5.74 RWF Lecture #12

Quasi-degenerate Perturbation Theory. Strong and Weak Coupling Limits

Reading: Chapter 9.3, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time: Non-degenerate perturbation theory for interaction between quasi-eigenstates with finite level-width

If we allow $\mathbf{H}^{(0)}$ to have complex energies along the diagonal, we have a basis for calculating how quasi-eigenstates share the property of decay rate.

Illustration that sharing of decay rate (NOT LIFETIME) is just like sharing of Zeeman tuning rate

* key is to use perturbation theory to obtain $\psi_i = \psi_i^{(0)} + \psi_i^{(1)}$.

* energy denominator is complex - rationalize and get corrections to ε and Γ

Problem of orthogonality — solved by biorthogonal basis set.

Today:

1. biorthogonality → completeness
2. 2×2 complex **H**
3. limiting cases
   strong & weak coupling limits
4. doorway state "dissolves in bath"
5. quantum beats .

Biorthogonality

When **H** is real everywhere except along the main diagonal

$$\mathbf{H}|i\rangle = E_i|i\rangle \qquad |i\rangle = \begin{pmatrix} \mathbf{a}_1^i \\ \vdots \\ \mathbf{a}_N^i \end{pmatrix}$$

then it must be true that

$$\mathbf{H}^*|\tilde{i}\rangle = E_i^*|\tilde{i}\rangle \qquad |\tilde{i}\rangle = \begin{pmatrix} \mathbf{a}_1^{i*} \\ \vdots \\ \mathbf{a}_N^{i*} \end{pmatrix}$$

but then we have

$$\langle\tilde{i}| = \left(\mathbf{a}_1^i \ldots \mathbf{a}_N^i\right)$$

and therefore

$$\langle \tilde{i} | i \rangle = \sum_j \left(\mathbf{a}^i_j\right)^2$$ which is not necessarily 1 and can even be complex.

Note that $\Psi(\mathbf{Q},t)$ cannot remain normalized to 1 at all t because $\mathrm{P}(t) = e^{-t\Gamma/\hbar}$!

So we are stuck with two awkwardnesses about normalization:

* cannot insist on normalization to 1 at all t
* usual normalization integral can give a complex number

We handle this by expressing the ortho-normalization condition as

$$\frac{\langle \tilde{j} | i \rangle}{\langle \tilde{j} | j \rangle} = \delta_{ij}$$

(the factor $\langle \tilde{j} | j \rangle$ in the denominator cancels the $e^{-t\Gamma_j/\hbar}$ decay of probability) and completeness as

$$\mathbb{1} = \sum_j \frac{|j\rangle\langle \tilde{j}|}{\langle \tilde{j} | j \rangle}.$$

Note that

non-zero only when $j = i$

$$\mathbb{1}|i\rangle = \sum_j \frac{|j\rangle\langle \tilde{j}|i\rangle}{\langle \tilde{j} | j \rangle} = |i\rangle$$

$$\langle \tilde{i}|\mathbb{1} = \sum_j \frac{\langle \tilde{i}|j\rangle\langle \tilde{j}|}{\langle \tilde{j} | j \rangle} = \langle \tilde{i}|$$

as expected, and, for a member of a different basis set

$$\mathbb{1}|K\rangle = \sum_j |j\rangle \underbrace{\left[\frac{\langle \tilde{j}|K\rangle}{\langle \tilde{j} | j \rangle}\right]}_{\text{expansion coefficient}}.$$

It turns out that all of the results for E_i and $|\psi_i\rangle$ from nondegenerate perturbation theory come out as expected. But it is important to remember that it is always necessary to include the factor of $[\langle\tilde{i}|i\rangle]^{-1/2}$ to renormalize $|i\rangle$.

Consider the <u>2×2 Problem with Complex Diagonal Elements</u>

From last lecture: real $\mathbf{H}^{(0)}$, Hermitian $\mathbf{H}$.

$$\mathbf{H} = \begin{pmatrix} E_A & \mathbf{H}_{AB} \\ \mathbf{H}_{AB}^* & E_B \end{pmatrix} = \begin{pmatrix} \overline{E} & 0 \\ 0 & \overline{E} \end{pmatrix} + \begin{pmatrix} \frac{E_A - E_B}{2} & \mathbf{H}_{AB} \\ \mathbf{H}_{AB}^* & \frac{E_A - E_B}{2} \end{pmatrix}$$

