

MIT OpenCourseWare
<http://ocw.mit.edu>

5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

Lecture #34: Wavepacket Dynamics

See pages 626-635 of SDDM for today, pages 635-649 and 659-667 for Wednesday. We mostly do frequency domain spectroscopy, yet we talk about dynamics. But eigenstates are stationary! How are dynamics encoded in a frequency domain spectrum?

Today: discuss the famous equivalence:

The Franck-Condon distribution in an absorption spectrum is identical to the Fourier transform of the autocorrelation function for a wavepacket created by transferring the initial state from potential surface g (or V'') to surface e (or V') at $t = 0$. The autocorrelation function describes the evolution of the g -state wavefunction on the e -state surface, where it is not an eigenstate.

The two pictures are mathematically equivalent, but yield quite different sets of insights. Key is that the wavepacket picture is inherently “local” and “ball-and-springs mechanistic”, whereas the traditional frequency domain picture is inherently “global” and quantum mechanical.

The stationary phase condition provides the reason why the localized picture emerges and why the autocorrelation function picture gives insights.

Next lecture: discuss various measures of dynamics

Absorption Spectrum is FT of autocorrelation function.

$$I(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \langle \psi(t) | \psi(0) \rangle dt$$

* Derive this by manipulating familiar stuff

* Interpret

$$I(\omega) = \sum_j I_j \delta(\omega - \omega_j)$$

spectrum is collection of lines of intensity I_j located at $\omega_j = (E_{v'_j} - E_{v''})/\hbar \equiv E_j/\hbar$

(define $E = 0$ at $E_{v''}$)

$$I_j = |M|^2 q_{v'_j v''}$$

$$= M^* \langle v'' | v'_j \rangle \langle v'_j | v'' \rangle M$$

FC factor times $|M|^2$ $M = \langle e | \mu | g \rangle$

$$|\psi(0)\rangle \equiv |v''\rangle M = \sum_j |v'_j\rangle \langle v'_j|v''\rangle M$$

$$\langle\psi(0)| = M^* \langle v''| = M^* \sum_j \langle v''|v'_j\rangle \langle v'_j|$$

$$\langle\psi(t)| = M^* \sum_j \langle v''|v'_j\rangle \langle v'_j| e^{iE_j t/\hbar}$$

return to this

$$\langle\psi(t)|\psi(0)\rangle = M^* \sum_{j,k} \langle v''|v'_j\rangle \langle v'_j| e^{iE_j t/\hbar} |v'_k\rangle \langle v'_k|v''\rangle M$$

$$= (M^* M) \sum_{j,k} e^{iE_j t/\hbar} \langle v''|v'_j\rangle \underbrace{\langle v'_j|v'_k\rangle}_{\delta_{kj}} \langle v'_k|v''\rangle$$

$$= |M|^2 \sum_j q_{v'_j v''} e^{iE_j t/\hbar}$$

$$\begin{aligned}
 \int_{-\infty}^{\infty} e^{-i\omega t} \langle \psi(t) | \psi(0) \rangle dt &= |M|^2 \int \sum_{v'_j} q_{v'_j v''} e^{i(\omega_j - \omega)t} dt \\
 &= |M|^2 \sum_{v'_j} q_{v'_j v''} \delta(\omega_j - \omega) \\
 &= \sum_j I_j \delta(\omega_j - \omega)
 \end{aligned}$$

$(E_{v'_j} - E_{v''})$

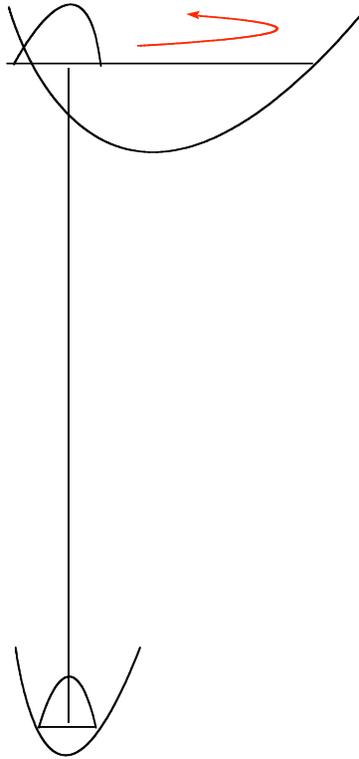
So we have shown that the absorption spectrum, $I(\omega)$, is FT of autocorrelation function.

But what is this autocorrelation function?

$$\begin{aligned}
 \langle \psi(t) | \psi(0) \rangle &= M^* \sum_j \langle v'' | v'_j \rangle \langle v'_j | e^{+i\omega_j t} | v'' \rangle M \\
 &= [M^* \langle v'' |] \sum_j \underbrace{|v'_j \rangle \langle v'_j | e^{+i\omega_j t}}_{e^{+i\mathbf{H}'t / \hbar}} [|v'' \rangle M]
 \end{aligned}$$

propagation of $\psi(0)$ on upper potential surface

Now we have a new picture \rightarrow spectrum is generated by a sequence of events occurring for a perfectly defined initial state propagating on unknown potential surface.



