5.74 RWF Lecture #5

When we create $\Psi(\mathbf{Q}, t = 0)$ that is not an eigenstate of the isolated molecule, time-independent **H**, that $|\Psi(\mathbf{Q},t)|^2$ will evolve.

Usually a nonstationary "coherent superposition of eigenstates" state is produced by a sudden perturbation, such as a short pulse of electromagnetic radiation.

We have looked at the evolution of a large number of "wavepackets" in 5.73 and 5.74. But there is a lack of a simple picture of how $\Psi(\mathbf{Q},0)$ is produced, what are the simple forces that cause it to evolve, and how all of this is related to the frequency domain spectrum.

We need to understand the nature of "the pluck".

Heller's formulation of the relationship between the absorption spectrum, $I(\omega)$, and the Fourier transform of the $\langle \Psi(t)^*\Psi(0)\rangle$ autocorrelation function provides a unified conceptual and computational framework. It was revolutionary!

$$\text{Electronic Absorption Spectrum} \leftrightarrow \text{FT of } \langle \Psi(t)|\Psi(0)\rangle$$

traditional frequency domain formulation
restated as Fourier Transform of the autocorrelation function

   *   wavepacket evolution as responsible for features in autocorrelation function
   *   what are the features of the wavepacket as determined by the upper and lower electronic potential surfaces
   *   <u>local</u> view of V($\mathbf{Q}$) from wavepacket/autocorrelation picture vs. <u>global</u> view from Franck-Condon picture.

   see Heller JCP **68**, 3891 (1978)

$$I_k(\omega) = \Sigma \; c_{k_j} \delta(\omega - \omega_{jk}) = \sum_j c_{k_j} \delta\left[\frac{1}{\hbar}\left(E - \left(E_j - E_k\right)\right)\right]$$

| initial state | transition intensity | transition frequency |

$$\omega_{jk} = \frac{1}{\hbar}\left(E_j - E_k\right)$$

notation e single prime, g double prime

$$I_{v_g''}(\omega) = \left|\mu_{eg}\right|^2 \sum_{v_e'} q_{v_e'v_g''} \delta\left(\omega - \omega_{v_e'v_g''}\right)$$

Franck-Condon factor

$$q_{v_e'v_g''} = \left|\langle v_e' | v_g'' \rangle\right|^2 \qquad \text{vibrational overlap squared}$$

It is necessary to know complete V'_e and V'_g up to at least energy of v'_e and v''_g and to integrate over all 3N–6 normal coordinate displacements. Usually do not have this information except for diatomic molecules. Use displaced harmonic oscillators and qualitative F-C factors derived from diatomic molecules. Problem when there is not a mode by mode correspondence between V'_e and V'_g. Duschinsky rotation.

Try to recast the standard frequency domain expression into wavepacket form.

Integral definition of δ-function

$$\delta\left(\omega - \omega_{v'_e v''_g}\right) = \frac{1}{2\pi}\int\,dt\exp\left[-i\left(\omega - \omega_{v'_e v''_g}\right)t\right].$$

Completeness of vibrational basis set to express lower state vibrational wavefunction as linear combination of upper state vibrational wavefunctions:

$$\chi_{v''_g}(R) \equiv \left\langle R\middle|v''_g\right\rangle$$

$$= \sum_{v'_e}\ \underbrace{\left\langle R\middle|v'_e\right\rangle\left\langle v'_e\middle|v''_g\right\rangle}_{\text{completeness}} = \sum_{v'_e}\ \chi_{v'_e}\underbrace{\left\langle v'_e\middle|v''_g\right\rangle}_{\text{vib. overlap}}.$$

Reassemble factors

$$I_{v''_g}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\,dt\exp\left[-i\left(\omega + \frac{E_{g,v''_g}}{\hbar}\right)t\right]\left\langle\Psi_i(t)\middle|\Psi_i(0)\right\rangle$$

$$\left\langle\Psi_i(t)\right| \equiv \underbrace{\left\langle g\middle|\boldsymbol{\mu}\middle|e\right\rangle}_{\mu^*_{eg}}\left\langle e\middle|\sum_{v'_e}\ \left(\left\langle v''_g\middle|v'_e\right\rangle\left\langle v'_e\middle|\underbrace{e^{iE_{e,v'_e}\,t/\hbar}}_{e^{i\mathbf{H}_e t/\hbar}}\right.\right.$$

excited state **H**

$$\left|\Psi_i(0)\right\rangle \equiv \left|e\right\rangle\underbrace{\left\langle e\middle|\boldsymbol{\mu}\middle|g\right\rangle}_{\mu_{eg}}\sum_{v'_e}\ \left|v'_e\right\rangle\left\langle v'_e\middle|v''_g\right\rangle.$$

gives E_{e,v'_e} when applied to $\left|e\right\rangle\left|v'_e\right\rangle$

Shaded equation is the Fourier transform of the initial ($t = 0$) (post-pluck) state formed from eigenstate $\left|g\right\rangle\left|v''_g\right\rangle$. It is the initial vibrational wavefunction transported onto the excited potential and allowed to evolve under the influence of $\mathbf{H}_e$.