$E_{\pm} = \overline{E} \pm \Delta$ change of notation $\qquad \mathbf{H}_{AB} = |\mathbf{H}_{AB}| e^{-i\phi}$

$$\overline{E} = \frac{E_A + E_B}{2}$$

$$\Delta = \left[\left(\frac{E_A - E_B}{2} \right)^2 + |\mathbf{H}_{AB}|^2 \right]^{1/2}$$

$$|\psi_{\pm}\rangle = \pm \left[\frac{\Delta \pm (E_A - E_B)/2}{2\Delta} \right]^{1/2} e^{-i\phi/2} |\psi_A\rangle + \left[\frac{\Delta \mp (E_A - E_B)/2}{2\Delta} \right]^{1/2} e^{i\phi/2} |\psi_B\rangle.$$

Now go to complex diagonal elements and simplified notation

$$E_A = \varepsilon_A - i\Gamma_A/2$$

$$E_B = \varepsilon_B - i\Gamma_B/2$$

$$\overline{\varepsilon} = \frac{\varepsilon_A + \varepsilon_B}{2} \qquad \delta\varepsilon = (\varepsilon_A - \varepsilon_B)/2$$

$$\Gamma = \frac{\Gamma_A + \Gamma_B}{2} \qquad \delta\Gamma = (\Gamma_A - \Gamma_B)/2$$

$\mathbf{H}_{AB} = \mathbf{H}_{AB}^* = V \qquad$ real

$$\mathbf{H} = \begin{pmatrix} \bar{\varepsilon} - i\bar{\Gamma}/2 & 0 \\ 0 & \bar{\varepsilon} - i\bar{\Gamma}/2 \end{pmatrix} + \begin{pmatrix} \delta\varepsilon - i\delta\Gamma/2 & V \\ V & -\delta\varepsilon + i\delta\Gamma/2 \end{pmatrix}$$

The complex energies are, $E_{\pm} = \left(\bar{\varepsilon} - i\bar{\Gamma}/2\right) \pm \mathscr{E}$

$$\mathscr{E} = \left[\delta\varepsilon^2 - \left(\delta\Gamma/2\right)^2 - i\delta\varepsilon\delta\Gamma + V^2\right]^{1/2}$$

This is the square root of a complex number. There is some extremely complicated algebra (including rejection of non-physical cases), but we eventually obtain

$$E_{\pm} = \left(\bar{\varepsilon} \pm \chi\right) - i\left(\bar{\Gamma}/2 \pm \delta\varepsilon\delta\Gamma/(2\chi)\right)$$
$$\chi = 2^{-1/2}\left\{\delta\varepsilon^2 - \delta\Gamma^2/4 + V^2 + \left[\left(-\delta\varepsilon^2 + \delta\Gamma^2/4 - V^2\right)^2 + \delta\varepsilon^2\delta\Gamma^2\right]\right\}^{1/2}$$
$$\chi > 0$$

NonLecture

for the eigenvectors, we have

$$|\psi_{\pm}\rangle = \alpha_{\pm}|\psi_A\rangle + \beta_{\pm}|\psi_B\rangle$$
$$\alpha_{+} = \beta_{-} = \left(\frac{\mathscr{E} + \delta\varepsilon - i\delta\Gamma/2}{2\mathscr{E}}\right)^{1/2}$$
$$\beta_{+} = -\alpha_{-} = \left(\frac{\mathscr{E} - \delta\varepsilon + i\delta\Gamma/2}{2\mathscr{E}}\right)^{1/2}$$

note that, as we feared,

$$\langle + | + \rangle = |\alpha_+|^2 + |\beta_+|^2 = \left(\frac{\mathcal{E}^2 + \delta\varepsilon^2 + \delta\Gamma^2/4 + 2\mathcal{E}\delta\varepsilon}{2\mathcal{E}} \right)^{1/2}$$

$$+ \left(\frac{\mathcal{E}^2 + \delta\varepsilon^2 + \delta\Gamma^2/4 - 2\mathcal{E}\delta\varepsilon}{2\mathcal{E}} \right)^{1/2}$$

$$\neq 1$$

$$\langle - | + \rangle = \alpha_-^{*}\;{}_{+} + \beta_-^{*}\beta \;\; = \left(-\beta_+^{*}\alpha_+\right) + \alpha_+^{*}\beta_+ = 2i\,\mathrm{Im}\left(\alpha_+^{*}\beta_+\right)$$

$$\neq 0$$

but, in the biorthogonal sense

Both "mixing fractions" are complex, but their sum is 1.

