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5.80 Small-Molecule Spectroscopy and Dynamics  
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# Lectures # 35 & 36: Wavepacket Dynamics II and III

An eigenstate does not move and the population in an eigenstate does not decay.

Quantum Beats: polarization vs. population.

Concept of “bright” and “dark” states

Nonradiative decay

into dense manifold of dark states

Fermi’s Golden Rule

Bixon-Jortner

into continuum: Complex  $\mathbf{H}^{\text{eff}}$  (SDDM, pages 671-683)

Dynamical Quantities

some are in real coordinate/momentum space

others are in state space

key is to reduce the quantity of information from what is contained

in  $\Psi(t)$  yet retain visibility that

\* reveals mechanism

\* suggests experiments

examples

\* probability density

\* density matrix

\* autocorrelation function

\* survival probability

\* transfer probability

\*  $\langle Q_i \rangle(t)$ ,  $\langle P_i \rangle(t)$  Ehrenfest’s Theorem

\*  $\langle E_i \rangle = \omega_i \langle \mathbf{a}_i^\dagger \mathbf{a}_i \rangle(t)$  OR anharmonic

$\langle v_i \rangle = \langle \mathbf{a}_i^\dagger \mathbf{a}_i \rangle(t)$

\* expectation values of resonance and transfer rate operators (SDDM, pages 694-701) .

It is also possible to go from a Quantum Mechanical  $\mathbf{H}^{\text{eff}}$  to a Classical Mechanical  $\mathcal{H}^{\text{eff}}$  and view structure and dynamics in an action-angle representation of phase space. Regular (quasi-periodic trajectories) and Chaotic regions of classical phase space.

An eigenstate  $\psi_j$ ,  $\Psi_j(t) = \psi_j e^{-iE_j t/\hbar}$ , from a harmonic oscillator potential surface

$$\langle \Psi_j(t) | \mathbf{Q} | \Psi_j(t) \rangle = \langle \psi_j | \mathbf{Q} | \psi_j \rangle = 0$$

because  $\mathbf{Q}$  is  $\Delta v = \pm 1$  off-diagonal.

Suppose  $\psi_j = \alpha \phi_v^0 + (1 - \alpha^2)^{1/2} \phi_{v+1}^0$  (a vibrationally mixed state)

$$\langle \psi_j | \mathbf{Q} | \psi_j \rangle = 2\alpha(1 - \alpha^2)^{1/2} \underbrace{\langle v+1 | \mathbf{Q} | v \rangle}_{\propto (v+1)^{1/2}} \neq 0.$$

Still no motion. Also

$$P_j = \langle \Psi_j(t) | \Psi_j(t) \rangle = \langle \psi_j | \psi_j \rangle = 1$$

does not decay.

Suppose, using a short pulse of radiation, we excite a coherent superposition of two eigenstates,  $\psi_j$  and  $\psi_k$ . Then

$$\begin{aligned} \Psi(0) &= \alpha \psi_j + (1 - \alpha^2)^{1/2} \psi_k \equiv \phi_B^0 \\ \Psi(t) &= \alpha \psi_j e^{-iE_j t/\hbar} + (1 - \alpha^2)^{1/2} \psi_k e^{-iE_k t/\hbar} \\ \Psi^*(t) \Psi(t) &= |\alpha|^2 |\psi_j|^2 + |1 - \alpha^2| |\psi_k|^2 \\ &\quad + \alpha^* \psi_j^* (1 - \alpha^2)^{1/2} \psi_k e^{-i(E_k - E_j)t/\hbar} + c.c. \\ &= |\alpha|^2 |\psi_j|^2 + |1 - \alpha^2| |\psi_k|^2 + \alpha^* (1 - \alpha^2)^{1/2} \psi_j^* \psi_k e^{-i\omega_{kj} t} + c.c. \\ &= |\alpha|^2 |\psi_j|^2 + |1 - \alpha^2| |\psi_k|^2 + 2\text{Re} [\alpha^* (1 - \alpha^2)^{1/2} \psi_j^* \psi_k] \cos \omega_{kj} t \\ &\quad + 2\text{Im} [\alpha^* (1 - \alpha^2)^{1/2} \psi_j^* \psi_k] \sin \omega_{kj} t. \end{aligned}$$

