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5.74 Introductory Quantum Mechanics II
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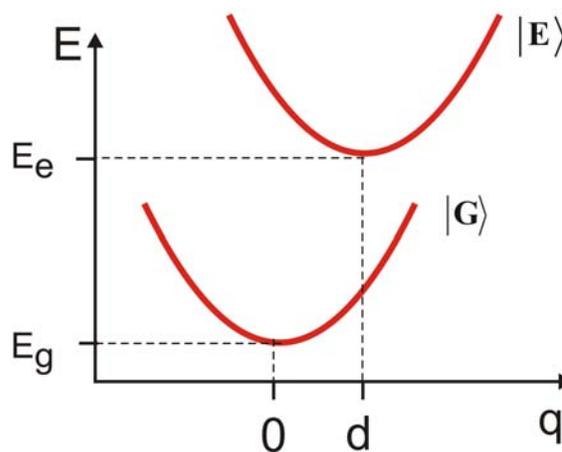
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6.4 NUCLEAR MOTION COUPLED TO ELECTRONIC TRANSITION¹

Here we will start with one approach to a class of widely used models for the coupling of nuclear motions to an electronic transition that takes many forms and 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 and vibrational states to intramolecular vibrations or solvent; or coupling of electronic states in solids or semiconductors to phonons. Further extensions of this model can be used to describe fundamental chemical rate processes, interactions of a molecule with a dissipative or fluctuating environment, and Marcus Theory for non-adiabatic electron transfer.

Two-electronic state as displaced harmonic oscillators

We are interested in describing the electronic absorption spectrum for the case that the electronic energy depends on nuclear configuration. The simplified model for this is two identical harmonic oscillators potentials displaced from one another along a nuclear coordinate, and whose 0-0 energy splitting is $E_e - E_g$. We will calculate the electronic absorption spectrum in the interaction picture ($H = H_0 + V(t)$) using the time-correlation



function for the dipole operator. The Hamiltonian for the matter represents two Born-Oppenheimer surfaces

$$H_0 = |G\rangle H_G \langle G| + |E\rangle H_E \langle E| \quad (6.1)$$

where the Hamiltonian describing the ground and excited states have contributions from the nuclear energy and the electronic energy

$$\begin{aligned} H_G &= E_g + H_g \\ H_E &= E_e + H_e \end{aligned} \quad (6.2)$$

The harmonic vibrational Hamiltonian has the same curvature in the ground and excited states, but the excited state is displaced by d relative to the ground state.

$$H_g = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (6.3)$$

$$H_e = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 (q-d)^2 \quad (6.4)$$

Now we are in a position to evaluate the dipole correlation function

$$C_{\mu\mu}(t) = \sum_{n=E,G} p_n \langle n | e^{iH_0 t/\hbar} \bar{\mu} e^{-iH_0 t/\hbar} \bar{\mu} | n \rangle. \quad (6.5)$$

with the time propagator

$$e^{-iH_0 t/\hbar} = |G\rangle e^{-i(H_g + E_g)t/\hbar} \langle G| + |E\rangle e^{-i(H_e + E_e)t/\hbar} \langle E| \quad (6.6)$$

We begin by making two approximations:

- 1) **Born-Oppenheimer Approximation**. Although this is implied in eq. (6.2) when we write the electronic energy as independent of q , specifically it means that we can write the state of the system as a product state in the electronic and nuclear configuration:

$$|G\rangle = |g, n\rangle \quad (6.7)$$

- 2) **Condon Approximation**. This approximation states that there is no nuclear dependence for the dipole operator. It is only an operator in the electronic states.

$$\bar{\mu} = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g| \quad (6.8)$$

Under all reasonable conditions, the system will only be on the ground electronic state at equilibrium, $|g, n\rangle$, and with the expression for the dipole operator (6.8), we find:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i(E_e - E_g)t/\hbar} \langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \rangle \quad (6.9)$$

Here the oscillations at the electronic energy gap are separated from the nuclear dynamics in the final factor, sometimes known as the dephasing function:

$$\begin{aligned} F(t) &= \langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \rangle \\ &= \langle U_g^\dagger U_e \rangle \end{aligned} \quad (6.10)$$

Note that physically the dephasing function describes the time-dependent overlap of the initial nuclear wavefunction on the ground state with the time-evolution of the same wavepacket on the when initially projected onto the excited state

$$F(t) = \langle \varphi_g(t) | \varphi_e(t) \rangle. \quad (6.11)$$

This is a perfectly general expression that does not depend on the particular form of the potential. If you have knowledge of the nuclear and electronic eigenstates or the nuclear dynamics on your ground and excited state surfaces, this expression is your route to the absorption spectrum.²

