12. COUPLING OF ELECTRONIC AND NUCLEAR MOTION

12.1. The Displaced Harmonic Oscillator Model

Here we will discuss the displaced harmonic oscillator (DHO), a widely used model that describes the coupling of nuclear motions to electronic states. Although it has many applications, we will look at the specific example of electronic absorption experiments, and thereby gain insight into the vibronic structure in absorption spectra. Spectroscopically, it can also be 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. As we will see, 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 nonadiabatic electron transfer.

The DHO and Electronic Absorption

Molecular excited states have geometries that are different from the ground state configuration as a result of varying electron configuration. This parametric dependence of electronic energy on nuclear configuration results in a variation of the electronic energy gap between states as one stretches bond vibrations of the molecule. We are interested in describing how this effect

influences the electronic absorption spectrum, and thereby gain insight into how one experimentally determines the coupling of between electronic and nuclear degrees of freedom. We consider electronic transitions between bound potential energy surfaces for a ground and excited state as we displace a nuclear coordinate q. The simplified model consists of two harmonic oscillators potentials whose 0-0 energy splitting is E_e - E_g and which depends on q. We will calculate the absorption



spectrum in the interaction picture using the time-correlation function for the dipole operator.

We start by writing a Hamiltonian that contains two terms for the potential energy surfaces of the electronically excited state $|E\rangle$ and ground state $|G\rangle$

$$H_0 = H_G + H_E \tag{12.1}$$

These terms describe the dependence of the electronic energy on the displacement of a nuclear coordinate q. Since the state of the system depends parametrically on the level of vibrational

excitation, we describe it using product states in the electronic and nuclear configuration, $|\Psi\rangle = |\psi_{elec}, \Phi_{nuc}\rangle$, or in the present case

$$|G\rangle = |g, n_g\rangle \quad |E\rangle = |e, n_e\rangle$$
(12.2)

Implicit in this model is a Born-Oppenheimer approximation in which the product states are the eigenstates of H_0 , i.e. $H_G | G \rangle = (E_g + E_{n_x}) | G \rangle$.

The Hamiltonian for each surface contains an electronic energy in the absence of vibrational excitation, and a vibronic Hamiltonian that describes the change in energy with nuclear displacement.

$$H_{G} = |g\rangle E_{g} \langle g| + H_{g} (q)$$

$$H_{E} = |e\rangle E_{e} \langle e| + H_{e} (q)$$
(12.3)

For our purposes, the vibronic Hamiltonian is harmonic and has the same curvature in the ground and excited states, however, the excited state is displaced by d relative to the ground state along a coordinate q.

$$H_g = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$$
(12.4)

$$H_{e} = \frac{p^{2}}{2m} + \frac{1}{2}m\omega_{0}^{2}(q-d)^{2}$$
(12.5)

The operator q acts only to changes the degree of vibrational excitation on the $|E\rangle$ or $|G\rangle$ surface.

We now wish to evaluate the dipole correlation function

$$C_{\mu\mu}(t) = \langle \overline{\mu}(t)\overline{\mu}(0) \rangle$$

= $\sum_{\ell=E,G} p_{\ell} \langle \ell | e^{iH_0 t/\hbar} \overline{\mu} e^{-iH_0 t/\hbar} \overline{\mu} | \ell \rangle$ (12.6)

Here p_{ℓ} is the joint probability of occupying a particular electronic and vibrational state, $p_{\ell} = p_{\ell,elec} p_{\ell,vib}$. The time propagator is

$$e^{-iH_0t/\hbar} = |G\rangle \ e^{-iH_Gt/\hbar} \langle G| + |E\rangle \ e^{-iH_Et/\hbar} \langle E|$$
(12.7)

We begin by making the Condon Approximation, which states that there is no nuclear dependence for the dipole operator. It is only an operator in the electronic states.

$$\overline{\mu} = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g|$$
(12.8)

This approximation implies that transitions between electronic surfaces occur without a change in nuclear coordinate, which on a potential energy diagram is a vertical transition. Under typical conditions, the system will only be on the ground electronic state at equilibrium, and substituting eqs. (12.7) and (12.8) into (12.6), we find:

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^{2} e^{-i(E_{e}-E_{g})t/\hbar} \left\langle e^{iH_{g}t/\hbar} e^{-iH_{e}t/\hbar} \right\rangle$$
(12.9)

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

$$F(t) = \left\langle e^{iH_g t/\hbar} e^{-iH_e t/\hbar} \right\rangle$$

= $\left\langle U_g^{\dagger} U_e \right\rangle$ (12.10)

The average $\langle \dots \rangle$ in equations (12.9) and (12.10) is only over the vibrational states $|n_g\rangle$. Note that physically the dephasing function describes the time-dependent overlap of the nuclear wavefunction on the ground state with the time-evolution of the same wavepacket initially projected onto the excited state

$$F(t) = \left\langle \varphi_g(t) \middle| \varphi_e(t) \right\rangle \tag{12.11}$$

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.¹

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

$$H_g = \hbar \omega_0 \left(a^{\dagger} a + \frac{1}{2} \right) \tag{12.12}$$

$$H_e = \hat{D}H_g\hat{D}^\dagger \tag{12.13}$$

Here \hat{D} is the spatial displacement operator

$$\hat{D} = \exp(-i\hat{p}d/\hbar) \tag{12.14}$$

which shifts an operator in space as:

$$\hat{D}\hat{q}\hat{D}^{\dagger} = \hat{q} - d \tag{12.15}$$

^{1.} For further on this see:

Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; Ch. 9. Reimers, J. R.; Wilson, K. R.; Heller, E. J., Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra. *J. Chem. Phys.* **1983**, *79*, 4749-4757.