What does this buy us?

We know $\left| v_g'' \right\rangle$ perfectly. It is a simple Gaussian if $v_g'' = 0$.

We move this up to the excited surface where it is not an eigenstate. We project it onto eigenstates $\left| v_e' \right\rangle$ and they evolve according to $\mathbf{H}_e$.

The averages $\langle \mathbf{R} \rangle$ and $\langle \mathbf{P} \rangle$ and are known perfectly at $t = 0$. $\langle \mathbf{P} \rangle_{t=0} = 0$, $\langle \mathbf{E} \rangle_{t=0} = \langle \mathbf{E} \rangle_t$. $\langle \mathbf{R} \rangle_{t=0}$ is $\left\langle v_g'' R v_g'' \right\rangle \approx R_e''$ if $v_g'' = 0$. Franck Condon principle gives $\langle \mathbf{E} \rangle_t -$ vertical transition (or turning point to turning point).

So we have a Gaussian of known ΔR, ΔP, E, $\langle \mathbf{R} \rangle$, $\langle \mathbf{P} \rangle = 0$ at $t = 0$. It is a particle like state. It's $\langle \mathbf{R} \rangle$, $\langle \mathbf{P} \rangle$ evolve on V_e' as a particle would evolve. The key is that we get the most important details in the spectrum from allowing the wavepacket to evolve for a very short time. It samples only the near $\left\langle v_g'' \mathbf{R} v_g'' \right\rangle$ region of the $V_e'(\mathbf{R})$.

See Figure 9.1   This shows a wavepacket starting at the Franck-Condon point on $V_e'(\mathbf{R})$. It feels a force which is minus gradient of V_e'. In this case gradient is in sym. stretch (v) direction which is bound. It starts at a saddle point wrt anti sym. stretch (u) which is unbound. The wavepacket is pulled apart along u. It oscillates and spreads along v and is pulled apart irreversibly along u.

Figures removed due to copyright reasons.

See Figure 9.2 This shows what happens to $\langle\Psi(t)|\Psi(0)\rangle$. At $t = 0$ it starts to move away from itself. Be careful, the moving away could be in either coordinate or momentum space. We will look at this next. At τ_e a small part of the wavepacket has returned to the F–C point along the sym. stretch (v). The motion is periodic of period $T = \frac{2\pi}{\omega}$. The initial FWHM is $\delta \approx 2(\tau_b - \tau_a)$. So we have damped periodic motion of a wavepacket with recurrences of nearly constant width. The FT of this is shown in the lower panel.

FT $\langle\Psi(t)|\Psi(0)\rangle \propto I(\omega)$

The slow recurrences give rapidly oscillating structure in $I(\omega)$,

$$\omega = \frac{2\pi}{T}.$$

The fast decays give an envelope of FWHM $\sim \frac{2\pi}{\delta}$.

So we know how to read off from the spectrum the key features of the dynamics of the wavepacket.

A key point is that we are looking at the evolution of the wavepacket on V_e' for a short time. The wavepacket does not move very far. It does not spread very far. It does not sample the F-C dark coordinates very much, even if they are anharmonically coupled to the FC bright coordinates.

Now we want to look at the actual form of the wavepacket and see how the shape of V_e' and the F-C point affect the evolution of the wavepacket.

Figures removed due to copyright reasons.

Heller, Sundberg, and Tannor JPC **86**, 1822 (1982)

for absorption from $v_g'' = 0$

$$\Psi_i(R, t = 0) = \left(\frac{2\mu\omega_g}{\hbar}\right)^{1/4} \exp\left[\left(\frac{-\mu\omega_g}{2\hbar}\right)(R - R_{e_g})^2\right]$$

$$\int dR|\Psi_i|^2 = 1 \qquad\qquad\qquad\qquad \boxed{\text{equilibrium R of the } V_g'' \text{ surface.}}$$

$$\Delta R \approx \text{FWHM}\left(\Psi_{v_g'' = 0}\right) = \left[\frac{\hbar 8 \ln 2}{\mu\omega_g}\right]^{1/2}$$

mass ↑ or w_g ↑ ΔR⇓

$$\omega_g = \left[k_g / \mu\right]^{1/2} \qquad k_g = \left.\frac{d^2 V_g}{dR^2}\right|_{R=R_{e_g}}$$