To evaluate $F(t)$, it helps to realize that we can write the nuclear Hamiltonians as

$$H_g = \hbar\omega_0 \left(a^\dagger a + \frac{1}{2} \right) \quad (6.12)$$

$$H_e = \hat{D}^\dagger H_g \hat{D}. \quad (6.13)$$

Here D is the spatial displacement operator

$$\hat{D} = \exp(-ipd/\hbar) \quad (6.14)$$

which shifts an operator in space:

$$\hat{D}^\dagger q \hat{D} = q + d. \quad (6.15)$$

This allows us to express the excited state Hamiltonian in terms of a shifted ground state Hamiltonian in eq. (6.13), but also allows us to relate the time-propagators on the ground and excited states

$$e^{-iH_e t/\hbar} = \hat{D}^\dagger e^{-iH_g t/\hbar} \hat{D}. \quad (6.16)$$

Substituting eq. (6.16) into eq. (6.10) allows us to write

$$\begin{aligned} F(t) &= \langle U_g^\dagger e^{-idp/\hbar} U_g e^{idp/\hbar} \rangle \\ &= \langle e^{-idp(t)/\hbar} e^{idp(0)/\hbar} \rangle \end{aligned} \quad (6.17)$$

since

$$p(t) = U_g^\dagger p(0) U_g. \quad (6.18)$$

Up to now, everything we've written is general to any form of the potential, but here we will continue by evaluating the results for the specific case of a harmonic nuclear potential. The time-evolution of p is obtained by evaluating eq. (6.18) by applying eq. (6.12) to

$$p = \frac{i}{\sqrt{2}} (a^\dagger - a) \sqrt{m\hbar\omega_0}. \quad (6.19)$$

Remembering $a^\dagger a = n$, we find

$$\begin{aligned}
U_g^\dagger a U_g &= e^{i n \omega_0 t} a e^{-i n \omega_0 t} = a e^{i(n-1)\omega_0 t} e^{-i n \omega_0 t} = a e^{-i \omega_0 t} \\
U_g^\dagger a^\dagger U_g &= a^\dagger e^{+i \omega_0 t}
\end{aligned}
\tag{6.20}$$

which gives

$$p(t) = i \sqrt{\frac{m \hbar \omega_0}{2}} (a^\dagger e^{i \omega_0 t} - a e^{-i \omega_0 t}). \tag{6.21}$$

So for the dephasing function we now have

$$F(t) = \left\langle \exp \left[\underline{d} (a^\dagger e^{i \omega_0 t} - a e^{-i \omega_0 t}) \right] \exp \left[-\underline{d} (a^\dagger - a) \right] \right\rangle, \tag{6.22}$$

where we have defined a dimensionless displacement variable

$$\underline{d} = d \sqrt{\frac{m \omega_0}{2 \hbar}}. \tag{6.23}$$

Since a^\dagger and a do not commute ($[a^\dagger, a] = -1$), we split the exponential operators using the identities

$$e^{\hat{A} + \hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2} [\hat{A}, \hat{B}]} \tag{6.24}$$

$$e^{\lambda a^\dagger + \mu a} = e^{\lambda a^\dagger} e^{\mu a} e^{\frac{1}{2} \lambda \mu}. \tag{6.25}$$

This leads to

$$\begin{aligned}
F(t) &= \left\langle \exp \left[\underline{d} a^\dagger e^{i \omega_0 t} \right] \exp \left[-\underline{d} a e^{-i \omega_0 t} \right] \exp \left[-\frac{1}{2} \underline{d}^2 \right] \right. \\
&\quad \left. \times \exp \left[-\underline{d} a^\dagger \right] \exp \left[\underline{d} a \right] \exp \left[-\frac{1}{2} \underline{d}^2 \right] \right\rangle
\end{aligned}
\tag{6.26}$$

Now to simplify our work, let's specifically consider the low temperature case in which we are only in the ground vibrational state at equilibrium $|n\rangle = |0\rangle$. Since $a|0\rangle = 0$ and $\langle 0|a^\dagger = 0$,

$$\begin{aligned}
e^{-\lambda a} |0\rangle &= |0\rangle \\
\langle 0| e^{\lambda a^\dagger} &= \langle 0|
\end{aligned}
\tag{6.27}$$

and

$$F(t) = e^{-\underline{d}^2} \left\langle 0 \left| \exp \left[-\underline{d} a e^{-i \omega_0 t} \right] \exp \left[-\underline{d} a^\dagger \right] \right| 0 \right\rangle. \tag{6.28}$$