We have a constant term and two oscillating terms. More insight is obtained if we ask for the time dependent probability of finding the system in  $\Psi(0) \equiv \phi_B^0$

$$\begin{aligned} P_B(t) &= |\langle \Psi(t) | \phi_B^0 \rangle|^2 = |\langle \Psi(t) | \Psi(0) \rangle|^2 \\ &= \langle \Psi(t) | \Psi(0) \rangle \langle \Psi(0) | \Psi(t) \rangle \\ &= [|\alpha|^2 e^{-iE_j t/\hbar} + |1 - \alpha^2| e^{-iE_k t/\hbar}] [|\alpha|^2 e^{iE_j t/\hbar} + |1 - \alpha^2| e^{iE_k t/\hbar}] \\ &= |\alpha|^4 + |1 - \alpha^2|^2 + |\alpha|^2 |1 - \alpha^2| (e^{i\omega_{kj} t} + e^{-i\omega_{kj} t}) \\ &= (1 + 2|\alpha|^4 - 2|\alpha|^2) + 2|\alpha|^2 |1 - \alpha^2| \cos \omega_{kj} t. \end{aligned}$$

The time dependent term is largest when  $\alpha = 2^{-1/2}$ , then

$$P_B(t) = \frac{1}{2}(1 + \cos \omega_{kj} t),$$

which oscillates sinusoidally between 1 (at  $t = 0, \frac{2\pi}{\omega_{kj}}, \frac{4\pi}{\omega_{kj}} \dots$ ) and 0 (at  $t = \frac{\pi}{\omega_{kj}}, \frac{3\pi}{\omega_{kj}}, \dots$ ).

Note that  $P_B(0) = 1$ , as it must be because it is the bright state that is initially populated. The modulation depth of the quantum beat is less than 100% when the mixing between bright and dark states is less than 50/50. For a simple 2-level QB it is always true that  $P(0) = 1$ . However, if you have *two* bright or *partially* bright basis states, the QB might be phase-shifted from a maximum at  $t = 0$ .

Polarization beats result when a  $\Delta M \neq 0$  coherence is produced. As a result, the angular distribution of the fluorescence is time-dependent.

Population beats result when one bright state and one dark zero-order state perturb each other. The beating is metaphorically the population flowing out of the bright state and back in again.

Problem for the class: suppose you know the radiative decay rates for  $\phi_{\text{Bright}}^0$  and  $\phi_{\text{Dark}}^0$ . What would be the decay behavior of the constant and modulated parts of the quantum beating  $I(t)$  signal?

## Non-radiative decay

For an absorption transition between two eigenstates, there is a definite relationship between the absorption cross-section and the zero-pressure radiative lifetime. In the 1960's, there was a lot of controversy about why (i) the fluorescence decay rates were faster than calculated from the absorption cross-section and (ii) the fluorescence quantum yield was smaller than unity. Predissociation and autoionization can be ruled out by thermodynamics. Is the observed effect due to extremely efficient collisional quenching or to some other phenomenon? Bixon and Jortner explained how a non-fragmenting, non-quenched molecular excited population can decay non-radiatively. They constructed a simple model of one bright state interacting with a manifold of equally spaced dark states.

Fermi's golden rule relates the decay rate to the density of states and the average squared matrix element between the bright state and the manifold of dark states.

Another way of understanding non-radiative decay is to allow the diagonal elements of an  $\mathbf{H}^{\text{eff}}$  to be complex.

$$\begin{aligned}\Psi_j(t) &= \psi_j e^{-iH_{jj}t/\hbar} \\ H_{jj} &= E_j - i\Gamma_j/2 \\ \Psi_j^*(t)\Psi_j(t) &= |\psi_j|^2 [e^{(+iE_j - \Gamma/2)t/\hbar} e^{(-iE_j - \Gamma/2)t/\hbar}] \\ &= |\psi_j|^2 e^{-\Gamma t/\hbar}\end{aligned}$$

where the lifetime is

$$\tau = \hbar/\Gamma.$$

See SDDM, pages 672-683 for non-degenerate and degenerate perturbation theory with complex  $\mathbf{H}^{\text{eff}}$  models.

