MIT Department of Chemistry
5.74, Spring 2004: Introductory Quantum Mechanics II
Instructor: Prof. Robert Field

Complex Energy H^{eff}: Nondegenerate Perturbation Theory

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

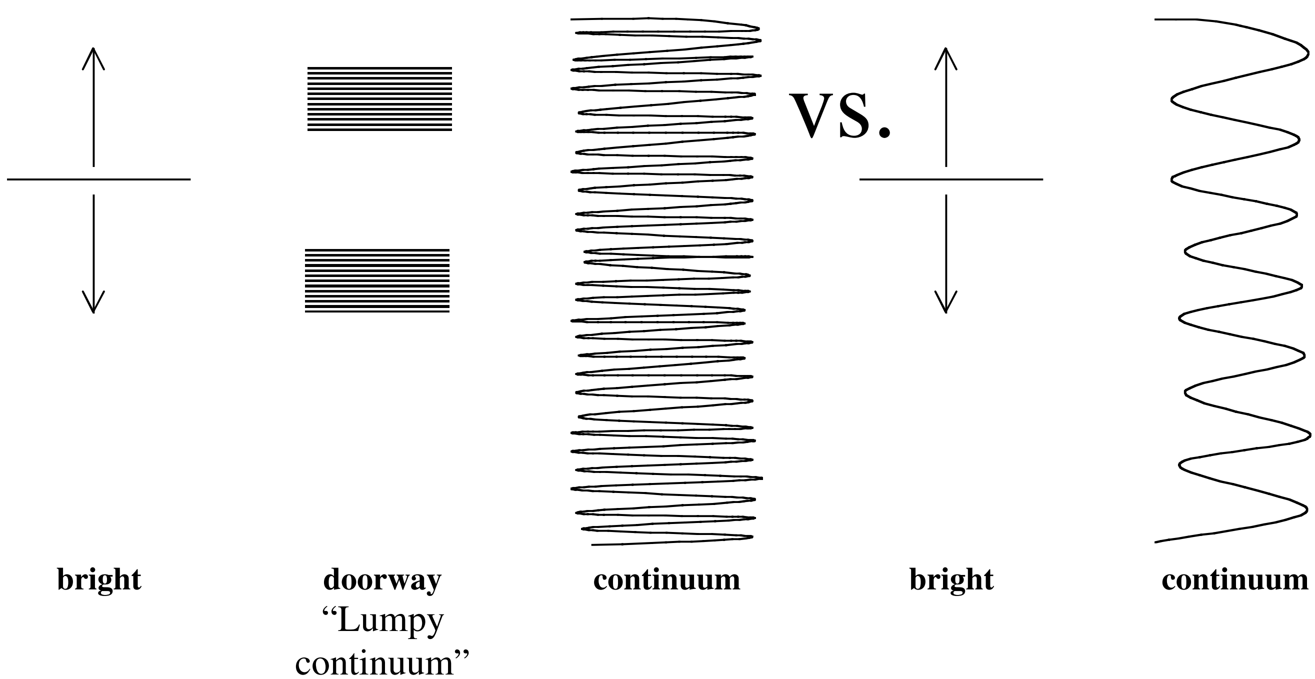
Last time:

$$\left.\begin{array}{c}\text{pure rotation}\\ \text{vibration - rotation}\\ \text{electronic - vibration - rotation}\end{array}\right\}\text{spectra } I(\omega)$$

genuinely localized plucks
grand recurrences

Supplements:
1. Stationary Phase for Vibration and Electronic Transitions (nature of pluck)
2. Heller's Fractionation Measure (inversely proportional to the fraction of state- or phase-space accessed.)

Today:
sharp bright state
broad doorway state
(broad because it couples to the quasi-continuum bath)
reduce many-state interactions to a simple two-level problem.



As the bright state is systematically tuned (perhaps by changing rotational level), it can mix either indirectly or directly with the continuous, dark bath.

Our goal is to find a shortcut for dealing with the interaction between a bright state and a bath, especially via a doorway state.

We can develop an intuitive understanding for a two- or three-level problem much more easily than for a large-dimension random matrix problem. It is also computationally much quicker.

