NUCLEAR MOTION COUPLED TO ELECTRONIC TRANSITION*

The following is a presentation of a widely used model for the coupling of nuclear motions to an electronic transition, which has many applications. We will look at the specific example of electronic absorption experiments, which leads to insight into the vibronic structure in absorption spectra. Spectroscopically it is also used to describe wavepacket dynamics; coupling of electronic states to intramolecular vibrations or solvent; coupling of electronic excitation/excitons in solids/semiconductors to phonons. Also, the same type of model can be used to describe fundamental chemical rate processes. We will develop extensions to Förster Theory for electronic energy transfer and Marcus Theory for non-adiabatic electron transfer.

Two-Electronic Level System: Displaced harmonic oscillators  

We will calculate the electronic absorption spectrum using T.C.F.

\[ H = H_0 + V(t) \]

\[ H_0 = |G\rangle H_G \langle G| + |E\rangle H_E \langle E| \]

\[ H_G = T(Q) + W_g(Q) + E_g \]

\[ H_E = T(Q) + W_e(Q) + E_e \]

\[ T(Q) : \text{Nuclear kinetic energy} \quad \Rightarrow \quad p^2 / 2m \]

\[ W_g(Q) / W_e(Q) : \text{Potential energy} \quad \Rightarrow \quad \frac{1}{2} m \omega_0^2 Q^2 \]

\[ E_e - E_g : \text{Electronic energy gap} \quad \Rightarrow \quad \frac{1}{2} m \omega_0^2 (Q - d)^2 \]

* See Mukamel, p. 217, also p. 189.
\[ H_e = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 (Q - d)^2 + E_e \quad = H_e + E_e \]
\[ H_g = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 Q^2 \quad = H_g + E_g \]

1) **Born-Oppenheimer Approximation**

\[ |G\rangle = |g\rangle |n\rangle \]

vibrational state
electronic state

2) **Condon Approximation**

No \( Q \) dependence to \( \bar{\mu} \) – The dipole operator is an operator only in the electronic states.

\[ V(t) = -\bar{\mu} \cdot E(t) \]
\[ \bar{\mu} = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g| \]

Now let’s calculate an absorption lineshape. Write dipole correlation function:

\[ \langle \bar{\mu}(t) \bar{\mu}(0) \rangle = \sum_n p_n \langle n | \bar{\mu}(t) \bar{\mu}(0) | n \rangle \]
\[ = \langle g, 0 | e^{iH_g t/\hbar} \bar{\mu} e^{-iH_g t/\hbar} \bar{\mu} | g, 0 \rangle \quad \text{since at low } T \text{ all population in } |g, 0\rangle \]

By substituting

\[ e^{-iH_g t/\hbar} = |G\rangle e^{-i(H_g + E_g) t/\hbar} \langle G| + |E\rangle e^{-i(H_e + E_e) t/\hbar} \langle E| \]

and dipole operator \( \bar{\mu} \) we find:

\[ C_{\mu\mu}(t) = |\mu_{eg}|^2 \left\langle 0 | e^{iH_g t/\hbar} e^{-iH_g t/\hbar} |0\rangle \right\rangle e^{-i(E_e - E_g) t/\hbar} \]

\[ F(t) \quad e^{-i\omega_{eg} t} \]
Note we can write our correlation function as $C(t) = \sum_n p_n |V_{mn}|^2 e^{-i\omega_0 (t - g(t))}$ where $g(t)$ is our lineshape function. Let's concentrate on $F(t) = \exp(-g(t))$, sometimes known as the dephasing function:

$$F(t) = \langle 0 | e^{iH_{dt}/\hbar} e^{-iH_{dt}/\hbar} | 0 \rangle$$

$$= \langle 0 | U_g^\dagger U_e | 0 \rangle$$

Using the displacement operator (From problem set 1):

$$e^{i\alpha p} O e^{-i\alpha p} = O + \alpha \hbar$$

$$\therefore \quad H_e = e^{-i\alpha p} H_g e^{i\alpha p} \quad \text{and} \quad e^{-iH_{dt}/\hbar} = e^{-i\alpha p} H_g e^{-i\alpha p}$$

