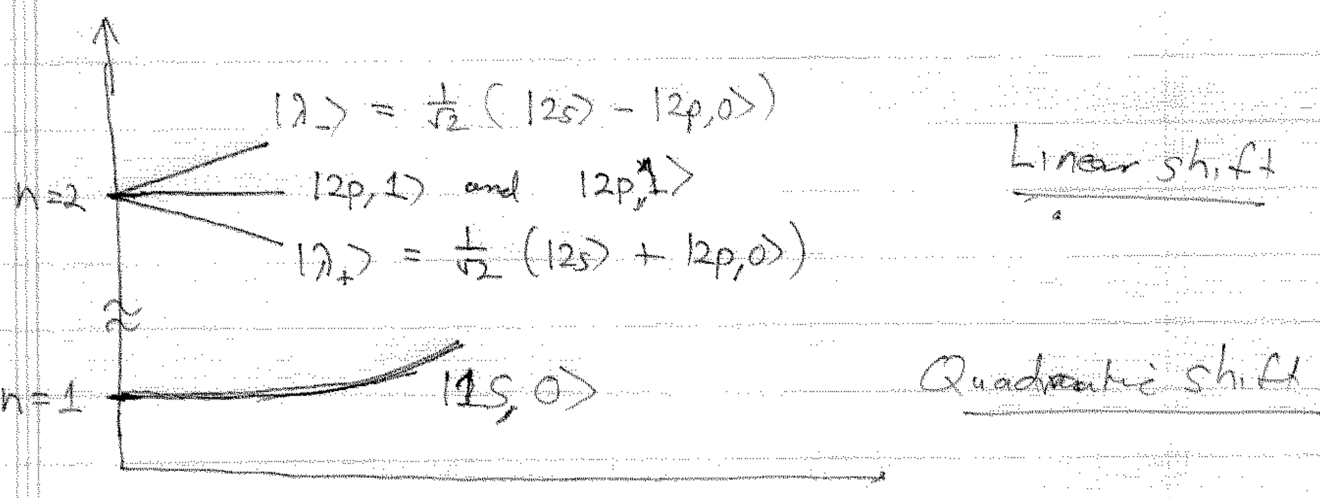
Secular equation $\det(\hat{H}_1 - \lambda \hat{\mathbb{1}}) = \lambda^2 - (\Delta E)^2 = 0$

$$\Rightarrow \lambda_{\pm} = \pm \Delta E = \mp 3 e \mathcal{E} a_0$$

Eigenvectors $|\lambda_\pm\rangle = \dfrac{|2s\rangle \pm |2p,0\rangle}{\sqrt{2}}$

Thus to first order the $n=2$ manifold

- $|\lambda_+\rangle = \dfrac{|2s\rangle - |2p,0\rangle}{\sqrt{2}}$, $E_- = E_2^{(0)} - \Delta E = \dfrac{-e^2}{8a_0} + 3e\mathcal{E}a_0$
- $|2p,1\rangle$, $|2p,-1\rangle$, $E_2^{(0)} = \dfrac{-e^2}{8a_0}$ (still degenerate)
- $|\lambda_-\rangle = \dfrac{|2s\rangle + |2p,0\rangle}{\sqrt{2}}$ $E_+ = E_2^{(0)} + \Delta E = \dfrac{-e^2}{8a_0} - 3e\mathcal{E}_0$

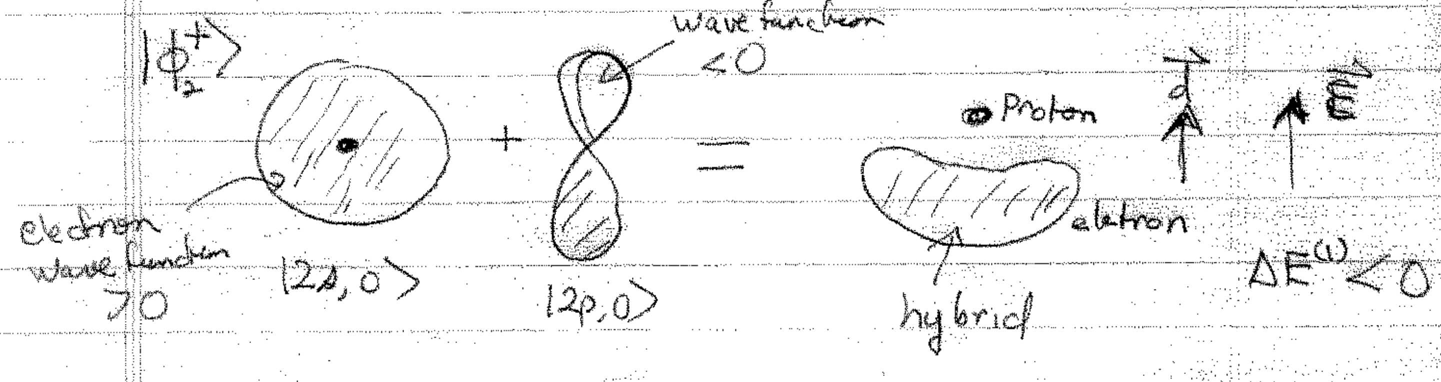


Note: The effect of the perturbation was to (at least partially) break the the degeneracies. A previously degenerate manifold now becomes split in energy by an amount depending on the perturbation Hamiltonian.

Note: Eventually, for huge field $\mathcal{E} \sim 10^4 \frac{\text{Volts}}{\text{cm}}$

$n=1$ and $n=2$ states become nearly degenerate. We must then apply perturbation theory again to this manifold.

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 $\vec{E}$

$\Longrightarrow$ Linear Stark effect