The basis for the idea is, if **H** is time-independent,

$$\Psi_j(\mathbf{Q},t) = \psi_j(\mathbf{Q}) e^{-iE_j t/\hbar}$$

$$\mathbf{H}\psi_j = E_j \psi_j$$

Suppose we allow E_j to be complex?

$$E_j = \varepsilon_j - i\gamma_j/2$$

$$e^{-iE_j t/\hbar} = e^{-i\varepsilon_j t/\hbar} e^{(-i)(-i)(\gamma_j/2)t/\hbar}$$

$$= e^{-i\varepsilon_j t/\hbar} \underbrace{e^{-\gamma_j t/2\hbar}}_{\text{exponential decay}}$$

$$P_j(t) = \langle \Psi_j(t) | \Psi_j(t) \rangle = e^{-\gamma_j t/\hbar} \qquad !$$

(an exponentially decaying population! Should come in handy.)

$$\frac{\hbar}{\gamma} = \tau \text{ or } \gamma = \frac{\hbar}{\tau}$$

γ has units of energy

Width of $P_j(t) = \langle \Psi_j(t) | \Psi_j(t) \rangle$ in energy or cm^{-1}?

Lorentzian $$L(\nu;\nu_0,\Delta\nu) = \frac{1}{\pi} \frac{(\Delta\nu/2)}{(\Delta\nu/2)^2 + (\nu-\nu_0)^2}$$

- * $\Delta\nu$ is FWHM
- * $\int d\nu L(\nu;\nu_0,\Delta\nu) = 1$ normalized to 1
- * $\Delta\nu[\text{cm}^{-1}] = \dfrac{1}{2\pi c\tau}$

FWHM of a Lorentzian line associated with exp. decay of probability with lifetime τ

$$P(t) = e^{-\gamma t/\hbar} \qquad \tau = \frac{\hbar}{\gamma}$$

← units of E

for our case:

$$\text{FWHM}[E] = \frac{\hbar}{\tau} = \gamma$$

We can think of decay rate as a property of a "quasi-eigenstate". We can just tack the decay rate onto the normal $\Psi_j(\mathbf{Q},t)$ without changing anything. Seems to be too good to be true!

One bad thing about allowing $\mathbf{H}^{\text{eff}}$ to have complex energies along the diagonal is that $\mathbf{H}^{\text{eff}}$ is no longer Hermitian. We will soon see the difficulties this causes and how to patch them up.

We would like to use non-degenerate and quasi-degenerate perturbation theory to describe the effects of interactions between states with finite lifetimes. [Decay rates is better concept than lifetimes. **Why**?]

Are decay rates shared between interacting states the way other properties are shared? Let's review what perturbation theory tells us about sharing of properties. Use the Zeeman tuning coefficient (g-value) as the shared property.

Non-degenerate perturbation theory

$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$$

$$E_j = E_j^{(0)} + E_j^{(1)} + E_j^{(2)}$$

$$\mathbf{H}^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$$

$$E_j = \mathbf{H}_{jj}^{(0)} + \mathbf{H}_{jj}^{(1)} + \sum_{k \neq j} \frac{\left|\mathbf{H}_{jk}^{(1)}\right|^2}{E_j^{(0)} - E_k^{(0)}}$$

$$\psi_j = \psi_j^{(0)} + \psi_j^{(1)} = \psi_j^{(0)} + \sum_{k \neq j} \frac{\mathbf{H}_{jk}^{(1)}}{E_j^{(0)} - E_k^{(0)}}\psi_k^{(0)}$$

Not normalized — must at least consider renormalization

$$\mathbf{H}^{\text{Zeeman}} = \mu_{\text{Bohr}} B_z (\mathbf{L}_z + 2\mathbf{S}_z)$$

$$E_j^{\text{Zeeman}} = \langle \psi_j | \mathbf{H}^{\text{Zeeman}} | \psi_j \rangle \big/ \langle \psi_j | \psi_j \rangle$$

$$= \frac{\mu_{\text{Bohr}} B_z}{\underbrace{1 + \sum_{k \neq j} \left(\frac{\mathbf{H}_{jk}^{(1)}}{E_j^{(0)} - E_k^{(0)}} \right)^2}_{\text{renormalization}}} \left[\langle \psi_j^{(0)} | \mathbf{L}_z + 2\mathbf{S}_z | \psi_j^{(0)} \rangle + \sum_{k \neq j} \underbrace{\left(\frac{\mathbf{H}_{jk}^{(1)}}{E_j^{(0)} - E_k^{(0)}} \right)^2}_{\text{mixing fraction}} \langle \psi_k^{(0)} | \mathbf{L}_z + 2\mathbf{S}_z | \psi_k^{(0)} \rangle \right]$$