Now, $H_g = \frac{\mathbf{p}^2}{2m} + \frac{1}{2} m \omega_0^2 \mathbf{Q}^2 = \hbar \omega_0 (a^\dagger a + \frac{1}{2})$

$$a^\dagger a = n$$

$$p = \frac{i}{\sqrt{2}} (a^\dagger - a) \sqrt{m \hbar \omega_0} \quad \text{and} \quad Q = \frac{1}{\sqrt{2}} (a + a^\dagger) \sqrt{\frac{m \omega_0}{\hbar}}$$

Note: $U_g^\dagger a U_g = e^{i\omega_0 t} a e^{-i\omega_0 t} = a e^{i(n-1)\omega_0 t} e^{-i\omega_0 t} = a e^{-i\omega_0 t}$

$$U_g^\dagger a^\dagger U_g = a^\dagger e^{i\omega_0 t}$$
So:  \[ p(t) = i\sqrt{\frac{m\hbar\omega_0}{2}} \left( a^e^{i\omega_0 t} - a e^{-i\omega_0 t} \right) \]

\[
F(t) = \left\langle 0 \left| \exp \left[ -d \left( a^e^{i\omega_0 t} - a e^{-i\omega_0 t} \right) \right] \exp \left[ -d \left( a^e - a \right) \right] \right| 0 \right\rangle \quad \text{with} \quad d = d\sqrt{\frac{m\omega_0}{2h}}
\]

Using the identity \( e^{\hat{A} + \hat{B}} = e^{\hat{A}} e^{-\frac{1}{2}[\hat{A},\hat{B}]} \) \quad \text{with} \quad [\hat{a}^e,\hat{a}] = -1

\[
e^{\lambda \hat{a}^e + \mu \hat{a}} = e^{\lambda \hat{a}^e} e^{\mu \hat{a}} e^{\frac{1}{2}(\lambda \mu)}
\]

So . . .

\[
F(t) = \left\langle 0 \left| \exp \left[ -d \hat{a}^e e^{i\omega_0 t} \right] \exp \left[ -d a e^{-i\omega_0 t} \right] \right| 0 \right\rangle
\]

\[
\times \exp \left[ -d \hat{a}^e \right] \exp \left[ -d a \right] \exp \left[ -\frac{1}{2} d^2 \right] \left| 0 \right\rangle
\]

since \( a \left| 0 \right\rangle = 0; \left\langle 0 \right| a^e = 0 \)

\[
F(t) = e^{-d^2} \left\langle 0 \left| \exp \left[ -d a e^{-i\omega_0 t} \right] \exp \left[ -d a^e \right] \right| 0 \right\rangle
\]

Note that the operator defined through expansion! So this is a bit tough to evaluate, as is. To help evaluate, we note that \( e^{-za} \left| 0 \right\rangle = 1; \left\langle 0 \right| e^{za} = 1 \). This would make evaluation of expression easier if we exchange order of operators. Since \( e^A e^B = e^B e^A e^{-[B,A]} \).

\[
F(t) = e^{-d^2} \left\langle 0 \left| \exp \left[ -d a e^{-i\omega_0 t} \right] \exp \left[ d^2 e^{-i\omega_0 t} \right] \right| 0 \right\rangle
\]

\[
= \exp \left[ \frac{d^2}{2} \left( e^{-i\omega_0 t} - 1 \right) \right]
\]

\[
\equiv e^{-g(t)} \quad \text{(where} \quad g(t) = -d^2 \left( e^{-i\omega_0 t} - 1 \right) \text{is the lineshape function)}
\]
So we have the dipole correlation function:

\[ C_{\mu\mu}(t) = \left| \mu_{eg} \right|^2 \exp \left[ -i\omega_{eg} t + D(e^{-i\omega_{0}t} - 1) \right] \]

Where \( D = d^2 = \frac{d^2 m \omega_0}{2\hbar} \) \text{ Huang-Rhys parameter}.