Since the operator defined through an expansion in raising operators, this expression is a bit tough to evaluate, as is. However, the evaluation becomes as easy as the previous step if we can exchange order of operators. Since

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{B}} e^{\hat{A}} e^{-[\hat{B}, \hat{A}]}, \quad (6.29)$$

we write

$$\begin{aligned} F(t) &= e^{-d^2} \langle 0 | \exp[-\underline{d} a^\dagger] \exp[-\underline{d} a e^{-i\omega_0 t}] \exp[\underline{d}^2 e^{-i\omega_0 t}] | 0 \rangle \\ &= \exp[\underline{d}^2 (e^{-i\omega_0 t} - 1)] \end{aligned} \quad (6.30)$$

So finally, we have the dipole correlation function:

$$C_{\mu\mu}(t) = |\mu_{eg}|^2 \exp[-i\omega_{eg}t + D(e^{-i\omega_0 t} - 1)] \quad (6.31)$$

D is known as the Huang-Rhys parameter, and is a dimensionless factor related to the mean square displacement

$$D = \underline{d}^2 = \frac{d^2 m \omega_0}{2\hbar} \quad (6.32)$$

It represents the strength of coupling to the nuclear degrees of freedom. Note we can write our correlation function as

$$C(t) = \sum_n p_n |\mu_{mn}|^2 e^{-i\omega_{mn}t - g(t)}. \quad (6.33)$$

Here $g(t)$ is our lineshape function

$$g(t) = -D(e^{-i\omega_0 t} - 1). \quad (6.34)$$

Absorption Lineshape and Franck-Condon Transitions

The absorption lineshape is obtained by Fourier transforming eq. (6.31)

$$\begin{aligned}\sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{\mu\mu}(t) \\ &= |\mu_{eg}|^2 e^{-D} \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg}t} \exp[De^{-i\omega_0 t}]\end{aligned}\quad (6.35)$$

If we now expand the final term as

$$\exp[De^{-i\omega_0 t}] = \sum_{j=0}^{\infty} \frac{1}{j!} D^j (e^{-i\omega_0 t})^j, \quad (6.36)$$

the lineshape is

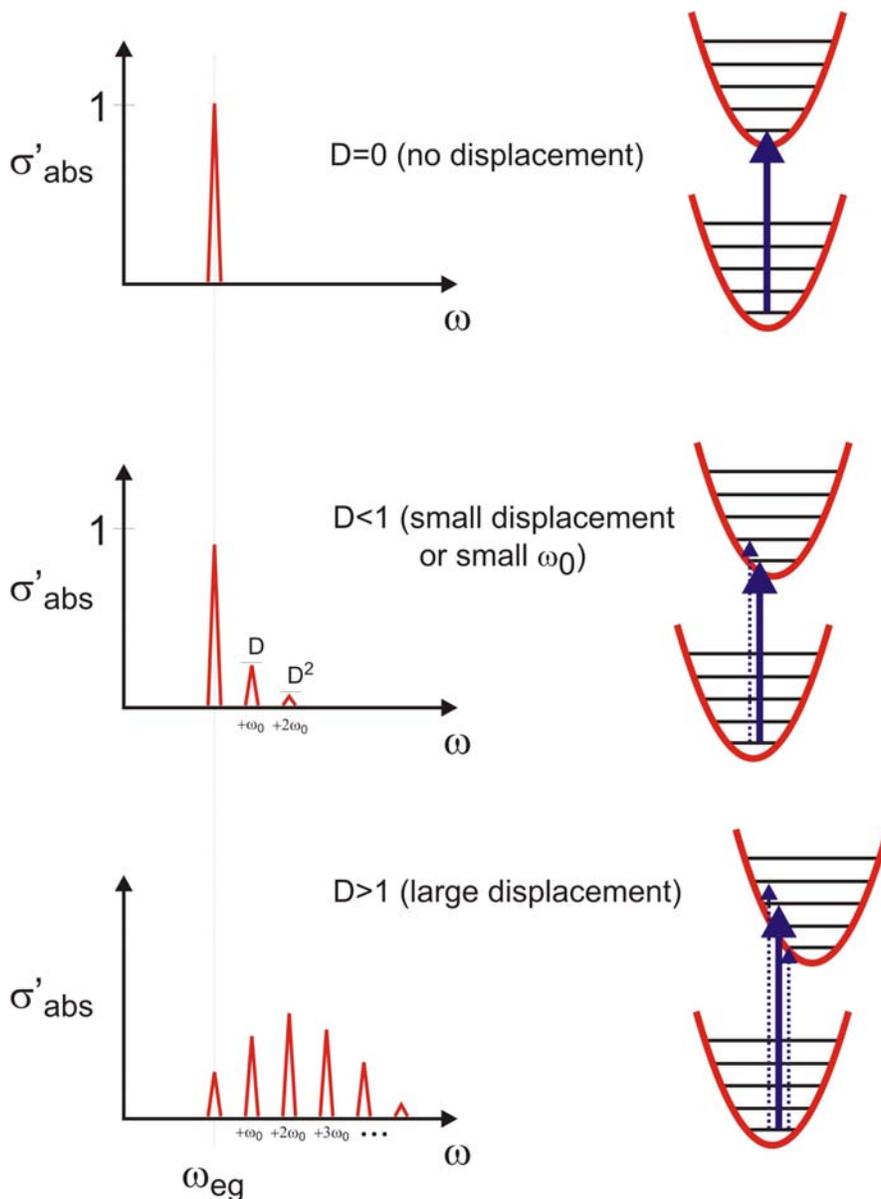
$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 \sum_{j=0}^{\infty} e^{-D} \frac{1}{j!} D^j \delta(\omega - \omega_{eg} - j\omega_0). \quad (6.37)$$

