5.74 Introductory Quantum Mechanics II
Spring 2009

7.4 <u>QUANTUM MECHANICAL TREATMENT OF FLUCTUATIONS</u>[§]

<u>Introduction</u>

In describing fluctuations in a quantum mechanical system, we will now address how they manifest themselves in an electronic absorption spectrum by returning to the Displaced Harmonic Oscillator model. As previously discussed, we can also interpret the DHO model in terms of an electronic energy gap which is modulated as a result of interactions with nuclear motion. While this motion is periodic for the case coupling to a single harmonic oscillator, we will look this more carefully for a continuous distribution of oscillators, and show the correspondence to classical stochastic equations of motion.

<u>Energy Gap Hamiltonian</u>

Now let's work through the description of the Energy Gap Hamiltonian more carefully. Remember that the Hamiltonian for coupling of an electronic transition to a harmonic degree of freedom is written as

$$H_0 = H_e + E_e + H_g + E_g \tag{7.48}$$

$$H_0 = \hbar\omega_{eg} + H_{eg} + 2H_g \tag{7.49}$$

where the Energy Gap Hamiltonian is

$$H_{eg} = H_e - H_g . \tag{7.50}$$

Note how eq. (7.49) can be thought of as an electronic "system" interacting with a harmonic "bath", where H_{eg} plays the role of the system-bath interaction:

$$H_0 = H_S + H_{SB} + H_B \tag{7.51}$$

We will express the energy gap Hamiltonian through reduced coordinates for the momentum, coordinate, and displacement of the oscillator

$$\underset{\sim}{p} = \sqrt{\frac{2}{\hbar\omega_0 m}}\,\hat{p} \ . \tag{7.52}$$

$$\underset{\sim}{q} = \sqrt{\frac{m\omega_0}{2\hbar}}\,\hat{q} \tag{7.53}$$

[§] See Mukamel, Ch. 8 and Ch. 7.

$$\underset{\sim}{d} = \sqrt{\frac{m\omega_0}{2\hbar}}\, d \tag{7.54}$$

$$H_e = \hbar\omega_0\left(\underset{\sim}{p}^2 + \left(\underset{\sim}{q} - \underset{\sim}{d}\right)^2 \right)$$

$$H_g = \hbar\omega_0\left(\underset{\sim}{p}^2 + \underset{\sim}{q}^2 \right) \tag{7.55}$$

From (7.50) we have

$$H_{eg} = -2\hbar\omega_0 \underset{\sim}{d}\, \underset{\sim}{q} + \hbar\omega_0 \underset{\sim}{d}^2$$

$$= -2\hbar\omega_0 \underset{\sim}{d}\, \underset{\sim}{q} + \lambda \tag{7.56}$$

So, we see that the energy gap Hamiltonian describes a linear coupling of the electronic system to the coordinate q. The slope of H_{eg} versus q is the coupling strength, and the average value of H_{eg} in the ground state, $H_{eg}(q{=}0)$, is offset by the reorganization energy λ.

To obtain the absorption lineshape from the dipole correlation function we must evaluate the dephasing function.

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\omega_{eg}t} F(t) \tag{7.57}$$

$$F(t) = \left\langle e^{iH_g t}\, e^{-iH_e t} \right\rangle = \left\langle U_g^\dagger U_e \right\rangle \tag{7.58}$$

We now want to rewrite the dephasing function in terms of the time dependence to the energy gap H_{eg}; that is, if $F(t) = \left\langle U_{eg} \right\rangle$, then what is U_{eg}? This involves a transformation of the dynamics to a new frame of reference and a new Hamiltonian. The transformation from the DHO Hamiltonian to the EG Hamiltonian is similar to our derivation of the interaction picture. Note the mapping

$$H_e = H_g + H_{eg} \qquad \Leftrightarrow \qquad H = H_0 + V \tag{7.59}$$

Then we see that we can represent the time dependence of H_{eg} by evolution under H_g. The time-propagators are
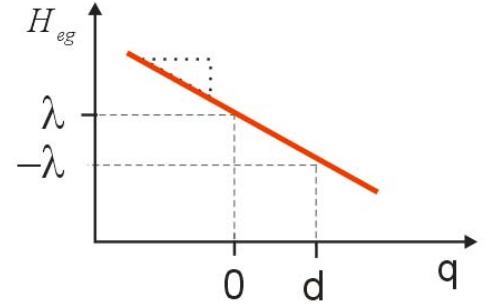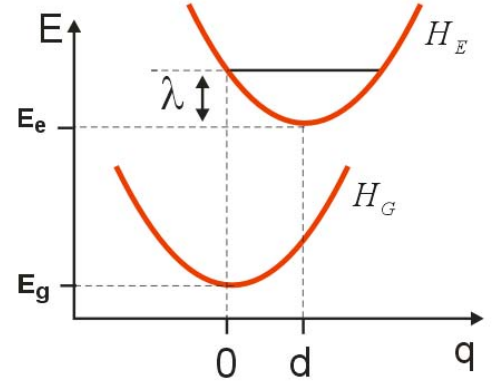
$$e^{-iH_e t/\hbar} = e^{-iH_g t/\hbar} \exp_+\left[\frac{-i}{\hbar} \int_0^t d\tau\, H_{eg}(\tau) \right]$$