Note \hat{p} is only an operator in the vibrational degree of freedom. We can now express the excited state Hamiltonian in terms of a shifted ground state Hamiltonian in eq. (12.13), and also relate the time propagators on the ground and excited states

$$e^{-iH_{e}t/\hbar} = \hat{D}e^{-iH_{g}t/\hbar}\hat{D}^{\dagger}$$
(12.16)

Substituting eq. (12.16) into eq. (12.10) allows us to write

$$F(t) = \left\langle U_{g}^{\dagger} e^{-idp/\hbar} U_{g} e^{idp/\hbar} \right\rangle$$

= $\left\langle \hat{D}(t) \hat{D}^{\dagger}(0) \right\rangle$ (12.17)

This says that the effect of the nuclear motion in the dipole correlation function can be expressed as a time-correlation function for the displacement of the vibration.

To evaluate eq. (12.17) we write it as

$$F(t) = \left\langle e^{-id\hat{p}(t)/\hbar} e^{id\hat{p}(0)/\hbar} \right\rangle$$
(12.18)

since

$$\hat{p}(t) = U_g^{\dagger} \, \hat{p}(0) U_g \tag{12.19}$$

The time-evolution of \hat{p} is obtained by expressing it in raising and lowering operator form,

$$\hat{p} = i\sqrt{\frac{m\hbar\omega_0}{2}} \left(a^{\dagger} - a\right) \tag{12.20}$$

and evaluating eq. (12.19) using eq. (12.12). Remembering $a^{\dagger}a = n$, we find

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

$$U_g^{\dagger} a^{\dagger} U_g = a^{\dagger} e^{+i\omega_0 t}$$
(12.21)

which gives

$$\hat{p}(t) = i\sqrt{\frac{m\hbar\omega_0}{2}} \left(a^{\dagger}e^{i\omega_0 t} - a e^{-i\omega_0 t}\right)$$
(12.22)

So for the dephasing function we now have

$$F(t) = \left\langle \exp\left[d\left(a^{\dagger}e^{i\omega_{0}t} - a e^{-i\omega_{0}t}\right)\right] \exp\left[-d\left(a^{\dagger} - a\right)\right]\right\rangle$$
(12.23)

where we have defined a dimensionless displacement variable

$$d = d\sqrt{\frac{m\omega_0}{2\hbar}}$$
(12.24)

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

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}\left[\hat{A},\hat{B}\right]}.$$
(12.25)

or specifically for a^{\dagger} and a,

$$e^{\lambda a^{\dagger} + \mu a} = e^{\lambda a^{\dagger}} e^{\mu a} e^{\frac{1}{2}\lambda\mu}$$
(12.26)

This leads to

$$F(t) = \left\langle \exp\left[\underline{d} \ a^{\dagger} e^{i\omega_{0}t}\right] \exp\left[-\underline{d} \ a \ e^{-i\omega_{0}t}\right] \exp\left[-\frac{1}{2} \ \underline{d}^{2}\right] \times \exp\left[-\underline{d} \ a^{\dagger}\right] \exp\left[\underline{d} \ a\right] \exp\left[-\frac{1}{2} \ \underline{d}^{2}\right] \right\rangle$$
(12.27)

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

$$e^{-\lambda a} |0\rangle = |0\rangle$$

$$\langle 0|e^{\lambda a^{\dagger}} = \langle 0|$$
(12.28)

and

$$F(t) = e^{-d^2} \left\langle 0 \left| \exp\left[-d \, a \, e^{-i\omega_0 t} \right] \exp\left[-d \, a^{\dagger} \right] \right| 0 \right\rangle$$
(12.29)

In principle these are expressions in which we can evaluate by expanding the exponential operators. However, the evaluation becomes much easier if we can exchange the order of operators. Remembering that these operators do not commute, and using

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{B}} e^{\hat{A}} e^{-\lfloor \hat{B}, \hat{A} \rfloor}$$
(12.30)

we can write

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

= $\exp\left[\underline{d}^2 \left(e^{-i\omega_0 t} - 1\right)\right]$ (12.31)

So finally, we have the dipole correlation function:

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 \exp\left[-i\omega_{eg}t + D\left(e^{-i\omega_0 t} - 1\right)\right]$$
(12.32)