Ψ is real, thus ⟨P⟩ = 0

Early time form of Gaussian wavepacket formed on V_e' from $v_g'' = 0$

$$\Psi_i(R, t) = \left(\frac{2\mu\omega_g}{\hbar}\right)^{1/4} \exp\left[-\frac{\mu\omega_g(t)}{2\hbar}(R - R(t))^2\right] \exp\left[\frac{i}{\hbar} P(t)(R - R(t))\right]$$

$$\times \exp\left[\frac{i}{\hbar}\gamma(t)\right]$$

3 factors: position, momentum, phase

$$R(t) = R_{e_g} + 0(t^2) \qquad\qquad \text{not moving at early time}$$

$$P(t) = -\left.\frac{dV}{dR}\right|_{R=R(t)} t + 0(t^2) \qquad \dot{P}(t) = -\left.\frac{dV}{dR}\right|_{R=R(t)}$$

$$\text{force } \dot{P} = -\text{gradient of potential}$$

$$\boxed{\begin{array}{l}\text{width in P changes at early time —}\\ \text{difference in curvature of } V_e + V_g\\ \text{at } R_{eg}\end{array}}$$

$$\omega_g(t) = \omega_g - i\left(\omega_g^2 - \frac{1}{\mu}\left.\frac{d^2 V_e}{dR^2}\right|_{R=R(t)}\right) t + 0(t^2)$$

$$\boxed{\begin{array}{l}\text{width in R does not}\\ \text{change at early time}\end{array}} \qquad\qquad \boxed{\left.\frac{1}{\mu}\frac{d^2 V_g}{dR^2}\right|_{R=R(t)=R_{e_g}}}$$

How do we know this? Stuff in exp $\Big\langle$

$$\text{real} \rightarrow \text{moments of R}$$

$$\text{imaginary} \rightarrow \text{moments of P}$$

$$P = \frac{\hbar}{i}\frac{\partial}{\partial R}$$

$$P\Psi = \frac{\hbar}{i}\frac{\partial \Psi}{\partial R} \qquad \text{gives } \frac{\hbar}{i}(ia+bR)\Psi$$

odd

$$\int \Psi *P\Psi dR \quad \text{gives } \hbar a + \int \ |\Psi|^2 RdR = 0$$

phase of the center E of wp

$$\gamma(t) = \gamma_0 - \Big[\Delta E_{eg} + V_e\big(R_{e_g}\big)\Big]t + 0(t^2)$$

arbitrary phase

min to min

Choose 0 of E at $V_g(R_{eg})$

$$V_e\big(R_{e_g}\big) \quad \begin{array}{c} \downarrow \\ \overline{} \\ \uparrow \end{array}$$

$\uparrow$

ΔE_{eg}

$\downarrow$ E = 0
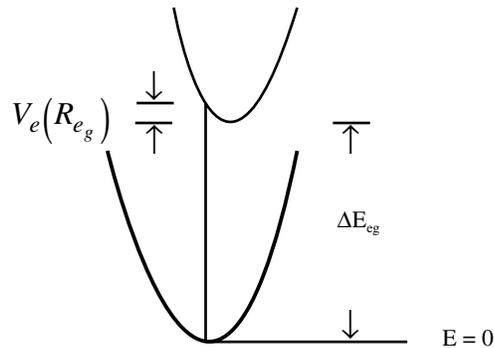
The dominant early time change in the wavepacket is in $\langle P \rangle$ and ΔP.

Rewriting $\Psi_i(R,t)$ we get

stationary $\langle R \rangle$ and ΔR

$$\Psi_i(R,t) = \left(\frac{2\mu\omega_g}{\hbar}\right)^{1/4} \exp\left[-\left(\frac{\mu\omega_g}{2\hbar}\right)(R-R_{e_g})^2\right]$$

acceleration of wp

$\langle P \rangle_t \propto t$

ordinary center-E phase

$$\times \exp\left[\left(\frac{it}{\hbar}\right)\left(\frac{dV_e}{dR}\bigg|_{R=R_{eg}}\right)(R-R_{eg}) + \Delta E_{eg} + V_e(R_{e_g})\right]$$

$$\times \exp\left[\frac{it\mu}{\hbar}(R-R_{eg})^2\left(\omega_g^2 - \frac{1}{\mu}\frac{d^2V_e}{dR^2}\bigg|_{R=R_{e_g}}\right)\right]\exp(i\dot{\gamma}_0\hbar)$$

spreading in P

Extend from diatomic molecule to Polyatomic molecule

FC active modes — get

$$\frac{d^2V_e'}{dQ_i^2}\bigg|_{Q_{i_g} = Q_{ie_g}}$$

along i-th g-state normal mode

equilibrium in mode i

also get ω_i

$$\frac{d^2V_e'}{dQ_i^2}_{Q_{ie_e}}$$

The $v=0 : v=1$ intensity ratio determines the gradient of V_e' at Q_{ie_g}.

What is wrong or incomplete with simple idea that initial state $\Psi(\mathbf{Q})$ is transferred intact and undistorted onto excited state potential energy surface?

* negative wavepacket on ground state energy surface is ignored

* assumes that the excitation pulse is sufficiently short and centered at the correct λ

* neglects $\boldsymbol{\mu}(\mathbf{Q})$

* neglects spatial (and temporal) distribution of excited molecules (especially the spatio-temporal correlation)

When are these simplifications justified?

What do we do when they are not justified?