Key is that a dark quasi-continuum (many discrete non-decaying eigenstates) may be lumped into one broad ( $\Gamma > 0$ ) super-eigenstate. This allows the interaction of one bright state with a manifold of many dark states to be reduced to a slightly non-standard two-level problem.

A key insight is a bifurcation of the dynamics that occurs when  $(\Gamma_k - \Gamma_j)/2 > |H_{kj}|$ .  
 strong-coupling: maps onto the ordinary two-level problem  
 weak-coupling: the sharp state can tune through the broader “state” without level shift or broadening.

## Goals of a Frequency Domain Experiment: First determine and then use the $\mathbf{H}^{\text{eff}}$

1. Use information in the spectrum to determine the parameters that define the  $\mathbf{H}^{\text{eff}}$ .

This is the usual first step. When the  $\mathbf{H}^{\text{eff}}$  model used is not sufficiently flexible to fit the spectrum, it is necessary to add local (perturbation) or global (polyad) interaction terms to  $\mathbf{H}^{\text{eff}}$ .

Sometimes mini-experiments (e.g. quantum beat, pair of “main” and “extra” relative intensity measurements) yield local determinations of specific parameters in  $\mathbf{H}^{\text{eff}}$ .

2. Once  $\mathbf{H}^{\text{eff}}$  is determined from the spectrum, (i) find out something not already known about stable large amplitude motions and dominant energy flow pathways; (ii) or discover unconventional diagnostics for the nature of an unknown state or unspecified pluck.

The key tool is the ability to select a variety of classes of “bright state.” The various dynamical measures, based on a *fitted but not fully understood*  $\mathbf{H}^{\text{eff}}$ , reveal the emergence and nature of new classes of local motions, dominant energy flow pathways, diagnostic patterns in a spectrum, schemes for designing an “optimal pluck” to gain access to a designed region of state space, or rational external control over dynamics. Examples: appearance of local modes, regular vs. ergodic dynamics, best design of an experiment (which bright state, optimal timing).

Now for a quick sprint through many dynamical quantities. For the initial state, denoted by  $I$  (not to be confused with the interaction representation),

$$\Psi_I(0) = \sum_j a_j \psi_j \quad \text{where } \{\psi_j\} \text{ are eigenstates and } \{E_j\} \text{ are eigenvalues of } \mathbf{H}$$

$$\Psi_I(t) = \sum_j a_j \psi_j e^{-iE_j t/\hbar}.$$

To get to this expression it is usually necessary to find the linear combination of eigenstates of  $\mathbf{H}^{\text{eff}}$  that corresponds to a Zero-Order Bright-State (ZOBS).  $\mathbf{H}^{\text{eff}}$  is expressed in the  $\{\phi_j^0\}$  basis set

$$\mathbf{U}^\dagger \mathbf{H}^{\text{eff}} \{\phi_j^0\} \mathbf{U} = \begin{pmatrix} E_1 & & 0 \\ & \ddots & \\ 0 & & E_n \end{pmatrix}$$

where  $\mathbf{U}$  is unitary.

We get

$$\phi_k^0 = \sum_j b_j^k \psi_j$$

from the columns of  $\mathbf{U}^\dagger$  (or is it  $\mathbf{U}$ ?). This gives us  $\Psi_I(t) = \sum_j b_j^k \psi_j e^{-iE_j t/\hbar}$ . We use  $\Psi_I(t)$  in many clever ways.