D is known as the Huang-Rhys parameter (which should be distinguished from the displacement operator \hat{D}). It is a dimensionless factor related to the mean square displacement

$$D = d^{2} = d^{2} \frac{m \omega_{0}}{2\hbar}$$
(12.33)

and therefore represents the strength of coupling of the electronic states to the nuclear degree of freedom. Note our correlation function has the form

$$C_{\mu\mu}(t) = \sum_{n} p_{n} \left| \mu_{mn} \right|^{2} e^{-i\omega_{mn}t - g(t)}$$
(12.34)

Here g(t) is our lineshape function

$$g(t) = -D(e^{-i\omega_0 t} - 1)$$
 (12.35)

To illustrate the form of these functions, below is plotted the real and imaginary parts of $C_{\mu\mu}(t)$, F(t), g(t) for D = 1, and $\omega_{eg} = 10 \omega_0$. g(t) oscillates with the frequency of the single vibrational mode. F(t) quantifies the overlap of vibrational wavepackets on ground and excited state, which peaks once every vibrational period. $C_{\mu\mu}(t)$ has the same information as F(t), but is also modulated at the electronic energy gap ω_{eg} .



Absorption Lineshape and Franck-Condon Transitions

The absorption lineshape is obtained by Fourier transforming eq. (12.32)

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{i\omega t} \, C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-D} \int_{-\infty}^{+\infty} dt \, e^{i\omega t} e^{-i\omega_{eg}t} \exp\left[De^{-i\omega_{0}t}\right].$$
(12.36)

If we now expand the final term as

$$\exp\left[D\,\mathrm{e}^{-i\omega_0 t}\right] = \sum_{n=0}^{\infty} \frac{1}{n!} D^n \left(e^{-i\omega_0 t}\right)^n \tag{12.37}$$

the lineshape is

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \sum_{n=0}^{\infty} e^{-D} \frac{D^n}{n!} \delta\left(\omega - \omega_{eg} - n\omega_0\right)$$
(12.38)

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

$$\left| \left\langle n_g = 0 \, \middle| \, n_e = n \right\rangle \right|^2 = \left| \left\langle 0 \, \middle| \, \hat{D} \, \middle| \, n \right\rangle \right|^2 = e^{-D} \, \frac{D^n}{n!} \tag{12.39}$$

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







Now let's investigate how the absorption lineshape depends on D.

For D = 0, there is no dependence of the electronic energy gap ω_{eg} on the nuclear coordinate, and only one resonance is observed. For D < 1, the dependence of the energy gap on q is weak and the absorption maximum is at ω_{eg} , with the amplitude of the vibronic progression falling off as D^n . For D > 1, the strong coupling regime, 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 $t < 1/\omega_0$ and for D>>1. If we approximate the oscillatory term in the lineshape function as

$$\exp\left(-i\omega_0 t\right) \approx 1 - i\omega_0 t - \frac{1}{2}\omega_0^2 t^2 \tag{12.40}$$

then the lineshape envelope is

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

$$\approx \left|\mu_{eg}\right|^{2} \int_{-\infty}^{+\infty} dt \ e^{i(\omega-\omega_{eg}t)} \ e^{D\left[-i\omega_{0}t-\frac{1}{2}\omega_{0}^{2}t^{2}\right]}$$

$$= \left|\mu_{eg}\right|^{2} \int_{-\infty}^{+\infty} dt \ e^{i(\omega-\omega_{eg}-D\omega_{0})t} \ e^{-\frac{1}{2}D\omega_{0}^{2}t^{2}}$$
(12.41)

This can be solved by completing the square, giving

$$\sigma_{env}(\omega) = \left|\mu_{eg}\right|^2 \sqrt{\frac{2\pi}{D\omega_0^2}} \exp\left[-\frac{\left(\omega - \omega_{eg} - D\omega_0\right)^2}{2D\omega_0^2}\right]$$
(12.42)

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

$$\omega = \omega_{eg} + D\omega_0 \tag{12.43}$$

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 vibrational energy in $|E\rangle$ on excitation at q = 0

$$\lambda = D\hbar\omega_0 = \frac{1}{2}m\omega_0^2 d^2 \tag{12.44}$$

 λ is known as the reorganization energy. This is the value of H_e at q=0, which reflects the excess vibrational excitation on the excited state that occurs on a vertical transition from the ground state. It is therefore the energy that must be dissipated by vibrational relaxation on the excited state surface as the system re-equilibrates following absorption.





Illustration of how the strength of coupling D influences the absorption lineshape σ (12.38) and dipole correlation function $C_{\mu\mu}$ (12.32). Also shown, the Gaussian approximation to the absorption profile (12.42), and the dephasing function (12.31).



Fluorescence

The DHO model also leads to predictions about the form of the emission spectrum from the electronically excited state. The vibrational excitation on the excited state potential energy surface induced by electronic absorption rapidly dissipates through vibrational relaxation, typically on picosecond time scales. Vibrational relaxation leaves the system in the ground vibrational state of the electronically excited surface, with an average displacement that is larger than that of the ground state. In the absence of other non-radiative processes relaxation processes, the most efficient way of relaxing back to the ground state is by emission of light, i.e., fluorescence. In



the Condon approximation this occurs through vertical transitions from the excited state minimum to a vibrationally excited state on the ground electronic surface. The difference between the absorption and emission frequencies reflects the energy of the initial excitation which has been dissipated non-radiatively into vibrational motion both on the excited and ground electronic states, and is referred to as the Stokes shift.

