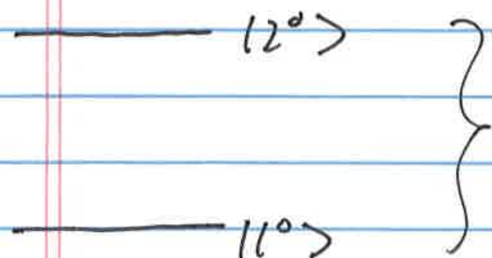
Optics & Spectroscopy — Lecture 16



2 levels coupled by "V"

Perturbation Theory:

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad E_1 = E_1^\circ + \langle 1^\circ|\hat{V}|1^\circ\rangle$$

$$E_2 = E_2^\circ + \langle 2^\circ|\hat{V}|2^\circ\rangle$$

rewrite as: $E_1 = E_1^\circ + V_{11}$

$$E_2 = E_2^\circ + V_{22}$$

wavefunctions: $$|2\rangle = |2^\circ\rangle + \frac{\langle 1^\circ|\hat{V}|2^\circ\rangle}{E_2^\circ - E_1^\circ}|1^\circ\rangle$$

$$|1\rangle = |1^\circ\rangle + \frac{\langle 2^\circ|\hat{V}|1^\circ\rangle}{E_1^\circ - E_2^\circ}|2^\circ\rangle$$

Note: define $2\Delta = E_2^\circ - E_1^\circ$ & $V = V_{12} = V_{21}$

write wavef's as: $$|2\rangle = |2^\circ\rangle + \frac{V}{2\Delta}|1^\circ\rangle$$

$$|1\rangle = |1^\circ\rangle - \frac{V}{2\Delta}|2^\circ\rangle$$

$|1\rangle$ and $|2\rangle$ are not normalized

$$\langle 1|1\rangle = \left\{\langle 1^0| - \frac{V}{2\Delta}\langle 2^0|\right\}\left\{|1^0\rangle - \frac{V}{2\Delta}|2^0\rangle\right\}$$

$$= 1 + V^2/4\Delta^2$$

$\Rightarrow$ Normalized wavef's are:

$$|1\rangle = \frac{1}{\sqrt{1+V^2/4\Delta^2}}\left\{|1^0\rangle - \frac{V}{2\Delta}|2^0\rangle\right\}$$

$$|2\rangle = \frac{1}{\sqrt{1+V^2/4\Delta^2}}\left\{|2^0\rangle + \frac{V}{2\Delta}|1^0\rangle\right\}$$

Note: $$\langle 1|2\rangle = \frac{1}{(1+V^2/4\Delta^2)}\left\{\langle 1^0| - \frac{V}{2\Delta}\langle 2^0|\right\} \times \left\{|2^0\rangle + \frac{V}{2\Delta}|1^0\rangle\right\}$$

$$= \frac{1}{(\quad)}\left\{\frac{V}{2\Delta} - \frac{V}{2\Delta}\right\} = 0$$

~ perturbation mixes the levels, we get "+" and "−" combinations

Exact Solution

~ rewrite in matrix form

$$\left.\begin{aligned} \hat{H}_0|1\rangle &= E_1|1\rangle \\ \hat{H}_0|2\rangle &= E_2|2\rangle \end{aligned}\right\} \text{ becomes } \left\{\begin{aligned} \hat{H}_0 &= \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \\ |1\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |2\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{aligned}\right.$$

$$\Rightarrow \langle 1|\hat{H}_0|1\rangle = E_1 \equiv (1 \; 0)\begin{pmatrix} E_1 & 0 \\ 0 & E_1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_1$$

~ the "perturbed" Hamiltonian is: $\hat{H} = \hat{H}_0 + \hat{V}$

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \quad w/ \quad V_{ij} = \langle i|\hat{V}|j\rangle$$

$$\Rightarrow H = \begin{pmatrix} E_1 + V_{11} & V_{12} \\ V_{21} & E_2 + V_{22} \end{pmatrix}$$