**Probability density:  $\Psi_I^*(t)\Psi_I(t)$  [not to be confused with  $\langle\Psi_I(t)|\Psi_I(t)\rangle = 1$ .]**

This is a moving wavepacket. It is real (and positive) everywhere and for all  $t$  because it is an observable quantity. It is a function of position and time. It is the basis of a lot of useful cartoons of coordinate space dynamics

$$\Psi_I^*(t)\Psi_I(t) = \sum_i \left\{ |a_i|^2 |\psi_i|^2 + \sum_{j>i} [2\text{Re}(a_i a_j^* \psi_i \psi_j^*) \cos \omega_{ji} t - 2\text{Im}(a_i a_j^* \psi_i \psi_j^*) \sin \omega_{ji} t] \right\}.$$

Note that the probability density is experimentally observable, whereas  $\Psi_I(t)$  is not observable. The disadvantage of the probability density is that it contains far more information than the wavepacket cartoons. It is often reduced to a moving and spreading Gaussian wavepacket.

Student exercises:

- (i) Draw a cartoon that describes the appearance of  $\Psi_I^*(t)\Psi_I(t)$  when the leading part of the wavepacket overlaps with the trailing part at a turning point.
- (ii) Contrast the behavior of a Gaussian wavepacket in a Harmonic and in a Morse potential. Choose  $\omega_{\text{Harmonic}} = \omega_{\text{Morse}}$  and  $D_{\text{Morse}}^e = 10(\hbar c \omega_{\text{Morse}})$ .

**Density Matrix:**  $\rho_I(t) = |\Psi_I(t)\rangle \langle \Psi_I(t)|$

This describes a freely evolving system after a specific initial preparation of the system. This is a state space quantity. It is implicitly integrated over coordinate (or momentum) space when we compute the implied matrix elements in the eigen-basis. One constructs the elements of the density matrix

$$\left(\rho_I^{(t)}\right)_{jk} = \langle \psi_j | \Psi_I(t) \rangle \langle \Psi_I(t) | \psi_k \rangle$$

where the diagonal elements are real, positive, and time-independent and are called *populations* and the off-diagonal elements are time-dependent and are called *coherences*.

$$\rho_I(t) = \sum_i \left\{ |a_i|^2 |\psi_i\rangle \langle \psi_i| + \sum_{j>i} [a_i a_j^* e^{-i\omega_{ij}t} |\psi_i\rangle \langle \psi_j| + cc.] \right\}.$$

Some coherences can radiate at  $\omega_{ij}$ .

Some off-diagonal elements of  $\rho_I(t)$  are complex, but  $\rho_I(t)$  is Hermitian.

The density matrix is useful for computing the time-dependent expectation value of any observable quantity,  $\mathbf{A}$ , where

$$\langle \mathbf{A} \rangle(t) = \text{Trace}(\rho \mathbf{A}) = \sum_{j,k} \rho_{jk} A_{kj}.$$

The density matrix is better suited for computing expectation values and other dynamical properties than for reduced-information visualization of dynamics.

$$i\hbar\dot{\rho} = [\mathbf{H}, \rho]$$

**Autocorrelation function:**  $\langle \Psi_I(t) | \Psi_I(0) \rangle = \sum_j |a_j|^2 e^{iE_j t/\hbar}$

It is a time-dependent state-space quantity because it is integrated over coordinate space. The absorption spectrum is the Fourier transform of the autocorrelation function.

Student exercise:

For a spectrum,  $I(\omega)$ , that looks like equally spaced Lorentzian lines of width  $\delta$  and the lines have a Lorentzian overall intensity distribution of width  $\Delta$ , what does  $\langle \Psi_I(t) | \Psi(0) \rangle$  look like?

The words “recurrence” and “dephasing” are used to describe features of the autocorrelation function. These features are usually explained by looking at the probability density representation of wavepackets.

**Survival Probability:**  $P_I(t) = |\langle \psi_I(t) | \Psi_I(0) \rangle|^2$

$P_I(t)$  describes how a wavepacket moves away from (and returns to) its  $t = 0$  form. It is integrated over coordinates, but is equally useful for explaining coordinate space or state-space pictures of dynamics:

$$P_I(t) = \sum_j \left[ |a_j|^4 + \sum_{k>j} 2|a_j|^2 |a_k|^2 \cos \omega_{jk} t \right].$$