From the DHO model, the emission lineshape can be obtained from the dipole correlation function assuming that the initial state is equilibrated in $|e,0\rangle$, centered at a displacement q = d, following the rapid dissipation of energy λ on the excited state. Based on the energy gap at q = d, we see that a vertical emission from this point leaves λ as the vibrational energy that needs to be dissipated on the ground state in order to re-equilibrate, and therefore we expect the Stokes shift to be 2λ .



Beginning with our original derivation of the dipole correlation function and focusing on emission, we find that fluorescence is described by

$$C_{fl} = \langle e, 0 | \mu(t) \mu(0) | e, 0 \rangle = C_{\mu\mu}^{*}(t)$$

$$= |\mu_{eg}|^{2} e^{-i\omega_{eg}t} F^{*}(t)$$

$$C_{fl} = \langle e, 0 | \mu(t) \mu(0) | e, 0 \rangle = C_{\mu\mu}^{*}(t)$$

$$= |\mu_{eg}|^{2} e^{-i\omega_{eg}t} F^{*}(t)$$

$$F^{*}(t) = \langle U_{e}^{\dagger} U_{g} \rangle$$

$$= \exp \left[D(e^{i\omega_{0}t} - 1) \right]$$
(12.45)
(12.46)

We note that $C^*_{\mu\mu}(t) = C_{\mu\mu}(-t)$ and $F^*(t) = F(-t)$. Then we can obtain the fluorescence spectrum

$$\sigma_{fl}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{i\omega t} \, C^*_{\mu\mu}(t)$$

$$= \left|\mu_{eg}\right|^2 \, \sum_{n=0}^{\infty} e^{-D} \frac{D^n}{n!} \, \delta\left(\omega - \omega_{eg} + n\omega_0\right)$$
(12.47)

This is a spectrum with the same features as the absorption spectrum, although with mirror symmetry about ω_{eg} .



A short time expansion confirms that the splitting between the peak of the absorption and emission lineshape envelopes is $2D\hbar\omega_0$, or 2λ . Further, one can establish that

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

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

$$g(t) = D(e^{-i\omega_{0}t} - 1)$$

(12.48)

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of the light-matter interaction, and in practice fluorescence involves spontaneous emission of light into a quantum mechanical light field. However, while the light field must be handled differently, the form of the dipole correlation function and the resulting lineshape remains unchanged. Additionally, we assumed that there was a time scale separation between the vibrational relaxation in the excited state and the time scale of emission, so that the system can be considered equilibrated in $|e, 0\rangle$. When this assumption is not valid then one must account for the much more complex possibility of emission during the course of the relaxation process.

Readings

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- 2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Section 12.5.
- 3. Reimers, J. R.; Wilson, K. R.; Heller, E. J., Complex time dependent wave packet technique for thermal equilibrium systems: Electronic spectra. J. Chem. Phys. **1983**, *79*, 4749-4757.
- 4. Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; Ch. 9.

12.2. Coupling to a Harmonic Bath

It is worth noting a similarity between the Hamiltonian for this displaced harmonic oscillator problem, and a general form for the interaction of an electronic "system" that is observed in an experiment with a harmonic oscillator "bath" whose degrees of freedom are invisible to the observable, but which influence the behavior of the system. This reasoning will in fact be developed more carefully later for the description of fluctuations. While the Hamiltonians we have written so far describe coupling to a single bath degree of freedom, the DHO model is readily generalized to many vibrations or a continuum of nuclear motions. Coupling to a continuum, or a harmonic bath, is the starting point for developing how an electronic system interacts with a continuum of intermolecular motions and phonons typical of condensed phase systems.

So, what happens if the electronic transition is coupled to many vibrational coordinates, each with its own displacement? The extension is straightforward if we still only consider two electronic states (e and g) to which we couple a set of independent modes, i.e., a bath of harmonic normal modes. Then we can write the Hamiltonian for N vibrations as a sum over all the independent harmonic modes

$$H_{e} = \sum_{\alpha=1}^{N} H_{e}^{(\alpha)} = \sum_{\alpha=1}^{N} \left(\frac{p_{\alpha}^{2}}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^{2} \left(q_{\alpha} - d_{\alpha} \right)^{2} \right)$$
(12.49)

each with their distinct frequency and displacement. We can specify the state of the system in terms of product states in the electronic and nuclear occupation, i.e.,

$$|G\rangle = |g; n_1, n_2, ..., n_N\rangle$$

= $|g\rangle \prod_{\alpha=1}^N |n_\alpha\rangle$ (12.50)

Additionally, we recognize that the time propagator on the electronic excited potential energy surface is

$$U_e = \exp\left[-\frac{i}{\hbar}H_e t\right] = \prod_{\alpha=1}^N U_e^{(\alpha)}$$
(12.51)

$$U_e^{(\alpha)} = \exp\left[-\frac{i}{\hbar}H_e^{(\alpha)}t\right]$$
(12.52)

where

Defining $D_{\alpha} = d_{\alpha}^2 (m\omega_{\alpha}/2\hbar)$

$$F^{(\alpha)} = \left\langle \left[U_{g}^{(\alpha)} \right]^{\dagger} U_{e}^{(\alpha)} \right\rangle$$

= $\exp \left[D_{\alpha} \left(e^{-i\omega_{\alpha}t} - 1 \right) \right]$ (12.53)

(12.55)

the dipole correlation function is then just a product of multiple dephasing functions that characterize the time-evolution of the different vibrations.