~ need to find the eigenvalues & eigenvectors for this matrix

define: $\tilde{E}_1 = E_1 + V_{11}$

$\tilde{E}_2 = E_2 + V_{22}$

← like the 1st order PT energies

$V = V_{21} = V_{12}$

$$\Rightarrow \hat{H} = \begin{pmatrix} \tilde{E}_1 & V \\ V & \tilde{E}_2 \end{pmatrix}$$

Mathematica

In[19]= $H = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}$;

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Eigenvalues[H]
Eigenvectors[H]
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Out[20]= $\left\{\frac{1}{2}\left(e_1 + e_2 - \sqrt{4\,V^2 + e_1^2 - 2\,e_1\,e_2 + e_2^2}\right), \frac{1}{2}\left(e_1 + e_2 + \sqrt{4\,V^2 + e_1^2 - 2\,e_1\,e_2 + e_2^2}\right)\right\}$

Out[21]= $\left\{\left\{-\frac{-e_1 + e_2 + \sqrt{4\,V^2 + e_1^2 - 2\,e_1\,e_2 + e_2^2}}{2\,V}, 1\right\}, \left\{-\frac{-e_1 + e_2 - \sqrt{4\,V^2 + e_1^2 - 2\,e_1\,e_2 + e_2^2}}{2\,V}, 1\right\}\right\}$

define $E_m = (\tilde{E}_1 + \tilde{E}_2)/2$

$\Delta = (\tilde{E}_2 - \tilde{E}_1)/2$

$$\Rightarrow \quad E = E_m \pm \frac{\sqrt{4V^2 + (\tilde{E}_2 - \tilde{E}_1)^2}}{2}$$

$$= E_m \pm \sqrt{V^2 + \Delta^2}$$

$$|+\rangle = \left(-\frac{\Delta}{V} + \frac{\sqrt{V^2+\Delta^2}}{V}\right)|1\rangle + |2\rangle$$

$$|-\rangle = \left(-\frac{\Delta}{V} - \frac{\sqrt{V^2+\Delta^2}}{V}\right)|1\rangle + |2\rangle$$

not normalized

$$\langle +|-\rangle = \left(\langle 2| + \left(-\frac{\Delta}{V} + \frac{\sqrt{\ }}{V}\right)\langle 1|\right)\left(\left(-\frac{\Delta}{V} - \frac{\sqrt{\ }}{V}\right)|1\rangle + |2\rangle\right)$$

$$= 1 - \left(-\frac{\Delta}{V} + \frac{\sqrt{\ }}{V}\right)\left(\frac{\Delta}{V} + \frac{\sqrt{\ }}{V}\right)$$

$$= 1 - \left(-\frac{\Delta^2}{V^2} + \frac{\Delta^2 + V^2}{V^2}\right) = 0$$

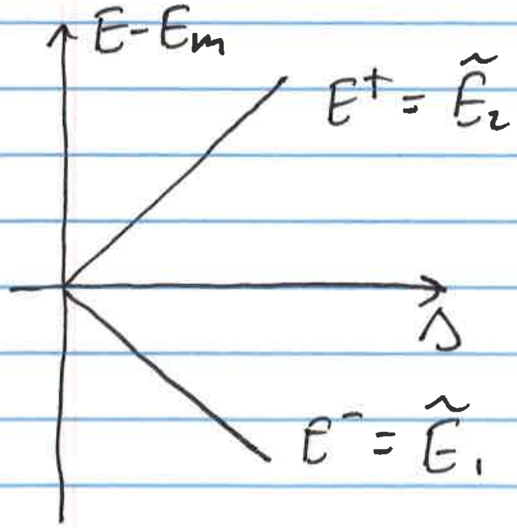
~ lets look at how the levels/mixings change as we change energy