$$U_e = U_g U_{eg}$$

(7.60)

and

$$H_{eg}(t) = e^{iH_g t/\hbar}\, H_{eg}\, e^{-iH_g t/\hbar}$$

$$= U_g^\dagger H_{eg} U_g$$

(7.61)

Remembering the equivalence between H_g and the bath mode(s) H_B indicates that the time dependence of the EG Hamiltonian reflects how the electronic energy gap is modulated as a result of the interactions with the bath. That is $U_g = U_B$.

Equation (7.60) immediately implies that

$$U_{eg}(\tau) = \exp_+\left[\frac{-i}{\hbar} \int_0^t d\tau\, H_{eg}(\tau) \right]$$

(7.62)

$$F(t) = \left\langle e^{iH_g t}\, e^{-iH_e t} \right\rangle = \left\langle \exp_+\left[\frac{-i}{\hbar} \int_0^t d\tau\, H_{eg}(\tau) \right] \right\rangle$$

(7.63)

Note: Transformation of time-propagators to a new Hamiltonian

If we have

$$e^{iH_A t}\, A\, e^{-iH_B t}$$

and we want to express this in terms of

$$A\, e^{-i(H_B - H_A)t} = A\, e^{-iH_{BA} t} ,$$

we will now be evolving the system under a different Hamiltonian H_{BA}. We must perform a transformation into this new frame of reference, which involves a unitary transformation under the reference Hamiltonian:

$$H_{new} = H_{ref} + H_{diff}$$

$$e^{-iH_{new} t} = e^{-iH_{ref} t} \exp_+\left[-\frac{i}{\hbar} \int_0^t d\tau\, H_{diff}(\tau) \right]$$

$$H_{diff}(\tau) = U_{ref}^\dagger H_{diff} U_{ref}$$

This is what we did for the interaction picture. Now, proceeding a bit differently, we can express the time evolution under the Hamiltonian of H_B relative to H_A as

$$H_B = H_A + H_{BA}$$

$$e^{-iH_B t} = e^{-iH_A t} \exp_+ \left[-\frac{i}{\hbar} \int_0^t d\tau \, H_{BA} (\tau) \right]$$

where $H_{BA} (\tau) = e^{+iH_A t} H_{BA} e^{-iH_A t}$. This implies:

$$e^{+iH_A t} e^{-iH_B t} = \exp_+ \left[-\frac{i}{\hbar} \int_0^t d\tau \, H_{BA} (\tau) \right]$$

Using the second-order cumulant expansion allows the dephasing function to be written as

$$F(t) = \exp \left[\frac{-i}{\hbar} \int_0^t d\tau \langle H_{eg} (\tau) \rangle \right.$$
$$\left. + \left(\frac{-i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle H_{eg} (\tau_2) H_{eg} (\tau_1) \rangle - \langle H_{eg} (\tau_2) \rangle \langle H_{eg} (\tau_1) \rangle \right] \tag{7.64}$$

Note that the cumulant expansion is here written as a time-ordered expansion here. The first exponential term depends on the mean value of H_{eg}

$$\langle H_{eg} \rangle = \hbar \omega_0 \underset{\sim}{d}^2 = \lambda \tag{7.65}$$

This is a result of how we defined H_{eg}. Alternatively, the EG Hamiltonian could also be defined relative to the energy gap at $Q = 0$: $H_{eg} = H_e - H_g - \lambda$. In fact this is a more common definition. In this case the leading term in (7.64) would be zero, and the mean energy gap that describes the high frequency (system) oscillation in the dipole correlation function is $\omega_{eg} + \lambda$.