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^{2} e^{-i\omega_{eg}t} \cdot \prod_{\alpha=1}^{N} F^{(\alpha)}(t)$$
(12.54)

or

with

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t + g(t)}$$
(12.55)
$$g(t) = \sum_{\alpha} D_{\alpha} \left(e^{-i\omega_{\alpha}t} - 1\right)$$
(12.56)

In the time domain this is a complex beating pattern, which in the frequency domain appears as a spectrum with several superimposed vibronic progressions that follow the rules developed above. Also, the reorganization energy now reflects to total excess nuclear potential energy required to make the electronic transition:

$$\lambda = \sum_{\alpha} D_{\alpha} \hbar \omega_{\alpha} \tag{12.57}$$

Taking this a step further, the generalization to a continuum of nuclear states emerges naturally. Given that we have a continuous frequency distribution of normal modes characterized by a density of states, $W(\omega)$, and a continuously varying frequency-dependent coupling, $D(\omega)$, we can change the sum in eq. (12.56) to an integral over the density of states:

$$g(t) = \int d\omega \ W(\omega) \ D(\omega) (e^{-i\omega t} - 1)$$
(12.58)

Here the product $W(\omega) D(\omega)$ is a coupling-weighted density of states, and is commonly 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. Coupling to a bath or continuum provides a way of introducing relaxation effects or damping of the electronic coherence in the absorption spectrum. You can see that if g(t) is associated with a constant Γ , we obtain a Lorentzian lineshape with width Γ . This emerges under certain circumstances, for instance if the distribution of states and coupling is large and constant, and if the integral in eq. (12.58) is over a distribution of



An Ensemble at Finite Temperature

As described above, the single mode DHO model above is for a pure state, but the approach can be readily extended to describe a canonical ensemble. In this case, the correlation function is averaged over a thermal distribution of initial states. If we take the initial state of the system to be in the electronic ground state and its vibrational levels (n_g) to be occupied as a Boltzmann distribution, which is characteristic of ambient temperature samples, then the dipole correlation function can be written as a thermally averaged dephasing function:

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} F(t)$$
(12.59)

$$F(t) = \sum_{n_g} p(n_g) \left\langle n_g \left| U_g^{\dagger} U_e \right| n_g \right\rangle$$
(12.60)

$$p(n_g) = \frac{e^{-\beta h n_g \omega_0}}{Z}$$
(12.61)

Evaluating these expressions using the strategies developed above leads to

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} \exp\left[D\left[(\overline{n}+1)(e^{-i\omega_0t}-1) + \overline{n}(e^{+i\omega_0t}-1)\right]\right]$$
(12.62)

 \overline{n} is the thermally averaged occupation number of the harmonic vibrational mode.

$$\overline{n} = \left(e^{\beta\hbar\omega_0} - 1\right)^{-1} \tag{12.63}$$

Note that in the low temperature limit, $\overline{n} \rightarrow 0$, and eq. (12.62) equals our original result eq. (12.32). The dephasing function has two terms underlined in (12.62), of which the first describes those electronic absorption events in which the vibrational quantum number increases or is unchanged ($n_e \ge n_g$), whereas the second are for those processes where the vibrational quantum number decreases or is unchanged ($n_e \le n_g$). The latter are only allowed at elevated temperature where thermally excited states are populated and are known as "hot bands".

Now, let's calculate the lineshape. If we separate the dephasing function into a product of two exponential terms and expand each of these exponentials, we can Fourier transform to give

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 e^{-D(2\overline{n}+1)} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \left(\frac{D^{j+k}}{j!k!}\right) (\overline{n}+1)^j \overline{n}^k \,\delta\left(\omega - \omega_{eg} - (j-k)\omega_0\right)$$
(12.64)

Here the summation over *j* describes $n_e \ge n_g$ transitions, whereas the summation over *k* describes $n_e \le n_g$. For any one transition frequency, $(\omega_{eg}+n\omega_0)$, the net absorption is a sum over all possible combination of transitions at the energy splitting with n=(j-k). Again, if we set $\overline{n} \rightarrow 0$, we obtain our original result eq. (12.38). The contributions where k<j leads to the hot bands.



Examples of temperature dependence to lineshape and dephasing functions for D = 1. The real part changes in amplitude, growing with temperature, whereas the imaginary part is unchanged.