**Transfer Probability:**  $P_{I \rightarrow F}(t) = |\langle \Psi_I(t) | \Psi_F(0) \rangle|^2$

This is useful to describe how a time-evolving wavepacket develops overlap with some sort of *a priori* specified target state.  $P_{I \rightarrow F}(t)$  is useful in combination with  $P_I(t)$ .

$$\begin{aligned} \Psi_I(0) &= \sum_j a_j \psi_j \quad , \quad \sum_j |a_j|^2 = 1 \\ \Psi_F(0) &= \sum_j b_j \psi_j \quad , \quad \sum_j |b_j|^2 = 1 \end{aligned}$$

$$P_{I \rightarrow F}(t) = \sum_j \left\{ |a_j|^2 |b_j|^2 + \sum_{k>j} 2\text{Re}(a_j^* a_k b_j b_k^*) \cos \omega_{jk} t - 2\text{Im}(a_j^* a_k b_j b_k^*) \sin \omega_{jk} t \right\}$$

$P_{I \rightarrow F}(t)$  is real, positive, and  $\leq 1$  at all  $t$ .

**Expectation values of coordinates and conjugate momenta:**  $\langle R \rangle_I(t), \langle P \rangle_I(t)$

The expectation values of coordinates and momenta follow the classical mechanical equations of motion (Ehrenfest's Theorem). This provides a simple representation of the motion of the "center" of a wavepacket, but tells us nothing about complicated shapes and widths of wavepackets.

**Expectation values of state-space quantities**

$$\begin{aligned} \langle v_j \rangle(t) &= \langle \mathbf{a}_j^\dagger \mathbf{a}_j \rangle(t) \\ \langle E_j \rangle(t) &= \frac{\hbar c \omega_e}{2} \left[ \langle \mathbf{a}_j^\dagger \mathbf{a}_j \rangle + \langle \mathbf{a}_j \mathbf{a}_j^\dagger \rangle \right] \\ &\quad + \frac{\hbar c x_e}{4} \left[ \langle \mathbf{a}_j^\dagger \mathbf{a}_j \rangle + \langle \mathbf{a}_j \mathbf{a}_j^\dagger \rangle \right]^2. \end{aligned}$$

$$\text{For a polyad where } P = 2v_1 + v_2 = 2 \langle \mathbf{a}_1^\dagger \mathbf{a}_1 \rangle + \langle \mathbf{a}_2^\dagger \mathbf{a}_2 \rangle$$

$$\langle v_2 \rangle = P - 2 \langle v_1 \rangle$$

so one expects  $\langle v_2 \rangle$  to oscillate opposite in phase and with twice the amplitude as  $\langle v_1 \rangle$ .

## Resonance Operators

See SDDM pages 646-649 and 694-700.

Dynamics occur as a result of off-diagonal matrix elements of  $\mathbf{H}$ . Dynamics are suppressed (or opposed) by large differences between diagonal elements of  $\mathbf{H}$ .

Suppose we partition  $\mathbf{H}^{\text{eff}}$

$$\mathbf{H}^{\text{eff}} = \mathbf{H}_{\text{diag}} + \mathbf{H}_{\text{res}}$$

where  $\mathbf{H}_{\text{res}}$  is exclusively off-diagonal.  $\mathbf{H}_{\text{res}}$  may be a sum of different resonance mechanisms

$$\mathbf{H}_{\text{res}} = \sum_k \mathbf{O}_k$$

and  $\mathbf{O}_k$  can always be expressed as a sum of two (not necessarily Hermitian) terms

$$\mathbf{O}_k = \mathbf{\Omega}_k + \mathbf{\Omega}_k^\dagger$$

because  $\mathbf{H}^{\text{eff}}$  is Hermitian (because  $\mathbf{O}_k^\dagger = \mathbf{O}_k$  as defined here). Every anharmonic resonance has the form, for example

$$\mathbf{\Omega}_k = k_{aabb} \mathbf{a}_a^{\dagger 2} \mathbf{a}_b^2$$

then

$$\mathbf{\Omega}_k^\dagger = k_{aabb}^* \mathbf{a}_a^2 \mathbf{a}_b^{\dagger 2}.$$