This is a dimensionless factor related to the mean square displacement. It represents the strength of coupling to the nuclear degrees of freedom.

**Absorption Lineshape**

\[
\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \left| \mu_{eg} \right|^2 e^{-i\omega_{eg}t} \exp \left[ D(e^{-i\omega_{0}t} - 1) \right] \]

(expand exponential)

\[
e^{-D} \sum_{j=0}^{\infty} \frac{1}{j!} D^j \left(e^{-i\omega_{0}t}\right)^j
\]

= \left| \mu_{eg} \right|^2 \sum_{j=0}^{\infty} e^{-D} \frac{1}{j!} D^j \delta \left( \omega - \omega_{eg} - j\omega_0 \right)

Spectrum is a progression of absorption peaks separated by \( \omega_0 \) with a Poisson distribution of intensities → vibrational progression!

The amplitudes are the Franck-Condon coefficients: \( \left| (0|v) \right|^2 = e^{-D} \frac{1}{v!} D^v \)

The intensities of these peaks are dependent on \( D \), which is a measure of the coupling strength between nuclear an electronic degrees of freedom.
Let’s plot the normalized absorption lineshape $\sigma'_\text{abs}(\omega) = \frac{\sigma_{\text{abs}}(\omega)}{e^{-D|\mu_{eg}|^2}}$ as a function of $D$. 

![Diagram showing the effect of $D$ on the normalized absorption lineshape](image)
Franck-Condon Transitions

Note that for $D < 1$ peak absorption at $n = 0$. For $D >> 1$ peak at $n \approx D$.
Note that $D$ is the number of quanta excited at $Q = 0 \rightarrow$ Franck-Condon principle.

The envelope for these transitions is Gaussian:

Short time expansion: $t < \frac{1}{\omega_0}$.

$$
\sigma_{\text{abs}}(\omega) = |\mu_{eg}|^2 \int_{-\infty}^{\infty} dt \ e^{i\omega t} e^{-i\omega_0 t} e^{D(\exp(-i\omega_0 t) - 1)}
$$

Here we expand the exponential keeping the first three terms: $1 - i\omega_0 t - \frac{1}{2} \omega_0^2 t^2$

$$
\approx |\mu_{eg}|^2 \int_{-\infty}^{\infty} dt \ e^{i(\omega - \omega_0) t} e^{\frac{-D}{\omega_0^2} t^2}
$$

$$
= |\mu_{eg}|^2 \int_{-\infty}^{\infty} dt \ e^{i(\omega - \omega_{eg} - D\omega_0) t} e^{-\frac{1}{2} \omega_0^2 t^2}
$$

Solve this by completing the square.

$$
= \sqrt{\pi} |\mu_{eg}|^2 \exp \left[ - \frac{(\omega - \omega_{eg} - D\omega_0)^2}{2\omega_0^2} \right]
$$

Gaussian profile centered at Franck-Condon vertical transition.

D: mean number of vibrational quanta excited in $|E\rangle$ on absorption.

Reorganization Energy

$$
\lambda = D \hbar \omega_0 = \frac{1}{2} m \omega_0^2 d^2 = \text{vibrational energy in } |E\rangle \text{ on excitation at } a = 0
$$

$$
= \text{vibrational energy in } |G\rangle \text{ at } Q = d
$$
Absorption: $h(\omega_{eg} + D\omega_0)$

Fluorescence: $h(\omega_{eg} - D\omega_0)$

Since vibrational energy on $|e\rangle$ is dissipated quickly, we expect fluorescence to be red-shifted by $2\lambda$ and have mirror symmetry:

$$
\sigma_{abs}(\omega) = \int_{-\infty}^{\infty} dt e^{i(\omega_{eg} - g) - g(t)}
$$

$$
\sigma_{fluor}(\omega) = \int_{-\infty}^{\infty} dt e^{i(\omega_{eg} - 2\lambda - g^*(t)}
$$

$$
g(t) = D(e^{-i\omega t} - 1)
$$

$2\lambda$: Stokes Shift
What if the electronic transition is coupled to many vibrational coordinates with own displacement?

