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

Visualizing IVR.

[*Chem. Phys. Lett.* 320, 553 (2000)]

Readings:	Chapter 9.4.9 and 9.4.10, *The Spectra and Dynamics of Diatomic Molecules*, H. Lefebvre-Brion and R. Field, 2nd Ed., Academic Press, 2004.

Last time:

Looking for causes of dynamics

$$\frac{d}{dt}\langle \mathbf{A} \rangle = \frac{1}{i\hbar}\langle [\mathbf{A},\mathbf{H}] \rangle$$

$$\frac{d^2}{dt^2}\langle \mathbf{A} \rangle = \left(\frac{1}{i\hbar}\right)^2 \langle [[\mathbf{A},\mathbf{H}],\mathbf{H}] \rangle$$

discussed 3 mode, 2 resonance model (H_2O)

derived many operator relationships for $\langle \mathbf{N}_j \rangle$ found that the cause of $\frac{d}{dt}\langle \mathbf{N}_j \rangle$ is transfer rate operators

# of quanta changed

e.g. $$\frac{d}{dt}\langle \mathrm{N}_2 \rangle = \frac{2}{i\hbar}\langle \mathbf{\Omega}_2 - \mathbf{\Omega}_2^\dagger \rangle$$

$k'_{11,33}\mathbf{a}_1^2\mathbf{a}_3^{\dagger 2}$ $\qquad$ $k'_{1,22}\mathbf{a}_1\mathbf{a}_2^{\dagger 2}$

$$\mathbf{H}^{(1)} = \left(\mathbf{\Omega}_1 + \mathbf{\Omega}_1^\dagger\right) + \left(\mathbf{\Omega}_2 + \mathbf{\Omega}_2^\dagger\right)$$

<u>The Two-Level Problem Again</u>

$$\mathbf{H} = \begin{pmatrix} \overline{E} & 0 \\ 0 & \overline{E} \end{pmatrix} + \begin{pmatrix} \delta E & 0 \\ 0 & -\delta E \end{pmatrix} + \mathbf{\Omega} + \mathbf{\Omega}^{\dagger}$$

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

$$\mathbf{\Omega} = \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} \qquad \mathbf{\Omega}^{\dagger} = \begin{pmatrix} 0 & 0 \\ V* & 0 \end{pmatrix}$$

We are going to let V be real

Suppose our pluck at $t = 0$ is ψ_A

$$|\Psi(0)\rangle = |\mathbf{A}\rangle = \cos\theta/2\ |+\rangle - \sin\theta/2\ |-\rangle$$

verify by plugging in

$$|+\rangle = \cos\theta/2|A\rangle + \sin\theta/2|B\rangle$$
$$|-\rangle = -\sin\theta/2|A\rangle + \cos\theta/2|B\rangle$$

$$\Psi(0)\rangle = \cos^2\theta/2\ A\rangle + \cos\theta/2\sin\theta/2\ B\rangle + \sin^2\theta/2\ A\rangle - \cos\theta/2\sin\theta/2\ B\rangle$$
$$= \left(\cos^2\theta/2 + \sin^2\theta/2\right) A\rangle.$$

✓ checks

Now put in t-dependence:

$$\Psi(0)\rangle = \cos\theta/2\, e^{-iE_+ t/\hbar}\ +\rangle - \sin\theta/2\, e^{-iE_- t/\hbar}\ -\rangle$$

in the +,– basis and

$$\Psi(t)\rangle = \cos\theta/2\, e^{-iE_+ t/\hbar}\left(\cos\theta/2\ A\rangle + \sin\theta/2\ B\rangle\right)$$
$$-\sin\theta/2\, e^{-iE_- t/\hbar}\left(-\sin\theta/2\ A\rangle + \cos\theta/2\ B\rangle\right)$$
$$= \left(\cos^2\theta/2\, e^{-iE_+ t/\hbar} + \sin^2\theta/2\, e^{-iE_- t/\hbar}\right) A\rangle$$
$$+\cos\theta/2\sin\theta/2\left(e^{-iE_+ t/\hbar} - e^{-iE_- t/\hbar}\right) B\rangle$$

$$E_{\pm} = E \pm \Delta$$
$$\Delta = \left[\delta E^2 + V^2\right]^{1/2}$$
$$\cos\theta/2 = \left[\frac{\Delta + \delta E}{2\Delta}\right]^{1/2} \qquad \sin\theta/2 = \left[\frac{\Delta - \delta E}{2\Delta}\right]^{1/2}$$

Let us ask several questions for this maximally simple problem that will give us insights into the relationships between observable properties and the fundamental control parameters in $\mathbf{H}^{\text{eff}}$.

1. $\langle \mathbf{H} \rangle \equiv \overline{E}$ is independent of t and $\overline{E} = E_A$ if $|\Psi(0)\rangle = |A\rangle$. This is going to tell us how to measure the energy of a zero-order state.

2. What is $\langle \mathbf{H}^{\text{diag}} \rangle_t = E_{\text{diag}}(t)$

   $\langle \mathbf{H}^{\text{res}} \rangle_t = \langle \mathbf{\Omega} + \mathbf{\Omega}^{\dagger} \rangle_t = E_{\text{res}}(t)$?