(i) weak coupling $|V| \ll |\Delta|$

$$E^+ = E_m + |\Delta| \; ; \quad E^- = E_m - |\Delta|$$

$$\Delta = (\tilde{E}_2 - \tilde{E}_1)/2 \; ; \quad E_m = (\tilde{E}_1 + \tilde{E}_2)/2$$

$$\Delta > 0 \quad (E_2 > E_1) \quad E^+ \simeq \tilde{E}_2 \; ; \quad E^- = \tilde{E}_1$$



$$|+\rangle \simeq \left(-\frac{\Delta}{V} + \frac{\Delta}{V}\right)|1\rangle + |2\rangle \simeq |2\rangle$$

$$|-\rangle \simeq \left(-\frac{\Delta}{V} - \frac{\Delta}{V}\right)|1\rangle + |2\rangle$$

$$= -\frac{2\Delta}{V}|1\rangle + |2\rangle \sim |1\rangle$$

$|\Delta| \gg |V|$

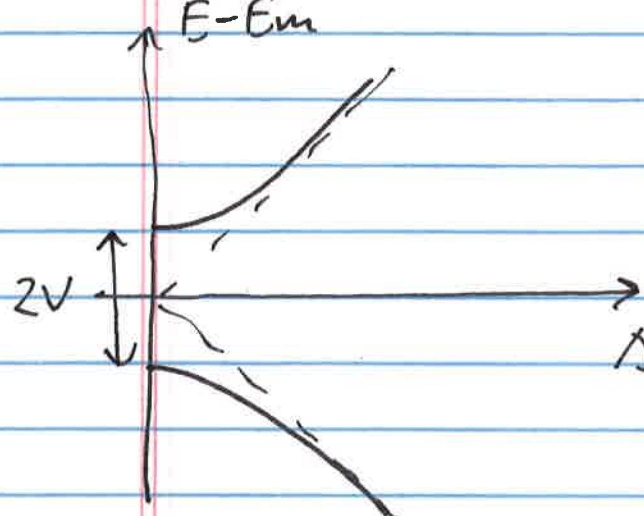
~ This is just like PT.

(ii) Strong coupling $|V| \gg |\Delta|$

$\sim$ $E^+ = E_m + \sqrt{V^2+\Delta^2}$

$E^- = E_m - \sqrt{V^2+\Delta^2}$

$\sim$ at $\Delta = 0$ $E^+ = E_m + V$; $E^- = E_m - V$



$\leftarrow$ levels now do not meet at $\Delta = 0$

"avoided crossing"

$\sim$ energy splitting at $\Delta = 0$ is $2V$

at $\Delta = 0$: $|+\rangle = |1\rangle + |2\rangle$

$|-\rangle = -|1\rangle + |2\rangle$

} wavefunctions are equal mixtures

normalized wavefunctions are

$$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

$$|-\rangle = \frac{1}{\sqrt{2}}(-|1\rangle + |2\rangle)$$

~ compare PT & exact results.