The spectrum is a progression of absorption peaks rising from ω_{eg} , separated by ω_0 with a Poisson distribution of intensities. This is a vibrational progression accompanying the electronic transition. The amplitude of each of these peaks are given by the Franck-Condon coefficients for the overlap of vibrational states in the ground and excited states

$$|\langle 0|v\rangle|^2 = e^{-D} \frac{1}{v!} D^v \quad (6.38)$$

The intensities of these peaks are dependent on D , which is a measure of the coupling strength between nuclear and electronic degrees of freedom.

Let's plot the normalized absorption lineshape $\sigma'_{abs}(\omega) = \frac{\sigma_{abs}(\omega)}{e^{-D} |\mu_{eg}|^2}$ as a function of D .



For $D < 1$, the dependence of the energy gap on q is weak and the absorption maximum is at ω_{eg} with $n = 0$, with the amplitude of the vibronic progression falling off at D^n . For $D \gg 1$ (strong coupling), the transition with the maximum intensity is found for peak at $n \approx D$. So D corresponds roughly to the mean number of vibrational quanta excited from $q = 0$ in the ground

state. This is the Franck-Condon principle, that transition intensities are dictated by the vertical overlap between nuclear wavefunctions in the two electronic surfaces.

To investigate the envelope for these transitions, we can perform a short time expansion of the correlation function applicable for $t < 1/\omega_0$. If we approximate the first term with damping

$$\exp(-i\omega_0 t) \approx 1 - i\omega_0 t - \frac{1}{2} \omega_0^2 t^2, \quad (6.39)$$

then the lineshape is

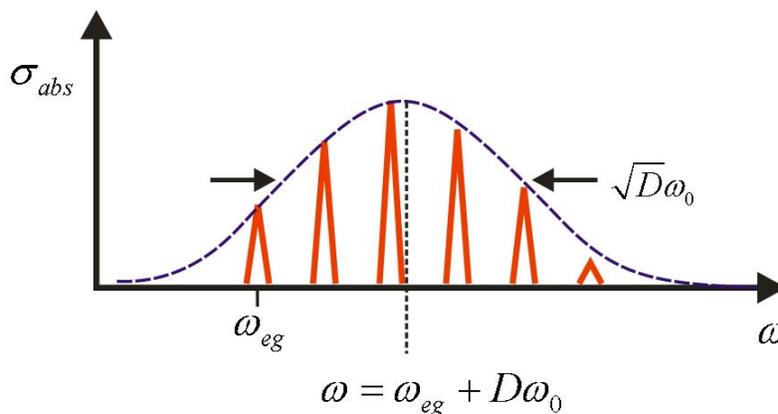
$$\begin{aligned} \sigma_{abs}(\omega) &= \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\omega_{eg} t} e^{D(\exp(-i\omega_0 t) - 1)} \\ &\approx \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} t)} e^{D[-i\omega_0 t - \frac{1}{2} \omega_0^2 t^2]} \\ &= \left| \mu_{eg} \right|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} - D\omega_0)t} e^{-\frac{1}{2} D\omega_0^2 t^2} \end{aligned} \quad (6.40)$$

This can be solved by completing the square, giving

$$\sigma_{abs}(\omega) = \sqrt{\pi} \left| \mu_{eg} \right|^2 \exp \left[-\frac{(\omega - \omega_{eg} - D\omega_0)^2}{2D\omega_0^2} \right]. \quad (6.41)$$