$$\langle \tilde{\pm} | \pm \rangle = (\alpha_\pm)^2 + (\beta_\pm)^2 = \frac{2\mathcal{E}}{2\mathcal{E}} = 1$$

$$\langle \tilde{\mp} | \pm \rangle = \alpha_\mp\alpha_\pm + \beta_\mp\beta_\pm = -\beta_\pm\alpha_\pm + \alpha_\pm\beta_\pm = 0$$

means we do not take complex conjugate

so all is well. The basis is biorthonormal.

Now consider the limiting cases for the complicated energy expressions.

Strong coupling limit:

$$V^2 >> \left|\delta\varepsilon^2 + \delta\Gamma^2/4\right| > \left|\delta\varepsilon^2 - \delta\Gamma^2/4\right|$$

we get

$$E_{\pm} = \left[\bar{\varepsilon} \pm |V|\left(1 + \frac{\delta\varepsilon^2 - \delta\Gamma^2/4}{2V^2}\right)\right] - i\left[\bar{\Gamma}/2 \pm \left(\frac{\delta\varepsilon\delta\Gamma}{2|V|}\right)\left(1 - \frac{\delta\varepsilon^2 - \delta\Gamma^2/4}{2V^2}\right)\right]$$

The real part of $E_+ - E_-$ differs from the $\delta\Gamma = 0$ familiar limit result $2\left[V^2 + \delta\varepsilon^2\right]^{1/2} \approx 2V + \frac{\delta\varepsilon^2}{|V|}$ or $2\delta\varepsilon + \frac{V^2}{\delta\varepsilon}$ by a small "level attraction" term (as we saw in non-degenerate p. t. last time) $\frac{-\delta\Gamma^2/4}{|V|}$.

The imaginary part shows that the difference in widths is

$$\delta\Gamma\left(\frac{\delta\varepsilon}{|V|}\right)\left(1 - \frac{\delta\varepsilon^2 - \delta\Gamma^2/4}{2V^2}\right)$$

original difference in widths

reduced if $|\delta\varepsilon| > |\delta\Gamma/2|$
increased if $|\delta\varepsilon| < |\delta\Gamma/2|$

But the important point is that if either $\delta\varepsilon$ or $\delta\Gamma = 0$, the two quasi-eigenstates have the same width.

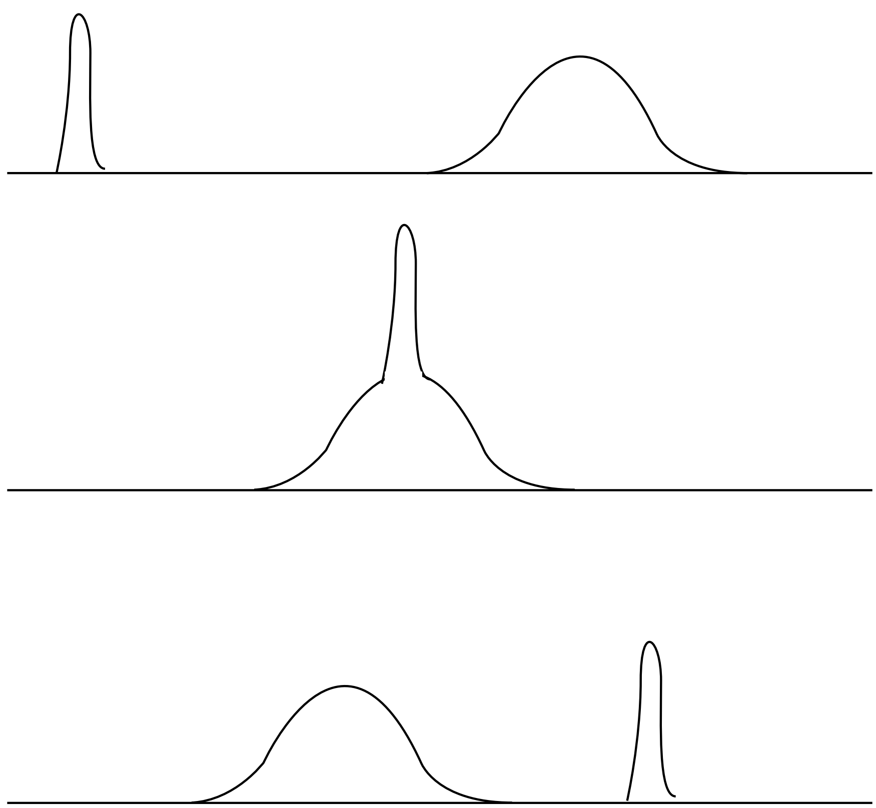
We knew that $\delta\Gamma = 0$ would have this effect from non-degenerate p. t. The $\delta\varepsilon = 0$ result is not a surprise because, in the ordinary 2-level problem, when $\delta\varepsilon = 0$, get 50/50 mixing. There is no difference in any property (including the width) except for the energy ($E_+ - E_- = 2V$).