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:

$$F(t) = \exp\left[\sum_{j} D_{j} \left[\left(\overline{n}_{j} + 1\right) \left(e^{-i\omega_{j}t} - 1 \right) + \overline{n}_{j} \left(e^{i\omega_{j}t} - 1 \right) \right] \right]$$
(12.65)

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

$$F(t) = \exp\left[\int d\omega \ W(\omega) \ D(\omega) \left[\left(\overline{n}(\omega) + 1\right) \left(e^{-i\omega t} - 1\right) + \overline{n}(\omega) \left(e^{i\omega t} - 1\right) \right] \right]$$
(12.66)

 $D(\omega)$ 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. (12.40)

$$F(t) = \exp\left[\int d\omega D(\omega) W(\omega) \left(-i\omega t - (2\overline{n} + 1)\frac{\omega^2 t^2}{2}\right)\right]$$
(12.67)

The lineshape is calculated from

$$\sigma_{abs}(\omega) = \int_{-\infty}^{+\infty} dt \, e^{i(\omega - \omega_{eg})t} \, \exp\left[-i\left\langle\omega\right\rangle t\right] \exp\left[-\frac{1}{2}\left\langle\omega^{2}\right\rangle \, t^{2}\right]$$
(12.68)

where we have defined the mean vibrational excitation on absorption

$$\langle \omega \rangle = \int d\omega W(\omega) D(\omega) \omega$$

= λ / \hbar (12.69)

and

$$\langle \omega^2 \rangle = \int d\omega W(\omega) D(\omega) \omega^2 (2\overline{n}(\omega) + 1)$$
 (12.70)

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

$$\sigma_{abs}(\omega) = \left|\mu_{eg}\right|^2 \sqrt{\frac{2\pi}{\langle\omega^2\rangle}} \exp\left[\frac{-\left(\omega - \omega_{eg} - \langle\omega\rangle\right)^2}{2\langle\omega^2\rangle}\right]$$
(12.71)

The lineshape is Gaussian, with a transition maximum at the electronic resonance plus reorganization energy. Although the frequency shift $\langle \omega \rangle$ is not temperature dependent, the width of the Gaussian is temperature-dependent as a result of the thermal occupation factor in eq. (12.70).

12.3 Semiclassical Approximation to the Dipole Correlation Function

In introducing the influence of dark degrees of freedom on the spectroscopy of a bright state, we made some approximations that are not always valid, such as the Condon approximation and the Second Cumulant Approximation. To develop tools that allow us to work outside of these approximations, it is worth revisiting the evaluation of the dipole correlation function and looking at this a bit more carefully. In particular, we will describe the semiclassical approximation, which is a useful representation of the dipole correlation function when one wants to describe the dark degrees of freedom (the bath) using classical molecular dynamics simulations.

For a quantum mechanical material system interacting with a light field, the full Hamiltonian is

$$H = H_0 + V(t)$$
 (12.72)

$$V(t) = -\overline{m} \cdot \overline{E}(t) \tag{12.73}$$

 $\overline{m} = \sum_{i} z_{i} \overline{r_{i}}$ is the quantum mechanical dipole operator, where z_{i} are charges. The absorption lineshape is given by the Fourier transformation of the dipole autocorrelation function $C_{\mu\mu}$:

$$C_{\mu\mu}(\tau) = \left\langle \overline{m}(t)\overline{m}(0) \right\rangle = Tr\left(\rho_{eq}\overline{m}(t)\overline{m}(0)\right)$$
(12.74)

and the time dependence in \overline{m} is expressed in terms of the usual time-propagator

$$\overline{m}(t) = \hat{U}_0^{\dagger} \overline{m} \hat{U}_0 \tag{12.75}$$

$$\hat{U}_{0} = e_{+}^{-\frac{i}{\hbar} \int_{0}^{t} H_{0}(t') dt'}$$
(12.76)

In principle, the time development of the dipole moment for all degrees of freedom can be obtained directly from *ab initio* molecular dynamics simulations.

For a more practical expression in which we wish to focus on one or a few bright degrees of freedom, we next partition the Hamiltonian into system and bath

$$H_{0} = H_{s}(Q) + H_{B}(q) + H_{sB}(Q,q)$$
(12.77)

For purposes of spectroscopy, the system H_S refers to those degrees of freedom (Q) with which the light will interacts, and which will be those in which we calculate matrix elements. The bath H_B refers to all of the other degrees of freedom (q), and the interaction between the two is accounted for in H_{SB} . Although the interaction of the light depends on how \overline{m} varies with Q, the dipole operator remains a function of system and bath coordinates: $\overline{m}(Q,q)$. We now use the interaction picture transformation to express the time propagator under the full material Hamiltonian \hat{U}_0 in terms of a product of propagators in the individual terms in H_0 :

$$\hat{U}_{0} = U_{S} U_{B} U_{SB} \tag{12.78}$$

$$\hat{U}_{0} = e_{+}^{-\frac{i}{\hbar}\int_{0}^{t}H_{0}dt'} = e^{-iH_{s}t}e_{+}^{-i\int_{0}^{t}H_{B}dt'}e_{+}^{-i\int_{0}^{t}\mathbf{H}_{sB}(t')dt'}$$
(12.79)

$$\mathbf{H}_{SB}(t) = e^{i(H_S + H_B)t} H_{SB} e^{-i(H_S + H_B)t}$$
(12.80)