The envelope has a Gaussian profile which is centered at Franck-Condon vertical transition

$$\omega = \omega_{eg} + D\omega_0. \quad (6.42)$$



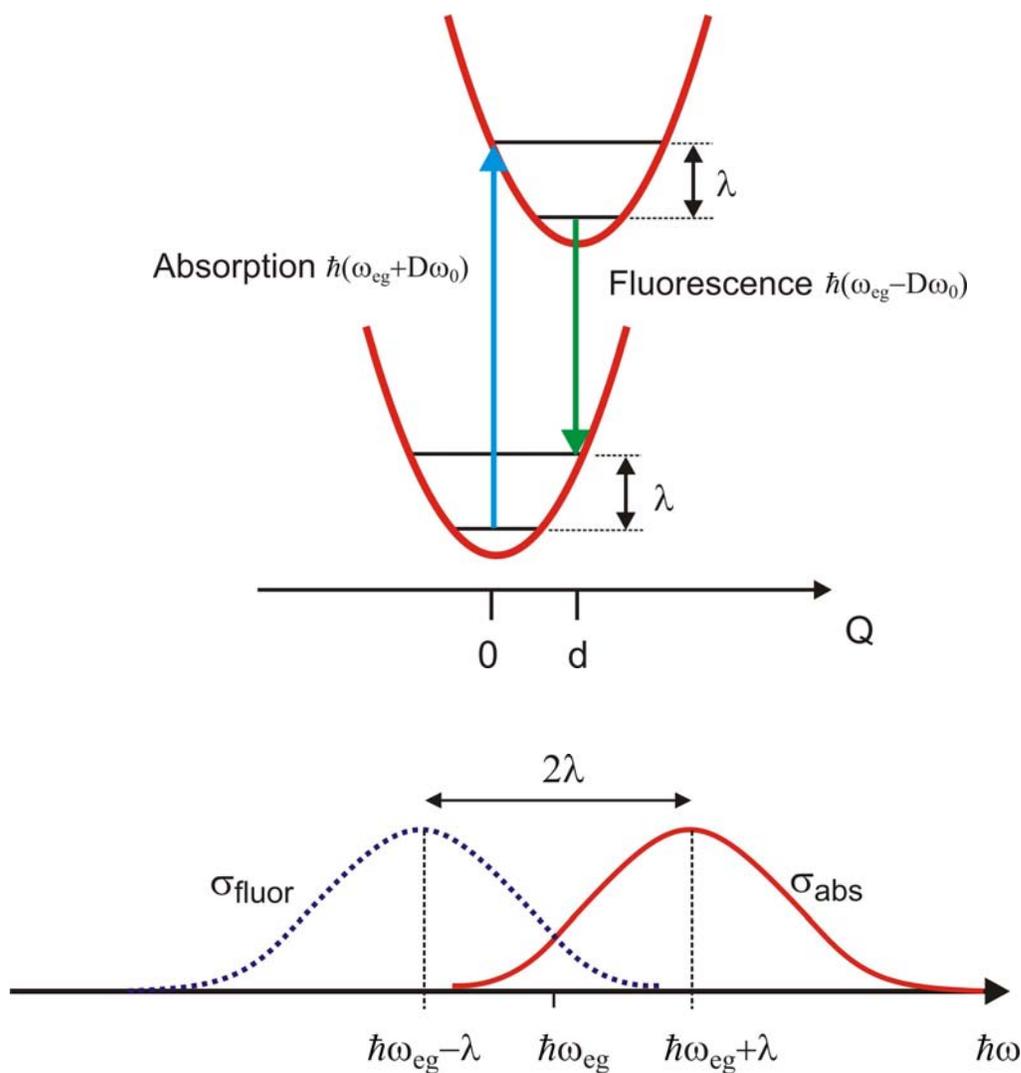
Thus we can equate D with the mean number of vibrational quanta excited in $|E\rangle$ on absorption from the ground state. Also, we can define the vibrational energy in $|E\rangle$ on excitation at $q = 0$

$$\lambda = D\hbar\omega_0 = \frac{1}{2} m\omega_0^2 d^2. \quad (6.43)$$

λ is known as the reorganization energy. This is the energy that must be dissipated for vibrational relaxation on the excited state surface.