<u>Weak coupling limit</u>: $V^2 << \left|\delta\Gamma^2/4 - \delta\varepsilon^2\right|$

$$E_{\pm} = \left[\bar{\varepsilon} \pm \delta\varepsilon\left(1 + \frac{V^2/2}{\delta\varepsilon^2 + \delta\Gamma^2/4}\right)\right] - i\left[\bar{\Gamma}/2 \pm \frac{\delta\Gamma}{2}\left(1 - \frac{V^2/2}{\delta\varepsilon^2 + \delta\Gamma^2/4}\right)\right]$$

The real part of $E_+ - E_-$ differs surprisingly from $2V + \frac{\delta\varepsilon^2}{|V|}$ or $2\delta\varepsilon + \frac{V^2}{\delta\varepsilon}$. When $\delta\varepsilon = 0$, the real part of $E_+ - E_-$ is zero! Level repulsion has turned off! Big surprise!

The imaginary part of $E_+ - E_-$ shows that the difference in level widths is reduced by the $E_1 \leftrightarrow E_2$ interaction EXCEPT, when $\delta\Gamma^2/4 >> V^2$, a narrow level tunes through resonance with a broad level without any significant change in width. BIG SURPRISE!

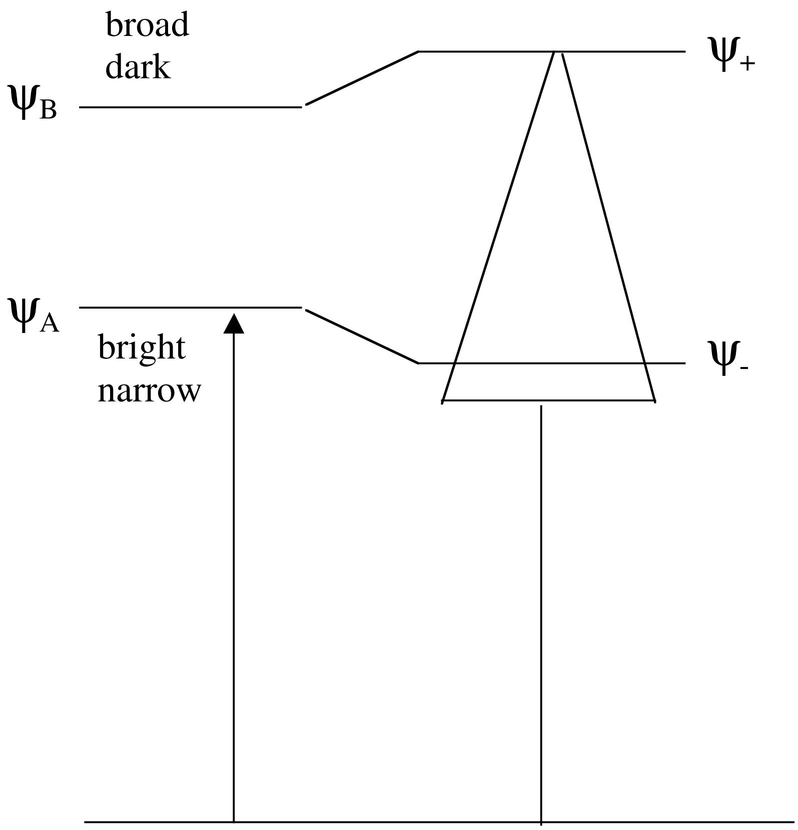


No level repulsion and no width sharing in the weak coupling limit!

The broad level is a doorway state broadened by its interaction with the dark continuum.

When the doorway state becomes broader than the sharp~broad matrix element, the interaction effectively turns off. The doorway state has "dissolved" in the bath.