Then the dipole autocorrelation function becomes

$$C_{\mu\mu} = \sum_{n} p_{n} \left\langle n \left| U_{SB}^{\dagger} U_{B}^{\dagger} U_{S}^{\dagger} \overline{m} U_{S} U_{B} U_{SB} \overline{m} \right| n \right\rangle$$
(12.81)

Where $p_n = \langle n | e^{-\beta H_0} | n \rangle / Tr(e^{-\beta H_0}).$

Further, to make this practical, we make an adiabatic separation between the system and bath coordinates, and say that the interaction between the system and bath is weak. This allows us to write the state of the system as product states in the system (a) and bath (α) , $|n\rangle = |a, \alpha\rangle$:

$$(H_{s} + H_{B})|a,\alpha\rangle = (E_{a} + E_{\alpha})|a,\alpha\rangle$$
(12.82)

With this we evaluate eq. (12.81) as

$$C_{\mu\mu} = \sum_{a,\alpha} p_{a} p_{\alpha} \left\langle a, \alpha \middle| U_{SB}^{\dagger} U_{B}^{\dagger} U_{S}^{\dagger} \overline{m} U_{S} U_{B} U_{SB} \overline{m} \middle| a, \alpha \right\rangle$$
$$= \sum_{\substack{a,b\\\alpha}} p_{a} p_{\alpha} \left\langle \alpha \middle| \left\langle a \middle| U_{SB}^{\dagger} U_{S}^{\dagger} U_{B}^{\dagger} \overline{m} U_{B} U_{S} U_{SB} \middle| b \right\rangle \overline{m}_{ba} \middle| \alpha \right\rangle$$
(12.83)

where $\overline{m}_{ba} = \langle b | \overline{m} | a \rangle$, and we have made use of the fact that H_S and H_B commute. Also, $p_a = e^{-E_a/kT}/Q_S$. Now, by recognizing that the time propagators in the system and system-bath Hamiltonians describe time evolution at the system eigenstate energy plus any modulations that the bath introduces to it

$$U_{S}U_{SB}|b\rangle = e^{-iH_{S}t}|b\rangle e^{-i\int_{0}^{t}dt'\delta E_{b}(t')} = |b\rangle e^{-i\int_{0}^{t}dt'E_{b}(t')}$$
(12.84)

and we can write our correlation function as

$$C_{\mu\mu} = \sum_{\substack{a,b\\\alpha}} p_a p_\alpha \left\langle \alpha \left| e^{i \int_0^t dt' E_a(t')} U_B^{\dagger} \overline{m}_{ab} U_B e^{-i \int_0^t dt' E_b(t')} \overline{m}_{ba} \right| \alpha \right\rangle$$
(12.85)

$$C_{\mu\mu} = \left\langle \overline{m}_{ab}(t) \overline{m}_{ba}(0) e^{-i \int_0^t dt' \omega_{ba}(t')} \right\rangle_B$$
(12.86)

$$\bar{m}_{ab}(t) = e^{-iH_{B}t}\bar{m}_{ab}e^{-iH_{B}t}$$
(12.87)

Equation (12.86) is the first important result. It describes a correlation function in the dipole operator expressed in terms of an average over the time-dependent transition moment, including its orientation, and the fluctuating energy gap. The time dependence is due to the bath and $\langle ... \rangle_B$ refers to a trace over the bath degrees of freedom.

Let's consider the matrix elements. These will reflect the strength of interaction of the electromagnetic field with the motion of the system coordinate, which may also be dependent on the bath coordinates. Since we have made an adiabatic approximation, to evaluate the matrix elements we would typically expand the dipole moment in the system degrees of freedom, Q. As an example for one system coordinate (Q) and many bath coordinates q, we can expand:

$$\overline{m}(Q,q) = \overline{m}_0 + \frac{\partial \overline{m}}{\partial Q}Q + \sum_{\alpha} \frac{\partial^2 \overline{m}}{\partial Q \partial q_{\alpha}}Qq_{\alpha} + \cdots$$
(12.88)

 \overline{m}_0 is the permanent dipole moment, which we can take as a constant. In the second term, $\partial \overline{m}/\partial Q$ is the magnitude of the transition dipole moment. The third term includes the dependence of the transition dipole moment on the bath degrees of freedom, i.e., non-Condon terms. So now we can evaluate

$$\overline{m}_{ab} = \left\langle a \left| \overline{m}_{0} + \frac{\partial \overline{m}}{\partial Q} Q + \sum_{\alpha} \frac{\partial^{2} \overline{m}}{\partial Q \partial q_{\alpha}} Q q_{\alpha} \right| b \right\rangle$$

$$= \frac{\partial \overline{m}}{\partial Q} \left\langle a \left| Q \right| b \right\rangle + \sum_{\alpha} \frac{\partial}{\partial q_{\alpha}} \frac{\partial \overline{m}}{\partial Q} \left\langle a \left| Q \right| b \right\rangle q_{\alpha}$$
(12.89)