The sum of a renormalization-corrected zero-order term (nominal character) plus expectation values of $\mathbf{H}^{\text{Zeeman}}$ weighted by the fractional character of each "remote perturber" state (borrowed character). This is exactly what we would expect for sharing of properties other than energy.

What about sharing of decay rates?

$$\mathbf{H} = \mathbf{H}^{(0)} + \mathbf{H}^{(1)}$$

$$\mathbf{H}^{(0)} \left| \psi_j^{(0)} \right\rangle = E_j^{(0)} \left| \psi_j^{(0)} \right\rangle = \left(E_j - i\Gamma_j / 2 \right) \left| \psi_j^{(0)} \right\rangle$$

$\mathbf{H}^{(0)}$ is not Hermitian! $\mathbf{H}^{(1)}$ is Hermitian. It has only real diagonal matrix elements.

The energy denominators from perturbation theory are complex.

$$\frac{1}{E_j^{(0)} - E_k^{(0)}} = \frac{1}{(\varepsilon_j - \varepsilon_k) - i(\Gamma_j - \Gamma_k)/2}$$

rationalize denominator

$$= \frac{(\varepsilon_j - \varepsilon_k)}{(\varepsilon_j - \varepsilon_k)^2 + (\Gamma_j - \Gamma_k)^2/4}$$

real part

$$+ \frac{i(\Gamma_j - \Gamma_k)/2}{(\varepsilon_j - \varepsilon_k)^2 + (\Gamma_j - \Gamma_k)^2/4}$$

imaginary part

This means that the borrowing and lending of decay rate follows the usual perturbation theory form, except for two subtle modifications, one in the numerator and one in the denominator. There is also a hidden surprise that can only be explored when ordinary, non-degenerate perturbation theory is invalid: $\left| \frac{\mathbf{H}_{jk}^{(1)}}{E_j^{(0)} - E_k^{(0)}} \right| > 1$.

Return to non-degenerate perturbation theory.

Real part:

Level shift $$\delta\varepsilon_j = \sum_{k \neq j} \frac{\left|\mathbf{H}_{jk}^{(1)}\right|^2 (\varepsilon_j - \varepsilon_k)}{(\varepsilon_j - \varepsilon_k)^2 + (\Gamma_j - \Gamma_k)^2 / 4}$$

* if $\varepsilon_j > \varepsilon_k$ *j*-th level gets pushed up as expected

* if $\varepsilon_j = \varepsilon_k$ (and, to stay in the non-degenerate perturbation theory limit, $\left|\mathbf{H}_{jk}^{(1)} / (\Gamma_j - \Gamma_k)/2\right| << 1$), then *there is no level shift at all* (surprise!)

* if $|\varepsilon_j - \varepsilon_k| >> |(\Gamma_j - \Gamma_k)/2|$, then a Taylor series expansion gives

$$\delta\varepsilon_j = \underbrace{\frac{\left|\mathbf{H}_{jk}^{(1)}\right|^2}{\varepsilon_j - \varepsilon_k}}_{\text{usual term}} \left\{1 - \underbrace{\left[\frac{(\Gamma_j - \Gamma_k)/2}{\varepsilon_j - \varepsilon_k}\right]^2}_{\text{reduced level repulsion}}\right\}.$$

Imaginary part:

Decay rate change $$\delta\Gamma_j = -\sum_{k \neq j} \frac{\left|\mathbf{H}_{jk}^{(1)}\right|^2 (\Gamma_j - \Gamma_k)/2}{(\varepsilon_j - \varepsilon_k)^2 + (\Gamma_j - \Gamma_k)^2 / 4}$$

* if $\Gamma_j > \Gamma_k$ (level-*k* decays more slowly than level-*j*) the decay rate of level-*j* is reduced (it lends decay rate to level-*k*). The *decay rates of levels j and k become more nearly equal.*

* if $\Gamma_j = \Gamma_k$ (and $\left|\frac{\mathbf{H}_{jk}^{(1)}}{\varepsilon_j - \varepsilon_k}\right| << 1$), then *there is no change of decay rate* (surprise!)