PT wavefunctions $|1\rangle = |1^0\rangle - \frac{V}{2\Delta}|2^0\rangle$

$|2\rangle = |2^0\rangle + \frac{V}{2\Delta}|1^0\rangle$

Define $\gamma = \left|\frac{V}{2\Delta}\right|$

$\Delta > 0$ $\quad |1\rangle = |1^0\rangle - \gamma|2^0\rangle$

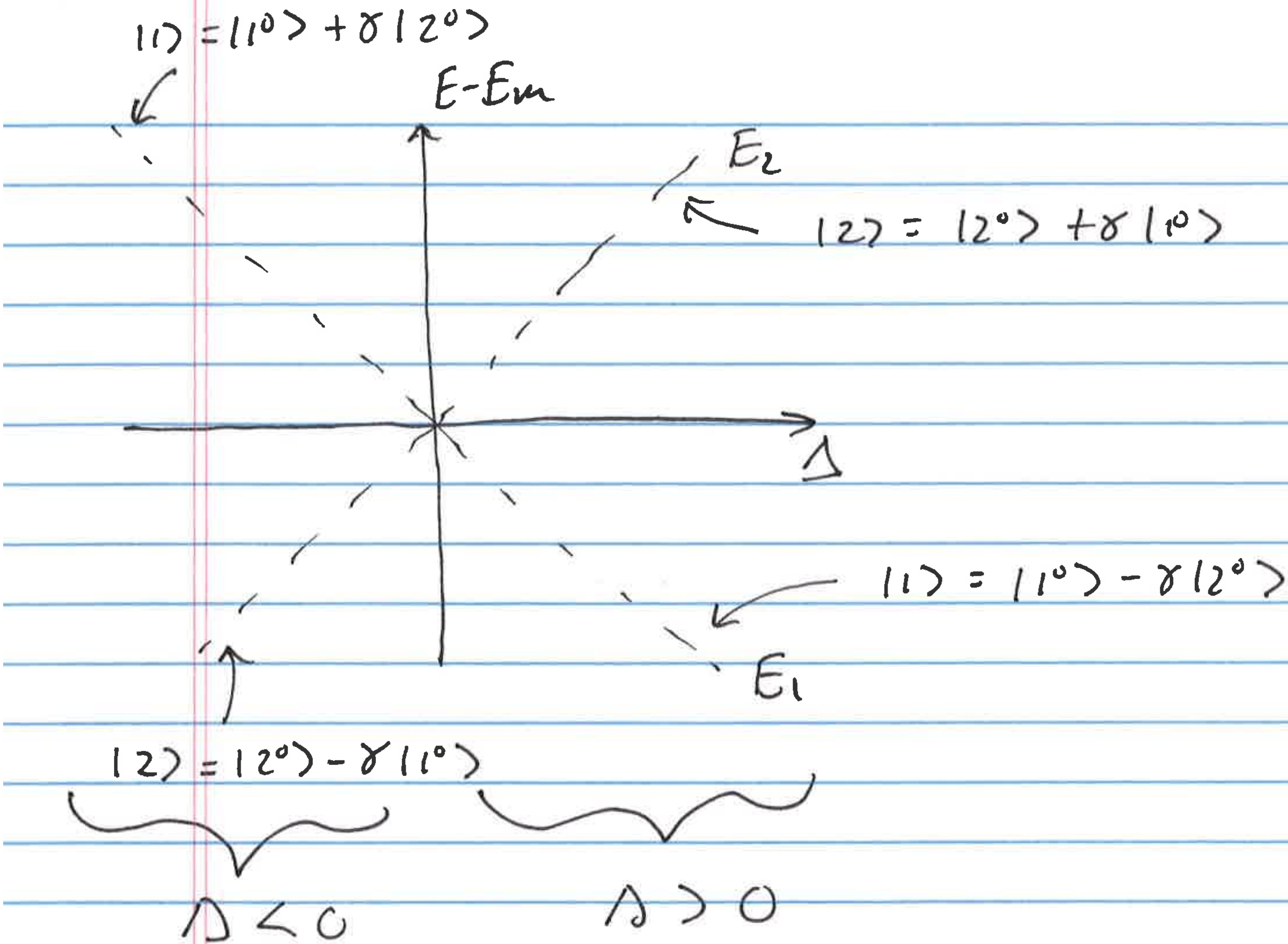
$|2\rangle = |2^0\rangle + \gamma|1^0\rangle$