We have set $\langle a | \overline{m}_0 | b \rangle = 0$. Now defining the transition dipole matrix element,

$$\overline{\mu}_{ab} = \frac{\partial \overline{m}}{\partial Q} \langle a | Q | b \rangle$$
(12.90)

we can write

$$\overline{m}_{ab} = \overline{\mu}_{ab} \left(1 + \sum_{\alpha} \frac{\partial \overline{\mu}_{ab}}{\partial q_{\alpha}} q_{\alpha} \right)$$
(12.91)

Remember that $\overline{\mu}_{ab}$ is a vector. The bath can also change the orientation of the transition dipole moment. If we want to separate the orientational and remaining dynamics this we could split the matrix element into an orientational component specified by a unit vector along $\partial \overline{m}/\partial Q$ and a scalar that encompasses the amplitude factors: $\overline{\mu}_{ab} = \hat{u}_{ab}\mu_{ab}$. Then eq. (12.86) becomes

$$C_{\mu\mu} = \left\langle \hat{u}_{ab}(t)\hat{u}_{ab}(0)m_{ab}(t)m_{ba}(0)e^{-i\int_{0}^{t}dt'\omega_{ba}(t')}\right\rangle_{B}$$
(12.92)

Mixed quantum-classical spectroscopy models apply a semiclassical approximation to equation (12.86). Employing the semiclassical approximation says that we will replace the quantum mechanical operator $\overline{m}_{ab}(t)$ with a classical $\overline{\mathcal{M}}_{ab}(t)$, i.e., we replace the time propagator U_B with classical propagation of the dynamics. Also, the trace over the bath in the correlation function becomes an equilibrium ensemble average over phase space.

How do you implement the semiclassical approximation? Replacing the time propagator U_B with classical dynamics amounts to integrating Newton's equations for all of the bath degrees of freedom. Then you must establish how the bath degrees of freedom influence $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$. For the quantum operator $\overline{m}(Q,q,t)$, only the system coordinate Q remains quantized, and following eq. (12.91) we can express the orientation and magnitude of the dipole moment and the dynamics depends on the classical degrees of freedom \tilde{q}_{α} .

$$\overline{m}_{ab} = \overline{\mu}_{ab} \left(1 + \sum_{\alpha} a_{\alpha} \tilde{q}_{\alpha} \right)$$
(12.93)

 a_{α} is a (linear) mapping coefficient, $a_{\alpha} = \partial \overline{\mu}_{ab} / \partial \tilde{q}_{\alpha}$, between the bath and the transition dipole moment.

In practice, use of this approximation has been handled in different ways, but practical considerations have dictated that $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$ are not separately calculated for each time step, but are obtained from a mapping of these variables to the bath coordinates q. This mapping may be to local or collective bath coordinates, and to as many degrees of freedom as are necessary to obtain a highly correlated single valued mapping of $\omega_{ba}(t)$ and $\overline{m}_{ab}(t)$. Examples of these mappings include correlating ω_{ba} with the electric field of the bath acting on the system coordinate.

Appendix

Let's evaluate the dipole correlation function for an arbitrary H_{SB} and an arbitrary number of system eigenstates. From eq. (12.83) we have

$$C_{\mu\mu} = \sum_{\substack{abcd\\\alpha}} p_a p_\alpha \left\langle \alpha \right| \left\langle a \middle| U_{SB}^{\dagger} \middle| c \right\rangle U_B^{\dagger} \left\langle c \middle| U_S^{\dagger} \overline{m} U_S \middle| d \right\rangle U_B \left\langle d \middle| U_{SB} \middle| b \right\rangle \left\langle b \middle| \overline{m} \middle| a \right\rangle \left| \alpha \right\rangle$$
(12.94)

$$\left\langle c \left| U_{S}^{\dagger} \overline{m} U_{S} \right| d \right\rangle = e^{-i(E_{d} - E_{c})t} \overline{m}_{cd}$$
(12.95)

$$\overline{m}_{cd}(t) = U_B^{\dagger} \overline{m}_{cd} U_B \tag{12.96}$$

$$\left\langle a \left| U_{SB}^{\dagger} \right| c \right\rangle = \left\langle a \right| e^{i \int_{0}^{t} dt' \mathbf{H}_{SB}(t')} \left| c \right\rangle = \exp \left[i \int_{0}^{t} dt' \left[\mathbf{H}_{SB} \right]_{ac}(t') \right]$$
(12.97)

$$C_{\mu\mu} = \sum_{abcd} p_a \left\langle e^{-i\omega_{dc}t} e^{i\int_0^t dt' [H_{SB}]_{ac}(t')} \overline{m}_{cd} e^{-i\int_0^t dt' [H_{SB}]_{db}(t')} \overline{m}_{ba} \right\rangle_B$$
(12.98)

$$C_{\mu\mu} = \left\langle \overline{m}_{cd}(t)\overline{m}_{ba}(0) \exp\left[-i\omega_{dc}t - i\int_{0}^{t} dt' \left[H_{SB}\right]_{db}(t') - \left[H_{SB}\right]_{ac}(t')\right] \right\rangle_{B}$$
(12.99)

Readings

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