* if $|\Gamma_j - \Gamma_k|/2 >> |\varepsilon_j - \varepsilon_k|$

$$\delta\Gamma_j = -\sum_{k \neq j} \frac{\mathbf{H}_{jk}^{(1)}}{(\Gamma_j - \Gamma_k)/2}\left[1 - \underbrace{\left(\frac{\varepsilon_j - \varepsilon_k}{(\Gamma_j - \Gamma_k)/2}\right)^2}_{\text{reduced decay rate attraction}}\right].$$

So part of this non-degenerate perturbation theory model seems reasonable, but there are some surprises. The surprises are most prominent when

$$\left|\frac{\mathbf{H}_{jk}^{(1)}}{E_j^{(0)} - E_k^{(0)}}\right| > 1$$

for which we must use quasi-degenerate perturbation theory. This is an algebraic nightmare, even in the $\Gamma = 0$ situation.

Recall

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

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

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

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

(CTDL, page 407)

$$\mathbf{H}_{AB} = |\mathbf{H}_{AB}| e^{-i\phi}$$

$$|\psi_+\rangle = \cos\theta/2\, e^{-i\phi/2} |\psi_A\rangle + \sin\theta/2\, e^{i\phi/2} |\psi_B\rangle$$

$$|\psi_-\rangle = -\sin\theta/2\, e^{-i\phi/2} |\psi_A\rangle + \cos\theta/2\, e^{i\phi/2} |\psi_B\rangle$$

$$\tan\theta = \frac{2|\mathbf{H}_{AB}|}{E_A - E_B} \qquad 0 \le \theta < \pi$$

$$\theta = \tan^{-1}\left(\frac{2|\mathbf{H}_{AB}|}{E_A - E_B}\right)$$

more explicitly (Herzberg, page 283)

$$\cos\theta/2 = \left[\frac{\delta E + (E_A - E_B)/2}{2\delta E}\right]^{1/2}$$

$$\sin\theta/2 = \left[\frac{\delta E - (E_A - E_B)/2}{2\delta E}\right]^{1/2}$$

verify that $|\psi_+\rangle$ belongs to $E_+ > E_-$ (you should always do this when using borrowed, rather than derived, equations).

$$\langle\psi_+|\mathbf{H}|\psi_+\rangle = \cos^2\theta/2\,\mathbf{H}_{AA} + \sin^2\theta/2\,\mathbf{H}_{BB} + e^{i\theta}\mathbf{H}_{AB}\cos\theta/2\sin\theta/2 + e^{-i\theta}\mathbf{H}_{BA}\cos\theta/2\sin\theta/2$$

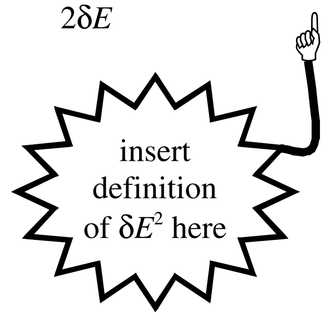
$$= \cos^2\theta/2\,E_A + \sin^2\theta/2\,E_B + 2|\mathbf{H}_{AB}|\cos\theta/2\sin\theta/2$$

$$= \frac{E_A[\delta E + (E_A - E_B)/2]}{2\delta E} + \frac{E_B[\delta E - (E_A - E_B)/2]}{2\delta E} + 2|\mathbf{H}_{AB}|\frac{\left(\delta E^2 - (E_A - E_B)^2/4\right)^{1/2}}{2\delta E}$$

$$= \frac{\delta E(E_A + E_B) + E_A^2/2 - E_A E_B + E_B^2/2 + 2|\mathbf{H}_{AB}|^2}{2\delta E}$$

$$= \frac{\delta E(E_A + E_B) + (E_A - E_B)/2 + 2|\mathbf{H}_{AB}|^2}{2\delta E}$$

$$= \frac{\delta E(E_A + E_B) + 2\delta E^2}{2\delta E} = \frac{E_A - E_B}{2} + \delta E = E_+$$



Confirmed. Regardless of sign of $\mathbf{H}_{AB}$ and $(E_A - E_B)$, $\mathbf{H}|\psi_+\rangle = E_+|\psi_+\rangle$.