$\Delta < 0$ $\quad |1\rangle = |1^0\rangle + \gamma|2^0\rangle$

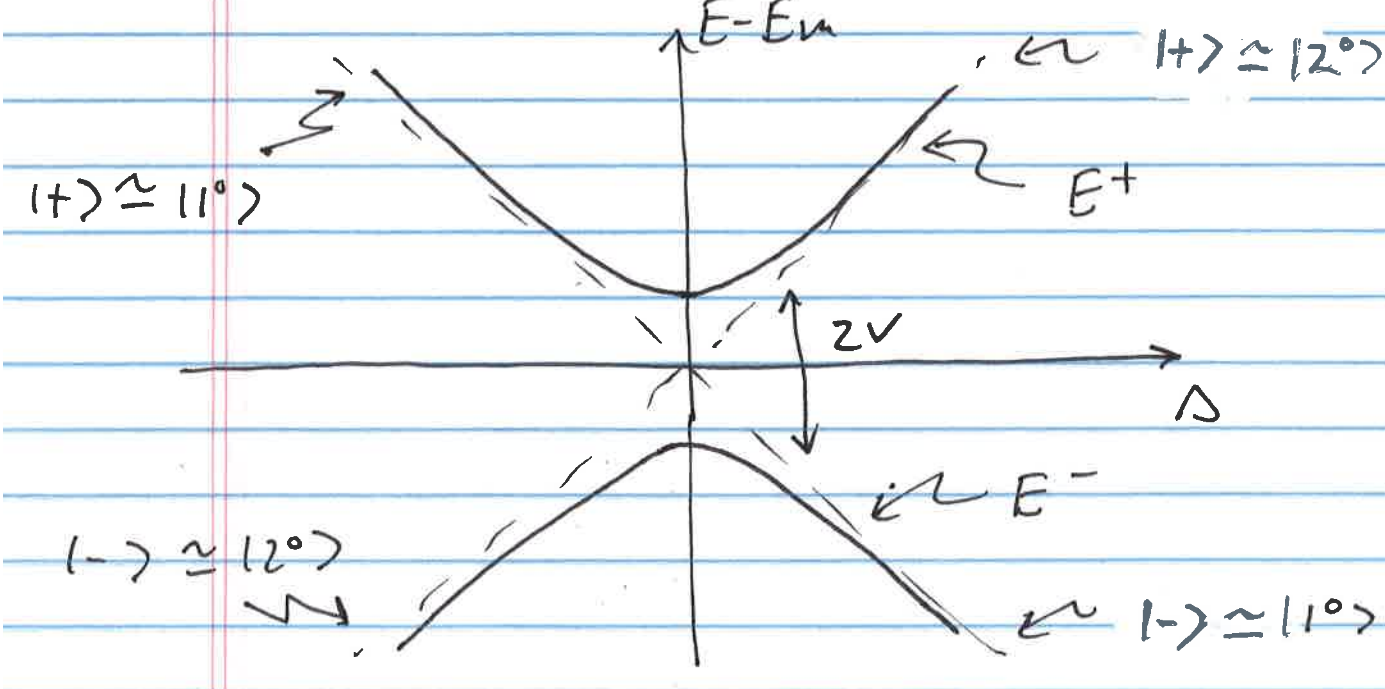
$|2\rangle = |2^0\rangle - \gamma|1^0\rangle$

$\Delta > 0 \Rightarrow E_2^0 > E_1^0$

$\Delta < 0 \Rightarrow E_2^0 < E_1^0$



~ "add in" exact energies / wave functions

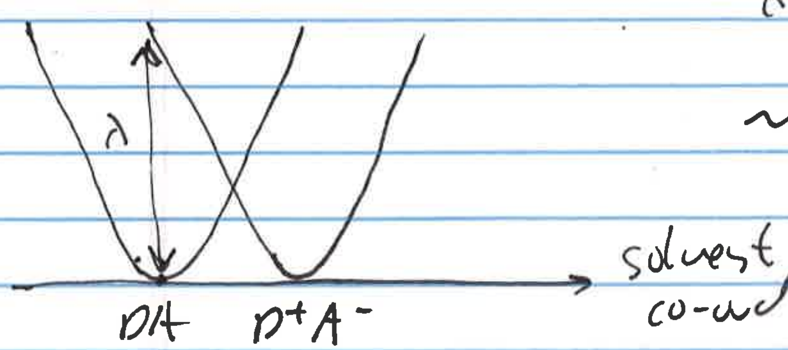


Note: wavefunctions change character as they go through the crossing region

Example: Electron transfer reactions

$DA \rightarrow D^+A^-$ ← different charge configurations ⇒ solvated differently

Weak Coupling: Marcus Theory



λ = "reorganization energy"

~ curves cross, system switches from one to the other at T.S.

Strong Coupling

~ "adiabatic" electron transfer