Quantum Beats: a pair of decaying quasi-eigenstates.



$$I(t) = I_+ e^{-t\Gamma_+/\hbar} + I_- e^{-t\Gamma_-/\hbar} + I_{\text{QB}} e^{-t\Gamma_{\text{QB}}/\hbar} \cos\left(\omega_{\text{QB}} t + \phi_{\text{QB}}\right)$$

solve for I_+, Γ_+, I_-, Γ_-, I_{QB}, Γ_{QB}, ω_{QB}, ϕ_{QB}

$$\Psi(0) = \psi_A = \left|\psi_+\right\rangle \underbrace{\left\langle\tilde{\psi}_+\middle|\psi_1\right\rangle}_{\boxed{\alpha_+}} + \left|\psi_-\right\rangle \underbrace{\left\langle\tilde{\psi}_-\middle|\psi_1\right\rangle}_{\boxed{\alpha_-}}$$

$$\Psi(t) = \alpha_+ \psi_+ e^{-i\varepsilon_+ t/\hbar} e^{-\Gamma_+ t/2\hbar} + \alpha_- \psi_- e^{-i\varepsilon_- t/\hbar} e^{-\Gamma_- t/2\hbar}$$

Intensity of fluorescence

$$I(t) = P_A(t) = \left|\left\langle\tilde{\Psi}_A(0)\middle|\Psi_A(t)\right\rangle\right|^2$$

$$I(t) = P_A(t) = \left(\alpha_+^2 e^{-iE_+ t/\hbar} + \alpha_-^2 e^{-iE_- t/\hbar}\right)\underbrace{\left(\alpha_+^{*2} e^{+iE_+^* t/\hbar} + \alpha_-^{*2} e^{+iE_-^* t/\hbar}\right)}_{\text{take complex conjugate of everything}}$$

$$= |\alpha_+|^4 e^{-\Gamma_+ t/\hbar} + |\alpha_-|^4 e^{-\Gamma_- t/\hbar} + \alpha_+^2\alpha_-^{*2} e^{-i\left(E_+ - E_-^*\right)t/\hbar} + \alpha_-^2\alpha_+^{*2} e^{-i\left(E_- - E_+^*\right)t/\hbar}$$

Expressions for $\alpha_\pm$ are complicated — see HLB-RWF Eq. 9.3.19.

$$= I_+ e^{-\Gamma_+ t/\hbar} + I_- e^{-\Gamma_- t/\hbar} + e^{-\Gamma_{\text{QB}} t/\hbar}\left[2\,\text{Re}\left(\alpha_+^2\alpha_-^{*2}\right)\cos\omega_{\text{QB}}t - 2\,\text{Im}\left(\alpha_+^2\alpha_-^{*2}\right)\sin\omega_{\text{QB}}t\right]$$

$$= I_+ e^{-\Gamma_+ t/\hbar} + I_- e^{-\Gamma_- t/\hbar} + e^{-\Gamma_{QB} t/\hbar}\left[I_{\text{QB}}\cos\left(\omega_{\text{QB}}t + \phi_{\text{QB}}\right)\right]$$

$$I_{\text{QB}} = 2\left|\alpha_+^2\alpha_-^{*2}\right|$$

$$\phi_{\text{QB}} = \tan^{-1}\frac{\text{Im}\left(\alpha_+^2\alpha_-^{*2}\right)}{\text{Re}\left(\alpha_+^2\alpha_-^{*2}\right)}$$

$$\omega_{\text{QB}} = (\varepsilon_+ - \varepsilon_-)/\hbar$$

$$\Gamma_{\text{QB}} = \frac{1}{2}(\Gamma_+ + \Gamma_-) = \overline{\Gamma}$$

$$\alpha_+ = \beta_- = \left(\frac{\mathcal{E} + \delta\epsilon - i\delta\Gamma/2}{2\mathcal{E}}\right)^{1/2} \qquad (9.3.19\text{a})$$

$$\beta_+ = -\alpha_- = \left(\frac{\mathcal{E} - \delta\epsilon + i\delta\Gamma/2}{2\mathcal{E}}\right)^{1/2} \qquad (9.3.19\text{b})$$

Easy to fit $I(t)$ to simple biexponentially decaying term (actually determining both Γ_+ and Γ_- is sometimes difficult) plus a beating term decaying at $\overline{\Gamma}$.