Note also that λ is the vibrational energy on the ground state surface at the excited state minimum $q = d$. This is the point for vertical transitions for emission from the excited state minimum to the ground state. Since vibrational energy on $|e\rangle$ is dissipated quickly, we expect fluorescence to be red-shifted by 2λ and have mirror symmetry with respect to the absorption:

$$\begin{aligned} \sigma_{abs}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg})t - g(t)} \\ \sigma_{fluor}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg} - 2\lambda)t - g^*(t)} \\ g(t) &= D(e^{-i\omega_0 t} - 1) \end{aligned} \tag{6.44}$$



Coupling to a Harmonic Bath

To further interpret this example, it is worth noting a similarity between the Hamiltonian for this displaced harmonic oscillator problem, and a general form for the coupling of an electronic “system” which is observed, and a harmonic oscillator “bath” whose degrees of freedom are dark to the observation, but which influence the behavior of the system. This is a preview of the concepts that we will develop more carefully later for the description of fluctuations in spectroscopy.

We demonstrated the electronic absorption lineshape derives from a dipole correlation function which describes the overlap between two wave packets evolving on the ground and excited surfaces $|E\rangle$ and $|G\rangle$.

$$\begin{aligned} C_{\mu\mu}(t) &= \langle G | e^{iH_0 t} \mu e^{-iH_0 t} \mu | G \rangle \\ &= \langle G | e^{iH_G t} \mu e^{-iH_E t} \mu | G \rangle \\ &\approx |\mu_{eg}|^2 \langle \varphi_g(t) | \varphi_e(t) \rangle e^{-i(E_e - E_g)t} \end{aligned} \quad (6.45)$$

$$\langle \varphi_g(t) | = \langle g | e^{iH_g t} \quad | \varphi_e(t) \rangle = e^{-iH_e t} | e \rangle \quad (6.46)$$

This is a perfectly general expression, which indicates that the absorption spectrum is the Fourier transform of the time-dependent overlap between excited and ground state nuclear wave packets.

Expressed in a slightly different physical picture, we can also conceive of this process as nuclear motions that act to modulate the electronic energy gap ω_{eg} . We can imagine re-writing the same problem in terms of a Hamiltonian that describes the electronic energy gap’s dependence on q , i.e. its variation relative to ω_{eg} . Defining an Energy Gap Hamiltonian:

$$H_{eg} = H_E - H_G - \hbar\omega_{eg} = H_e - H_g \quad (6.47)$$

We can see that this leads to a problem for an electronic transition linearly coupled to a harmonic oscillator:

$$\begin{aligned} H_0 &= H_e + E_e + H_g + E_g \\ &= \hbar\omega_{eg} + H_{eg} + 2H_g \end{aligned} \quad (6.48)$$

Noting that

$$H_g = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (6.49)$$

we see

$$\begin{aligned}
 H_{eg} &= \frac{1}{2} m \omega_0^2 (q-d)^2 - \frac{1}{2} m \omega_0^2 q^2 \\
 &= -m \omega_0^2 d q + \frac{1}{2} m \omega_0^2 d^2 \\
 &= c q + \lambda
 \end{aligned}
 \tag{6.50}$$

The Energy Gap Hamiltonian describes a linear coupling between the electronic transition and a harmonic oscillator. The strength of the coupling is c and the Hamiltonian has a constant energy offset value given by the reorganization energy.

This discussion illustrates how the displaced harmonic oscillator and Energy Gap Hamiltonian are isomorphic with a Hamiltonian for an electronic “system” coupled to a harmonic oscillator “bath”:

$$H_0 = H_S + H_B + H_{SB} \tag{6.51}$$

$$\begin{aligned}
 H_S &= |e\rangle (E_e + \lambda) \langle e| + |g\rangle E_g \langle g| \\
 H_B &= \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \\
 H_{SB} &= m \omega_0^2 d q
 \end{aligned}
 \tag{6.52}$$

Here H_{SB} describes the interaction of the electronic system (H_S) with the vibrational bath (H_B). It is a linear coupling Hamiltonian, meaning that it is linear in the bath coordinate has a strength-of-coupling term ($m \omega_0^2 d$).

Coupling to Multiple Vibrations or a Continuum

The Hamiltonians we have written so far describe coupling to a single bath degree of freedom, but the results can be generalized to many vibrations or a continuum of nuclear motions. This approach is used to treat the spectroscopy of dissipative systems, through the interaction of a system with a continuum of states that are dark to the field, and which we treat in a statistical manner, in addition to describing fluctuations in spectroscopy.

So, what happens if the electronic transition is coupled to many vibrational coordinates, each with its own displacement? The extension is straightforward if the modes are independent, i.e. we can conceive of the bath vibrations as harmonic normal modes. 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 in the electronic and nuclear occupation, i.e. $|G\rangle = |g; n_1, n_2, \dots, n_i\rangle$.