   And what do $E_{\text{diag}}(t)$ and $E_{\text{res}}(t)$ tell us?

Evaluate $\langle \mathbf{H} \rangle$.

We can evaluate this in either the $|A\rangle$, $|B\rangle$, or $|+\rangle$, $|-\rangle$ basis set.

In the A,B basis set

$$\begin{aligned}\boldsymbol{\rho}(t) = &\left[\cos^4\theta/2 + \sin^4\theta/2 + \cos^2\theta/2\sin^2\theta/2(\ \cos\omega_{+-}t)\right]|A\rangle\langle A| \\ &+\left[\cos^2\theta/2\sin^2\theta/2(2 - 2\cos\omega_{+-}t)\right]|B\rangle\langle B| \\ &+\left[\cos^3\theta/2\sin\theta/2\left(1 - e^{-i\omega_{+-}t}\right) + \cos\theta/2\sin^3\theta/2\left(e^{+i\omega_{+-}t} - 1\right)\right]|A\rangle\langle B| \\ &+\left[\cos^3\theta/2\sin\theta/2\left(1 - e^{+i\omega_{+-}t}\right) + \cos\theta/2\sin^3\theta/2\left(e^{-i\omega_{+-}t} - 1\right)\right]|B\rangle\langle A|\end{aligned}$$

simplify

$$\begin{aligned}\boldsymbol{\rho}(t) = &\left[1 - \frac{V^2}{2\left(V^2 + \delta E^2\right)}(1 - \cos\omega_{+-}t)\right]|A\rangle\langle A| \\ &+\left[\frac{V^2}{2\left(V^2 + \delta E^2\right)}(1 - \cos\omega_{+-}t)\right]|B\rangle\langle B| \\ &+\left[\frac{V\delta E}{2\left(V^2 + \delta E^2\right)}(1 - \cos\omega_{+-}t) + \frac{iV\sin\omega_{+-}t}{2\left[V^2 + \delta E^2\right]^{1/2}}\right]|A\rangle\langle B| \\ &+\left[\frac{V\delta E}{2\left(V^2 + \delta E^2\right)}(1 - \cos\omega_{+-}t) - \frac{iV\sin\omega_{+-}t}{2\left[V^2 + \delta E^2\right]^{1/2}}\right]|B\rangle\langle A|\end{aligned}$$

in the +,– basis

$$\boldsymbol{\rho}(t) = \cos^2\theta/2|+\rangle\langle+| + \sin^2\theta/2|-\rangle\langle-|$$
$$-\sin\theta/2\cos\theta/2\, e^{-i\omega_{+-}t}|+\rangle\langle-|$$
$$-\sin\theta/2\cos\theta/2\, e^{+i\omega_{+-}t}|-\rangle\langle+|$$
$$= \left(\frac{\Delta+\delta E}{2\Delta}\right)|+\rangle\langle+| + \left(\frac{\Delta-\delta E}{2\Delta}\right)|-\rangle\langle-|$$
$$-\left(\frac{\Delta^2-\delta E^2}{4\Delta^2}\right)^{1/2}\left[e^{-i\omega_{+-}t}|+\rangle\langle-| + e^{+i\omega_{+-}t}|-\rangle\langle+|\right]$$

Want $\langle\mathbf{H}\rangle_t = \text{Trace}(\boldsymbol{\rho}H) = \sum_{j,k} \boldsymbol{\rho}_{jk}\mathbf{H}_{kj}$

$$= \boldsymbol{\rho}_{11}\mathbf{H}_{11} + \underbrace{\boldsymbol{\rho}_{12}\mathbf{H}_{21} + \boldsymbol{\rho}_{21}\mathbf{H}_{12}} + \boldsymbol{\rho}_{22}\mathbf{H}_{22}$$

= 0 in +,– basis
because $\mathbf{H}_{21} = \mathbf{H}_{12} = 0$

in the +,– basis

$$\langle\mathbf{H}\rangle_t = \left(\frac{\Delta+\delta E}{2\Delta}\right)E_+ + \left(\frac{\Delta-\delta E}{2\Delta}\right)E_-$$

$$E_\pm = \overline{E} \pm \Delta$$

$$\langle\mathbf{H}\rangle_t = \frac{2\Delta}{2\Delta}\overline{E} + \frac{2\delta E\Delta}{2\Delta} = \overline{E} + \delta E = E_A!$$

So we have our first really important result. If you know your pluck perfectly, then, for any **H**,

$\langle\mathbf{H}\rangle_t = E_{\text{pluck}}$ independent of time.

To determine the energy of the plucked zero-order state, simply measure the intensity weighted average energy in the absorption spectrum.

Now let us divide $\mathbf{H}$ into $\mathbf{H}^{\text{diag}}$ and $\mathbf{H}^{\text{res}} = \mathbf{\Omega} + \mathbf{\Omega}^{\dagger}$

$$E_{\text{diag}}(t) = \left\langle \mathbf{H}^{\text{diag}} \right\rangle_t$$

$$E_{\text{res}}(t) = \left\langle \mathbf{\Omega} + \mathbf{\Omega}^{\dagger} \right\rangle_t$$

of course $\overline{E} = E_{\text{diag}}(t) + E_{\text{res}}(t)$ must be independent of t, but E_{diag} and E_{res} are certainly time-dependent.