The second exponential term in (7.64) is a correlation function that describes the time dependence of the energy gap

$$\langle H_{eg} (\tau_2) H_{eg} (\tau_1) \rangle - \langle H_{eg} (\tau_2) \rangle \langle H_{eg} (\tau_1) \rangle$$
$$= \langle \delta H_{eg} (\tau_2) \delta H_{eg} (\tau_1) \rangle \tag{7.66}$$

where $$\delta H_{eg} = H_{eg} - \langle H_{eg} \rangle. \tag{7.67}$$

Defining the time-dependent energy gap frequency in terms of the EG Hamiltonian as

$$\delta \omega_{eg} \equiv \frac{\delta H_{eg}}{\hbar} \tag{7.68}$$

we obtain

$$C_{eg}(\tau_2, \tau_1) = \left\langle \delta \omega_{eg}(\tau_2 - \tau_1) \delta \omega_{eg}(0) \right\rangle \tag{7.69}$$

$$F(t) = \exp\left[\frac{-i}{\hbar} \lambda t - \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \, C_{eg}(\tau_2 - \tau_1)\right] \tag{7.70}$$

So, the dipole correlation function can be expressed as

$$C_{\mu\mu}(t) = \left|\mu_{eg}\right|^2 e^{-i\left(E_e - E_g + \lambda\right)t/\hbar} \, e^{-g(t)} \tag{7.71}$$

$$g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \left\langle \delta \omega_{eg}(\tau_2 - \tau_1) \delta \omega_{eg}(0) \right\rangle. \tag{7.72}$$

This is the correlation function expression that determines the absorption lineshape for a time-dependent energy gap. It is a perfectly general expression at this point. The only approximation made for the bath is the second cumulant expansion.

Now, let's look specifically at the case where the bath we are coupled to is a single harmonic mode. Evaluating the energy gap correlation function

$$\begin{aligned} C_{eg}(t) &= \sum_n p_n \left\langle n \left| \delta \omega_{eg}(t) \delta \omega_{eg}(0) \right| n \right\rangle \\ &= \frac{1}{\hbar^2} \sum_n p_n \left\langle n \left| e^{iH_g t/\hbar} \delta H_{eg} \, e^{-iH_g t/\hbar} \delta H_{eg} \right| n \right\rangle \\ &= \omega_0^2 D\left[(\bar{n}+1)e^{-i\omega_0 t} + \bar{n}\, e^{+i\omega_0 t}\right] \end{aligned} \tag{7.73}$$

Here, as before, $D = \underline{d}^2$, and $\bar{n}$ is the thermally averaged occupation number for the oscillator

$$\bar{n} = \sum_n p_n \left\langle n \left| a^\dagger a \right| n \right\rangle = \left(e^{\beta \hbar \omega_0} - 1\right)^{-1}. \tag{7.74}$$

Note that C_{eg} is a complex quantity with

$$C_{eg}(t) = C_{eg}{}' + iC_{eg}{}'' \tag{7.75}$$

$$\begin{aligned} C_{eg}'(t) &= \omega_0^2 \, D \coth\left(\beta \hbar \omega_0/2\right) \cos\left(\omega_0 t\right) \\ C_{eg}''(t) &= \omega_0^2 \, D \sin\left(\omega_0 t\right) \end{aligned} \tag{7.76}$$

Here $\coth(x) = \left(e^x + e^{-x}\right)/\left(e^x - e^{-x}\right)$. As the temperature is raised well beyond the frequency of the oscillator, C_{eg} becomes real, $\left|C_{eg}{}'\right| \gg \left|C_{eg}{}''\right|$, and $C_{eg}(t) \sim \cos \omega_0 t$. This is the simple classical limit in which the energy gap is modulated at the frequency of the oscillator.

Evaluating (7.72) gives the lineshape function

$$g(t) = D\left[\coth\left(\beta\hbar\omega_0/2\right)\left(1-\cos\omega_0 t\right) + i\left(\sin\omega_0 t - \omega_0 t\right)\right]$$
$$= g' + ig''$$

(7.77)

We also have real (g') and imaginary (g'') contributions to $F(t)$. Alternatively, we can write this in a form that more closely parallels our earlier DHO expressions

$$g(t) = D\left[\bar{n}\left(e^{-i\omega_0 t} - 1 + e^{+i\omega_0 t} - 1\right) + \left(e^{-i\omega_0 t} - 1\right)\right] - iD\omega_0 t$$
$$= D\left[\left(\bar{n}+1\right)\left(e^{-i\omega_0 t} - 1\right) + \bar{n}\left(e^{+i\omega_0 t} - 1\right)\right] - iD\omega_0 t$$

(7.78)

The leading term gives us a vibrational progression, the second term leads to hot bands, and the final term is the reorganization energy.