The dipole correlation function is then

$$\begin{aligned} C_{\mu\mu}(t) &= |\mu_{eg}|^2 e^{-i\omega_{eg}t} \cdot F_1(t) \cdot F_2(t) \cdots F_N(t) \\ &= |\mu_{eg}|^2 e^{-i\omega_{eg}t} \left[\prod_{i=1}^N \exp\left[D_i(e^{-i\omega_i t} - 1)\right] \right] \\ &= |\mu_{eg}|^2 e^{-i\omega_{eg}t - g(t)} \end{aligned} \quad (6.53)$$

with

$$g(t) = \sum_i D_i (e^{-i\omega_i t} - 1) \quad (6.54)$$

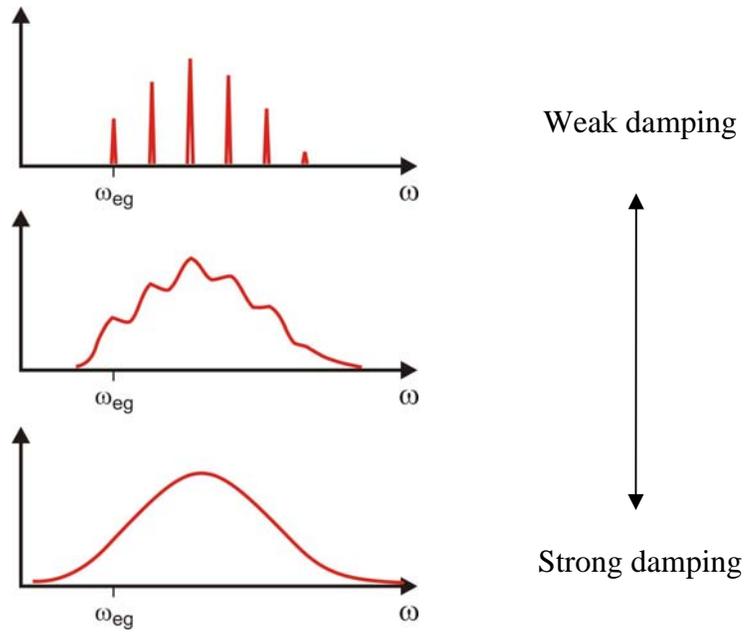
For independent modes, the dipole correlation function is just a product of multiple dephasing functions that characterize the time-evolution of the different vibrations. In the time-domain this would lead to a complex beating pattern, which in the frequency domain appears as a spectrum with several superimposed vibronic progressions that follow the rules developed above.

Taking this a step further, the generalization to a continuum of nuclear states should be apparent. This approach describes the absorption lineshape that results from dephasing or irreversible relaxation induced by coupling to a continuum. Given that we have a continuous frequency distribution of normal modes characterized by a density of states, $W(\omega)$, and a frequency dependent coupling, $D(\omega)$, we can change the sum in eq. (6.54) to an integral over the distribution

$$g(t) = \int d\omega W(\omega) D(\omega) (e^{-i\omega t} - 1). \quad (6.55)$$

Here the product $W(\omega) D(\omega)$ can be considered a coupling-weighted density of states, sometimes referred to as a spectral density.

What this treatment does is provide a way of introducing a bath of states that the spectroscopically interrogated transition couples with. You can see that if the distribution of states is very broad and coupling is a constant, we can associate $g(t)$ with a constant Γ , and we obtain a Lorentzian lineshape. So coupling to a continuum or bath provides a way of introducing relaxation effects or damping of the electronic coherence in the absorption spectrum. More generally the lineshape function will be complex, where the real part describes damping and the imaginary part modulates the primary frequency and leads to fine structure.



Displaced Harmonic Oscillator Model at Finite Temperature

If you solve the problem for coupling to a single vibrational mode at finite temperatures, where excited vibrational levels in the ground state are initially populated, you find

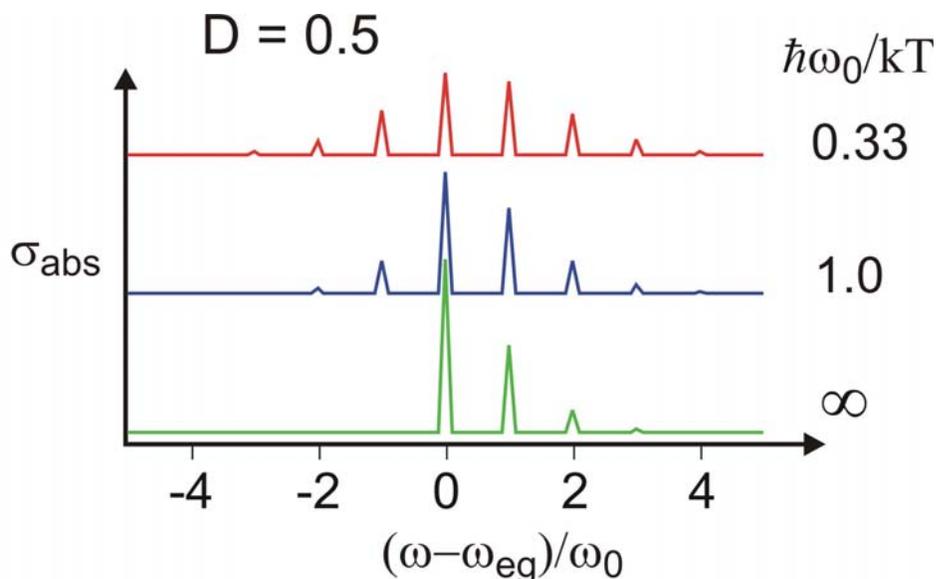
$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} \exp\left[D\left[(\bar{n}+1)(e^{-i\omega_0 t} - 1) + \bar{n}(e^{+i\omega_0 t} - 1)\right]\right]. \quad (6.56)$$