For our $|\Psi(0)\rangle = |A\rangle$ pluck of a two-level system, we want to express both $\mathbf{H}$ and $\boldsymbol{\rho}$ in the A, B Basis set.

$$\begin{aligned}
\boldsymbol{\rho}(t) = & \left[1 - \frac{V^2}{2(V^2 + \delta E^2)}(1 - \cos\omega_{+-}t)\right]|A\rangle\langle A| \\
& + \left[\frac{V^2}{2(V^2 + \delta E^2)}(1 - \cos\omega_{+-}t)\right]|B\rangle\langle B| \\
& + \left[\frac{V\delta E}{2(V^2 + \delta E^2)}(1 - \cos\omega_{+-}t) + \frac{iV\sin\omega_{+-}t}{2\left[V^2 + \delta E^2\right]^{1/2}}\right]|A\rangle\langle B| \\
& + \left[\frac{V\delta E}{2(V^2 + \delta E^2)}(1 - \cos\omega_{+-}t) - \frac{iV\sin\omega_{+-}t}{2\left[V^2 + \delta E^2\right]^{1/2}}\right]|B\rangle\langle A|
\end{aligned}$$

Thus

$$\left\langle \mathbf{H}^{\text{diag}} \right\rangle_t = \text{Trace } \boldsymbol{\rho}\mathbf{H}^{\text{diag}} = \boldsymbol{\rho}_{AA}\mathbf{H}^{\text{diag}}_{AA} + \boldsymbol{\rho}_{BB}\mathbf{H}^{\text{diag}}_{BB}$$

$$= \boldsymbol{\rho}_{AA} \overset{\bar{E}+\delta E}{E_A} + \boldsymbol{\rho}_{BB} \overset{\bar{E}-\delta E}{E_B} = (\boldsymbol{\rho}_{AA} + \boldsymbol{\rho}_{BB})\bar{E} + (\boldsymbol{\rho}_{AA} - \boldsymbol{\rho}_{BB})\delta E$$

$$= \bar{E} - \frac{V^2 \delta E}{V^2 + \delta E^2}(1 - \cos\omega_{+-}t) + \delta E$$

$$\left(\text{at } t = 0 \qquad \left\langle \mathbf{H}^{\text{diag}} \right\rangle = \bar{E} + \delta E = E_A \right)$$

$$\left\langle \mathbf{H}^{\text{res}} \right\rangle_t = \boldsymbol{\rho}_{AB}\mathbf{H}_{BA} + \boldsymbol{\rho}_{BA}\mathbf{H}_{AB}$$

$$= \frac{V^2 \delta E}{V^2 + \delta E}(1 - \cos\omega_{+-}t)$$

$$\left(\text{at } t = 0 \qquad \left\langle \mathbf{H}^{\text{res}} \right\rangle_t = 0 \right)$$

$$\left\langle \mathbf{H}^{\text{diag}} \right\rangle_t + \left\langle \mathbf{H}^{\text{res}} \right\rangle_t = \bar{E} + \delta E = E_A$$

In a more general situation, when there are several resonances, we have a polyad $\mathbf{H}^{\text{eff}}$ that is larger than 2×2, we need help sorting out which resonance is most important for the post-pluck dynamics of each conceivable pluck.

See HLB-RWF Chapter 9.4.10 and *Chem. Phys. Lett*. **320**, 553 (2000).

Let $E_{\text{res}}(t) = \sum_{j} \left\langle \mathbf{\Omega}_j + \mathbf{\Omega}_j^{\dagger} \right\rangle$

(↑ sum over resonances)

we still have $E = E_{\text{diag}}(t) + \sum_{\text{j}} E_{\text{res},j}(t)$

two useful quantities:

$$\overline{E_{\text{res},j}} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \left(\left\langle \mathbf{\Omega}_k + \mathbf{\Omega}_k^{\dagger} \right\rangle \right)$$

and fractional importance, for a specific pluck, of the j-th resonance

$$f_j = \left| \frac{\overline{E}_{\text{res},j}}{\overline{E}_{\text{res}}} \right|$$

What do we do with $E_{\text{res},j}$, $\overline{E_{\text{res},j}}$, and f_j?

We attempt to correlate what we see in the spectrum to the various resonance terms that could cause the observed effects.

We look for a pluck which is maximally sensitive to one particular resonance term.

In order to do this, we need a working model for $\mathbf{H}^{\text{eff}}$. We then use insights guided by the resonance operator dynamics.

See **Figure 9.11**. The survival probability of the plucked state is directly observable because it is the F. T. of the pluck-related piece of the spectrum. The dynamical features in the survival probability encode Fourier components and amplitudes associated with each of the dynamically important resonance operators. We want to know what causes each of the dynamical features present in any do-able experiment.

Strategy: use computed simple dynamical quantities to sharpen up correspondences with observable dynamical features.

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