* Recurrences at $T = \frac{1}{\nu} = \text{classical period} = \frac{1}{\Delta E / h}$
 $= \frac{1}{\omega_e c}$

* Initial decay — gradient of potential is Force

How long does it take for a wavepacket of spatial width Δ to move a distance $\Delta/2$ away from its initial location? Call this time $t_{1/2}$.

[Actually, this is an over-simplification. The motion of the wavepacket occurs in both coordinate and momentum space, respectively at rates of order t^2 and t .]

$$F = -\frac{dV}{dR} = m\ddot{R} \quad (\text{equation of motion})$$

$$R(0) = R_{<} \quad (\text{inner turning point})$$

$$\dot{R}(0) = 0$$

$$\dot{R}(t) = -\frac{1}{m} \left. \frac{dV}{dR} \right|_{R_{<}} t \quad \text{integrated equation of motion with respect to } t$$

$$R(t) = -\frac{1}{2m} \left. \frac{dV}{dR} \right|_{R_{<}} t^2 + R_{<} \quad \text{integrated again}$$

$$t_{1/2} \text{ related to } \frac{dV}{dR} \quad R(t_{1/2}) - R(0) \equiv \Delta/2 \quad \text{What is } t_{1/2}?$$

$$\left[\left(\frac{-2m}{\frac{dV}{dR}} \right) \frac{\Delta}{2} \right]^{1/2} = t_{1/2}$$

For a harmonic upper electronic state potential

$$V'(R) = \frac{1}{2}k'(R - R'_e)^2$$

$$k' = m(2\pi c\omega'_e)^2$$

$$F = -\frac{dV'}{dR} = -k'(R - R'_e) = -m(2\pi c\omega'_e)^2 (R - R'_e)$$

$$t_{1/2} = \left[\frac{-m\Delta}{-m(2\pi c\omega'_e)^2 (R - R'_e)} \right]^{1/2} = \frac{1}{2\pi c\omega'_e} \left| \frac{\Delta}{R - R'_e} \right|^{1/2}$$

If the initial wavepacket is created from $v'' = 0$ of the initial state, $R(t=0) = (R_< \text{ or } R_>) = R''_e$,

$$\Delta = R''_>(v'' = 0) - R''_<(v'' = 0)$$

$$\Delta = \frac{1}{\pi} \left[\frac{h}{mc\omega''_e} \right]^{1/2}$$

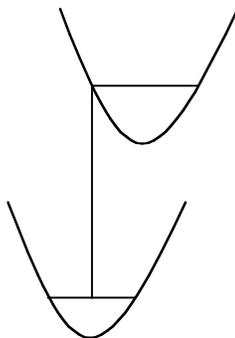
ω''_e is initial state frequency, ω'_e is final state frequency. Note that the time required for the wavepacket to move half its spatial width from its initial location at an upper state turning point is

$$t_{1/2} \propto \frac{1}{\omega'_e} |R''_e - R'_e|^{-1/2}.$$

Questions

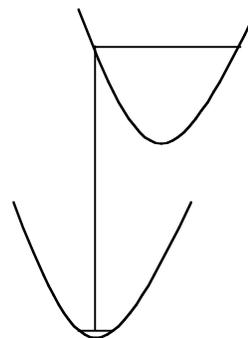
1. $V(R) = \frac{1}{2}k(R - R_e)^2$

Two Harmonic oscillators of identical k but different R_e .



small displacement

VS.



large displacement

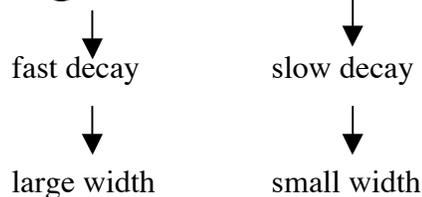
which $\langle \psi(t) | \psi(0) \rangle$ decays faster?

What does this imply about $I(\omega)$? [use time dependent approach instead of old FC envelope ideas to answer.]

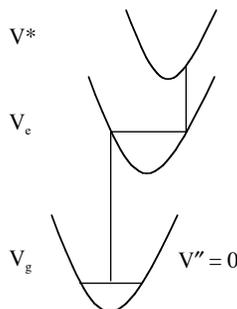
Does this give correct limiting behavior when $\Delta R_e = 0$?

2. For 2 vibrational modes of same $R'_e - R''_e$, which will give wider FC region from $v'' = 0$?

large ω' or small ω' ?



3. For 2 modes of same ω' , but different $R'_e - R''_e$, which will give longer FC progression?
4. pictures of OODR.



What does this picture tell you about the optimal timing and center frequencies for excitation from state g to state $*$ via state e ?