Correlation function is a straightforward extension if the modes are independent. We imagine an electronic transition coupled to a set of normal modes for the molecule or lattice. Then we write the state of the system as product states, i.e. $|G\rangle = |g; n_1, n_2, \ldots, n_i\rangle$

$$C_{gg'}(t) = |\mu_{eg}|^2 e^{-i\omega_0 t} \cdot F_1(t) \cdot F_2(t) \cdots F_N(t)$$

$$= |\mu_{eg}|^2 e^{-i\omega_0 t} \left[ \prod_{i=1}^{N} \exp \left[ D_i \left( e^{-i\omega t} - 1 \right) \right] \right]$$

$$= |\mu_{eg}|^2 e^{-i\omega_0 t} g(t)$$

$$g(t) = \sum_i D_i \left( e^{-i\omega t} - 1 \right)$$
Displaced Harmonic Oscillator Model at Finite Temperature

If you want to solve the same problem at finite temperatures, where excited vibrational levels are populated, you find:

\[
C_{\mu\nu}(t) = |\mu_{\text{eg}}|^2 e^{-i\omega_0 t} \exp\left[ D \left( \frac{1}{\bar{n} + 1} + \frac{1}{\bar{n}} \right) + \frac{1}{\bar{n}} \left( \frac{1}{\omega_{eg} - \omega} - \frac{1}{\omega_{eg} + \omega} \right) \right]
\]

\[
\bar{n} = \left( e^{\hbar \omega_0 T} - 1 \right)^{-1}
\]

Here \( \bar{n} \) is the thermally averaged occupation number of the harmonic vibrational mode. Now, let's calculate the lineshape. Expanding exponentials in the dephasing function as we did before gives

\[
\sigma_{\text{abs}}(\omega) = |\mu_{\text{eg}}|^2 \sum_{j=0}^{\infty} \frac{e^{-D j}}{j!} D^j \left( \frac{1}{\bar{n} + 1} \right)^j \omega_{eg} - \omega + \frac{1}{\bar{n}} \left( \frac{1}{\omega_{eg} - \omega} - \frac{1}{\omega_{eg} + \omega} \right)
\]

The first term looks similar to before, but the second term now includes “hot bands”: transitions upward from thermally populated vibrational states with a net decrease in quantum number on excitation. Note the amplitudes depend on the thermal occupation. At low temperature the first term dominates – giving our previous result, and at high temperatures, we have additional contributions which gives a progression of transitions to frequencies below \( \omega_{eg} \): \( \omega = \omega_{eg} - j\omega_0 \).
For the coupling of electronic transitions to nuclear motion, we often want to describe coupling to a large number of modes. A continuous distribution can be used to describe relaxation processes—remember that coupling to a continuum leads to irreversible relaxation. If the nuclear degrees of freedom don’t interact, we can write the state of the system in terms of the electronic state and the nuclear quantum numbers, i.e. \( |E\rangle = |e; n_1, n_2, n_3 \ldots \rangle \), and from that:

\[
F(t) = \exp \left[ \sum_j D_j \left( (\bar{n}_j + 1) \left( e^{-i\omega_j t} - 1 \right) + \bar{n}_j \left( e^{+i\omega_j t} - 1 \right) \right) \right]
\]

or changing to an integral over a continuous frequency distribution of normal modes characterized by a density of states, \( W(\omega) \):

\[
F(t) = \exp \left[ \int d\omega \ W(\omega) \ D(\omega) \left( (\bar{n}(\omega) + 1) \left( e^{-i\omega t} - 1 \right) + \bar{n}(\omega) \left( e^{+i\omega t} - 1 \right) \right) \right]
\]

Here \( D(\omega) \) is a frequency dependent coupling to the vibrational mode at frequency \( \omega \). Let’s look at the envelope of the nuclear structure on the transition by doing a short-time expansion on the complex exponential

\[
e^{-i\omega t} = 1 - i\omega t - \frac{\omega^2 t^2}{2} + \ldots
\]