$$\bar{n} = (e^{\beta\hbar\omega_0} - 1)^{-1} \quad (6.57)$$

\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 and Fourier transforming gives

$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 e^{-D(2\bar{n}+1)} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \left(\frac{D^{j+k}}{j!k!}\right) (\bar{n}+1)^j \bar{n}^k \delta(\omega - \omega_{eg} - (j-k)\omega_0) \quad (6.58)$$

The first summation over j (setting all k to zero) looks as before, but the second summation now includes “hot bands”: transitions upward from thermally populated vibrational states with a net decrease in vibrational quantum number on excitation. Note their amplitudes depend on the thermal occupation.



We can extend this description to describe coupling to a many independent nuclear modes or coupling to a continuum. We write the state of the system in terms of the electronic state and the nuclear quantum numbers, i.e. $|E\rangle = |e; n_1, n_2, n_3 \dots\rangle$, and from that:

$$F(t) = \exp \left[\sum_j D_j \left[(\bar{n}_j + 1) (e^{-i\omega_j t} - 1) + \bar{n}_j (e^{+i\omega_j t} - 1) \right] \right] \quad (6.59)$$

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

$$F(t) = \exp \left[\int d\omega W(\omega) D(\omega) \left[(\bar{n}(\omega) + 1) (e^{-i\omega t} - 1) + \bar{n}(\omega) (e^{i\omega t} - 1) \right] \right] \quad (6.60)$$

$D(\omega)$ is the frequency dependent coupling. Let's look at the envelope of the nuclear structure on the transition by doing a short-time expansion on the complex exponential as in eq. (6.39)

$$F(t) = \exp \left[\int d\omega D(\omega) W(\omega) \left(-i\omega t - (2\bar{n} + 1) \frac{\omega^2 t^2}{2} \right) \right]. \quad (6.61)$$

The lineshape is calculated from

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt e^{i(\omega - \omega_{eg})t} \exp[-i\langle\omega\rangle t] \exp\left[-\frac{1}{2}\langle\omega^2\rangle t^2\right] \quad (6.62)$$

where we have defined the mean vibrational excitation on absorption

$$\begin{aligned} \langle\omega\rangle &= \int d\omega W(\omega) D(\omega) \omega \\ &= \lambda / \hbar \end{aligned} \quad (6.63)$$

and

$$\langle\omega^2\rangle = \int d\omega W(\omega) D(\omega) \omega^2 (2\bar{n}(\omega) + 1). \quad (6.64)$$

$\langle\omega^2\rangle$ reflects the thermally averaged distribution of accessible vibrational states. Completing the square, eq. (6.62) gives

$$\sigma_{abs}(\omega) = |\mu_{eg}|^2 \sqrt{\frac{\pi}{\langle\omega^2\rangle}} \exp \left[\frac{-(\omega - \omega_{eg} - \langle\omega\rangle)^2}{2\langle\omega^2\rangle} \right] \quad (6.65)$$

The lineshape is Gaussian, with a transition maximum at the electronic resonance plus reorganization energy. The width of the Gaussian is temperature-dependent and given by eq. (6.64).

Readings

1. See also:

Mukamel, S. *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995), p. 217, also p. 189.

Nitzan, A. *Chemical Dynamics in Condensed Phases* (Oxford University Press, New York, 2006). Chapter 12, Sec. 5.

2. For further on this see:

Chapter 9 of Schatz, G. C. & Ratner, M. A. *Quantum Mechanics in Chemistry* (Dover Publications, Mineola, NY, 2002).

Also, Reimers, JR, Wilson, KR, Heller, EJ Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra. *J. Chem. Phys.* **79**, 4749 (1983).