This means that we automatically know how to write  $\mathbf{H}_{\text{res}}$  as

$$\mathbf{H}_{\text{res}} = \sum_k \mathbf{O}_k = \sum_k (\mathbf{\Omega}_k + \mathbf{\Omega}_k^\dagger).$$

It will be informative to compute the expectation value of every  $\mathbf{O}_k$  term for each plausible bright state pluck, which is expressed as

$$\Psi_I(t) \text{ for } \Psi_I(0) = \phi_{\text{bright}}^0.$$

We can ask questions:

- (i) What is the fractional importance of the  $k^{\text{th}}$  resonance operator relative to the totality of resonance operators, for a given pluck?
- (ii) Which Fourier components of the  $\langle \mathbf{H}_{\text{diag}} \rangle (t)$  are due to  $\mathbf{O}_k$ ?
- (iii) What is the term in  $\mathbf{H}$  that is responsible for the time dependence of  $\langle \mathbf{O}_k \rangle (t)$ ?

Let's do some analysis

$$i\hbar \frac{d}{dt} [\langle \mathbf{O}_k \rangle (t)] = \langle [\mathbf{O}_k, \mathbf{H}] \rangle (t).$$

If it is possible to evaluate  $[\mathbf{O}_k, \mathbf{H}]$  by operator algebra, then we know the operator responsible for the time dependence of any pluck of  $\mathbf{O}_k$ .

For a freely evolving, isolated system

$$\langle \mathbf{H} \rangle = E.$$

The total energy for any pluck state  $\Psi_I(t)$  is time-independent.

This means that it is instructive to compare  $\langle \mathbf{H}_{\text{diag}} \rangle$  to the corresponding expectation value of each of the resonance operators

$$\begin{aligned} E &= \langle \mathbf{H}_{\text{diag}} \rangle (t) + \langle \mathbf{H}_{\text{res}} \rangle (t) \\ &= \langle \mathbf{H}_{\text{diag}} \rangle (t) + \sum_k \langle \mathbf{O}_k \rangle (t). \end{aligned}$$

The dynamical features of  $\langle \mathbf{H}_{\text{diag}} \rangle (t)$  "caused by"  $\mathbf{O}_k$  will be those that have the same Fourier components but opposite phase as  $\langle \mathbf{O}_k \rangle (t)$ . The fractional importance for a particular  $\mathbf{O}_k$  relative to the totality of  $\mathbf{O}_k$  terms is given by

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \langle \mathbf{O}_k \rangle &\equiv \bar{E}_{\text{res},k} \\ \bar{E}_{\text{res}} &= \sum_k \bar{E}_{\text{res},k}. \end{aligned}$$

Thus the fractional importance of the  $k^{\text{th}}$  resonance term is

$$f_k = \left| \frac{\bar{E}_{\text{res},k}}{\bar{E}_{\text{res}}} \right|.$$

The fractional importance of the  $k^{\text{th}}$  resonance term will depend on which basis state is chosen as the initial pluck of the system.

See Jacobson and Field, *Chem. Phys. Lett.* **320**, 553 (2000).

## “Intramolecular Radiationless Transitions” by M. Bixon and J. Jortner

*J. Chem. Phys.* **48**, 715-726 (1967).

### ABSTRACT

In this paper we consider a theory for intramolecular radiationless transitions in an isolated molecule. The Born-Oppenheimer zero-order excited states are not pure in view of configuration interaction between nearly degenerate zero-order states, leading to the broadening of the excited state, the line shape being Lorentzian. The optically excited state can be described in terms of a superposition of molecular eigenstates, and the resulting wavefunction exhibits an exponential nonradiative decay. The linewidth and the radiationless lifetime are expressed in terms of a single molecular parameter, that is the square of the interaction energy between the zero-order state and the manifold of all vibronic states located within one energy unit around that state. The validity criteria for the occurrence of an unimolecular radiationless transition and for exponential decay in an isolated molecule are derived. Provided that the density of vibrational states is large enough (i.e., exceeds the reciprocal of the interaction matrix element) radiationless transitions are expected to take place. The gross effects of molecular structure on the relevant molecular parameters are discussed.