Now we will retain the first three terms, since the third term is the first to look like damping. We can write:

\[
F(t) = \exp \left[ \int d\omega \ D(\omega) W(\omega) \left( -i\omega t - (2\bar{n} + 1) \frac{\omega^2 t^2}{2} \right) \right]
\]

\[
\sigma_{abs} (\omega) = \int_{-\infty}^{+\infty} dt \ e^{(i(\omega-\omega_0)t)} \ exp\left[-i \ \langle \omega \rangle \ t \right] \ exp\left[-\frac{1}{2} \ \langle \omega^2 \rangle \ t^2 \right]
\]
Where

\[
\langle \omega \rangle = \int d\omega W(\omega) D(\omega) \omega \\
= \lambda / h
\]

Average vibrational excitation on absorption

\[
\langle \omega^2 \rangle = \int d\omega W(\omega) D(\omega) \omega^2 \left( 2\pi(\omega) + 1 \right)
\]

\(\langle \omega^2 \rangle\) reflects the thermally averaged distribution of accessible vibrational states. Temperature dependent damping.

Completing the square, we have:

\[
\sigma_{\text{avr}}(\omega) = |\mu_{eg}|^2 \left( \frac{\pi}{\langle \omega^2 \rangle} \right)^{\frac{1}{2}} \exp \left[ -\frac{(\omega - \omega_{eg} - \langle \omega \rangle)^2}{2\langle \omega^2 \rangle} \right]
\]

Gaussian centered at electronic resonance plus reorganization energy. Width is temperature dependent.

**Relaxation**

We didn’t include damping originally, but clearly, this will lead to broadening of delta function transitions. In fact, we can think of coupling to a continuous distribution of harmonic oscillators as described above as a damping of the electronic coherence.
Time Correlation Functions Describe Electronic Spectra

What we demonstrated was that the lineshape is the Fourier transform of the dipole correlation function.

\[ C_{\mu\mu}(t) = \sum_{i} p_{i} \langle i | e^{iH_{\mu}/\hbar} \mu e^{-iH_{\mu}} \mu | i \rangle \]

where \(|i\rangle = |g,n\rangle, |e,n\rangle\). We note that this was written then as the overlap between two time-resolving wave packets on the initial and final surfaces \(|E\rangle\) and \(|G\rangle\).

\[ C_{\mu\mu}(t) = \langle G | e^{iH_{\mu}/\hbar} \mu e^{-iH_{\mu}} \mu | G \rangle \]
\[ = \langle G | e^{iH_{\mu}} \mu e^{-iH_{\mu}} \mu | G \rangle \]
\[ \approx |\mu_{eg}|^{2} \langle \phi_{g}(t) | \phi_{e}(t) | e^{-i(E_{e}-E_{g})t} \rangle \]
\[ \langle \phi_{g} \rangle = \langle g | e^{iH_{\mu}} | \phi_{e} = e^{-iH_{\mu}} | e \rangle \]

This is a perfectly general expression, and need not only apply to two displaced harmonic oscillators. The absorption spectrum is the Fourier transform of the time-dependent overlap between excited and ground state nuclear wave packets.

One way of calculating this for thermal distributions is given by Ratner (Ch. 7) and Heller (1983). We can write the correlation function as:

\[ C_{\mu\mu}(t) = \frac{1}{Z} Tr \left\{ e^{iH_{\mu}/\hbar} \mu e^{-iH_{\mu}} \mu e^{-\beta H} \right\} \]

where the equilibrium density matrix is \(e^{-\beta H}\) and \(Z = Tr(e^{-\beta H})\). Now from the cyclic invariance to the trace:

\[ C_{\mu\mu}(t) = \frac{1}{Z} Tr \left\{ e^{-\beta H} e^{iH_{\mu}/\hbar} \mu e^{-iH_{\mu}} \mu \right\} \]
\[ = \frac{1}{Z} Tr \left\{ e^{iH_{\mu}(t+\tau)} \mu e^{-iH_{\mu}} \mu \right\} \]

where \(\tau = -i\beta \hbar\). So, we can interpret this as an overlap between a wave packet in the excited state and time evolution on the ground state with a complex time assignment.