One can tune E_A relative to E_B using $\Delta BJ(J+1)$ or using a magnetic field.

Once can adjust the interaction matrix element using an electric field (ψ_B has the wrong parity for excitation from the ground state).

See Figure 9.10 on the next page.

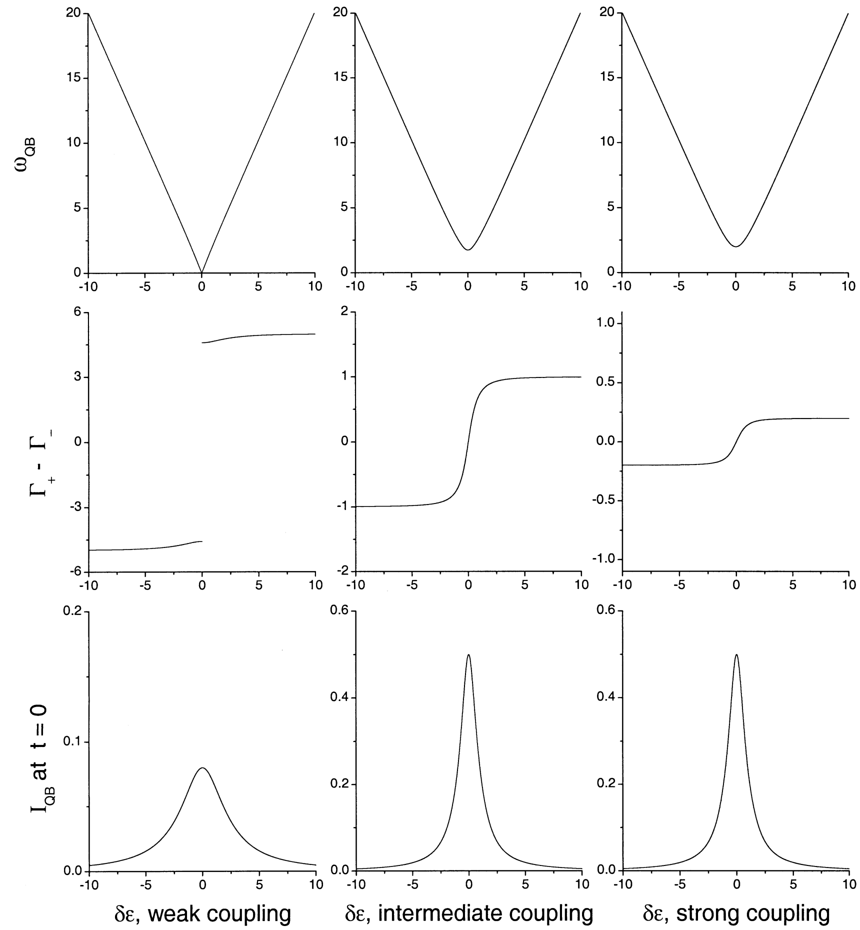


Figure courtesy of Kyle Bittinger. Used with permission.

Figure 9.10. Level Anticrossings between states with complex energies in the strong and weak coupling limits. The quantum beat frequency, ω_{QB}, the difference between the widths of the levels at higher and lower real energy, $\Gamma_+ - \Gamma_-$, and the intensity of the quantum beat, I_{QB}, are plotted vs. the difference between the real part of the zero-order energy, $\delta\varepsilon$, at constant coupling strength (V), for three values of the difference between the imaginary parts of the zero-order energy, dΓ: strong coupling ($V = 5\delta\Gamma$), intermediate coupling ($V = \delta\Gamma$), and weak coupling ($V = \delta\Gamma/5$). Note the use of different vertical scales for the three $\Gamma_+ - \Gamma_-$ and I_{QB} plots. The ω_{QB} plots illustrate the reduction in level repulsion from the strong coupling value of minimum (ω_{QB}) = $2V$ that occurs in the weak coupling limit. That the sharp level tunes, without level repulsion, through the broad level in the weak coupling limit, is illustrated by the linearity of the vee-shaped ω_{QB} curve and the discontinuity in the $\Gamma_+ - \Gamma_-$ curve. The I_{QB} curves illustrate that, in the weak coupling limit, the product of mixing fractions is significantly reduced at the level crossing (dynamical decoupling) but the FWHM of the $I_{QB} = 2\left|\alpha_+^2\alpha_-^{*2}\right|$ mutually-mixed region is increased (figure prepared by Kyle Bittinger).