Now we are ready to try to solve for $E_\pm$, $|\psi_\pm\rangle$ using an **H** that has complex diagonal elements.

But we also have to worry about a big problem!

If we use perturbation theory to define $\psi_j = \psi_j^{(0)} + \psi_j^{(1)}$, then ψ_j and ψ_k are not orthogonal!

Consider a 2-state basis set, $|\psi_A\rangle$ and $|\psi_B\rangle$, and let $\mathbf{H}_{AB}$ be real.

$$\left|\psi_A\right\rangle = N\left[\left|\psi_A^{(0)}\right\rangle + \frac{\mathbf{H}_{AB}}{(\varepsilon_A-\varepsilon_B)-i(\Gamma_A-\Gamma_B)/2}\left|\psi_B^{(0)}\right\rangle\right]$$

$$\left\langle\psi_A\middle|\psi_A\right\rangle = |N_A|^2\left[1+\frac{\mathbf{H}_{AB}^2}{(\varepsilon_A-\varepsilon_B)^2-i(\Gamma_A-\Gamma_B)^2/4}\right]$$

$$|N_A| = \left[\frac{(\varepsilon_A-\varepsilon_B)^2+(\Gamma_A-\Gamma_B)^2/4}{\mathbf{H}_{AB}^2+(\varepsilon_A-\varepsilon_B)^2+(\Gamma_A-\Gamma_B)^2/4}\right]^{1/2}$$

$$\left\langle\psi_B\middle|\psi_B\right\rangle = |N_B|^2\left[1+\frac{\mathbf{H}_{AB}^2}{(\varepsilon_B-\varepsilon_A)^2+(\Gamma_B-\Gamma_A)^2/4}\right]$$

$$|N_A| = |N_B|$$

$$\begin{aligned}\left\langle\psi_A\middle|\psi_B\right\rangle &= |N_A|^2\left[\frac{\mathbf{H}_{BA}}{(\varepsilon_B-\varepsilon_A)-i(\Gamma_B-\Gamma_A)/2}+\frac{\mathbf{H}_{BA}}{(\varepsilon_A-\varepsilon_B)+i(\Gamma_A-\Gamma_B)/2}\right]\\ &= |N_A|^2\mathbf{H}_{BA}\left[\frac{1}{(\varepsilon_B-\varepsilon_A)-i(\Gamma_B-\Gamma_A)/2}-\frac{1}{(\varepsilon_B-\varepsilon_A)+i(\Gamma_B-\Gamma_A)/2}\right]\\ &= |N_A|^2\mathbf{H}_{BA}\,\frac{i(\Gamma_B-\Gamma_A)}{(\varepsilon_B-\varepsilon_A)^2+(\Gamma_B-\Gamma_A)^2/4}\neq 0!\end{aligned}$$

The usual orthogonality integral is not 0 and is pure imaginary. Something is wrong! Cannot use either orthogonality or completeness to expand $\left|\psi_j^{(1)}\right\rangle$. So we cannot use the results of ordinary non-degenerate perturbation theory without a correction.

The concept of "biorthogonality" saves us.

When **H** is not Hermitian, $|\psi_i\rangle$ are eigenfunctions of **H** in the sense $\mathbf{H}\,|\psi_i\rangle = E_i\,|\psi_i\rangle$

but $\langle\tilde{\psi}_i|$ are the conjugate transpose of $|\tilde{\psi}_i\rangle$, which are eigenfunctions of **H*** in the sense

$$\mathbf{H}^*\left|\tilde{\psi}_i\right\rangle = E_i^*\left|\tilde{\psi}_i\right\rangle \;\; !$$