Looking at the low temperature limit for this expression, $\coth\left(\beta\hbar\omega_0/2\right) \to 1$ and $\bar{n} \to 0$, we have

$$g(t) = D\left[1 - \cos\omega_0 t + i\sin\omega_0 t - i\omega_0 t\right]$$
$$= D\left[1 - e^{-i\omega_0 t} - i\omega_0 t\right]$$

(7.79)

Combining with

$$F(t) = e^{-i\lambda t/\hbar - g(t)} = e^{-iD\omega_0 t - g(t)}$$

(7.80)

we have our old result:

$$F(t) = \exp\left[D\left(e^{-i\omega_0 t} - 1\right)\right].$$

(7.81)

In the high temperature limit $\coth\left(\beta\hbar\omega/2\right) \to 2/\beta\hbar\omega$ and $g' \gg g''$. From eq. (7.77) we obtain

$$F(t) = \exp\left[\frac{-2D}{\beta\hbar\omega_0}\left(1 - \cos\left(\omega_0 t\right)\right)\right]$$
$$= e^{-2DkT/\hbar\omega_0}\sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{2DkT}{\hbar\omega_0}\right)^j\cos^j\left(\omega_0 t\right)$$

(7.82)

which leads to an absorption spectrum which is a series of sidebands equally spaced on either side of ω_{eg}.

Spectral representation of energy gap correlation function

Since time- and frequency domain representations are complementary, and one form may be preferable over another, it is possible to express the frequency correlation function in terms of its spectrum. We define a Fourier transform pair that relates the time and frequency domain representations:

$$\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} C_{eg}(t)\, dt \qquad = 2\,\mathrm{Re}\int_{0}^{+\infty} e^{i\omega t} C_{eg}(t)\, dt . \tag{7.83}$$

$$C_{eg}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t} \tilde{C}_{eg}(\omega)\, dt \tag{7.84}$$

The second equality in eq. (7.83) follows from $C_{eg}(-t) = C_{eg}^{*}(t)$. Also it implies that

$$\tilde{C}_{eg}(\omega) = \tilde{C}_{eg}'(\omega) + \tilde{C}_{eg}''(\omega) \tag{7.85}$$

Where $\tilde{C}_{eg}'(\omega)$ and $\tilde{C}_{eg}''(\omega)$ are the Fourier transforms of the real and imaginary components of $C_{eg}(t)$, respectively. Note that $\tilde{C}_{eg}(\omega)$ is an entirely real quantity.

With these definitions in hand, we can the spectrum of the energy gap correlation function for coupling to a single harmonic mode spectrum (eq. (7.73)):

$$\tilde{C}_{eg}(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha)\big[(\bar{n}_\alpha + 1)\delta(\omega - \omega_\alpha) + \bar{n}_\alpha\,\delta(\omega + \omega_\alpha)\big]. \tag{7.86}$$

This spectrum characterizes the thermally averaged balance between upward energy transition of the system and downward in the bath $\delta(\omega - \omega_\alpha)$ and vice versa in $\delta(\omega + \omega_\alpha)$. This is given by the detailed balance expression

$$\tilde{C}(-\omega) = e^{-\beta\hbar\omega}\tilde{C}(\omega). \tag{7.87}$$
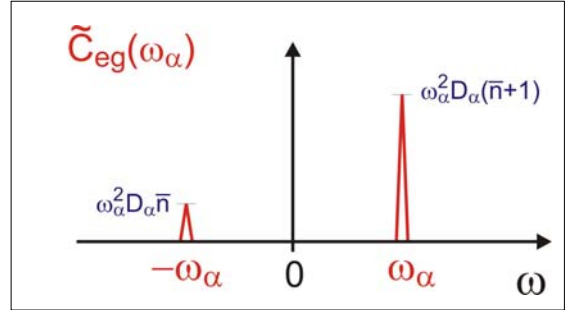
The balance of rates tends toward equal with increasing temperature. Fourier transforms of eqs. (7.76) gives two other representations of the energy gap spectrum

$$\tilde{C}_{eg}'(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha)\coth(\beta\hbar\omega_\alpha/2)\big[\delta(\omega - \omega_\alpha) + \delta(\omega + \omega_\alpha)\big] \tag{7.88}$$

$$\tilde{C}_{eg}''(\omega_\alpha) = \omega_\alpha^2 D(\omega_\alpha)\big[\delta(\omega - \omega_\alpha) + \delta(\omega + \omega_\alpha)\big]. \tag{7.89}$$

The representations in eqs. (7.86), (7.88), and (7.89) are not independent, but can be related to one another through the detailed balance expression:

$$\tilde{C}'_{eg}(\omega_\alpha) = \coth\left(\beta\hbar\omega_\alpha/2\right)\tilde{C}''_{eg}(\omega_\alpha) \tag{7.90}$$

$$\tilde{C}_{eg}(\omega_\alpha) = \left(1 + \coth\left(\beta\hbar\omega_\alpha/2\right)\right)\tilde{C}''_{eg}(\omega_\alpha) \tag{7.91}$$

Due to its independence on temperature, $\tilde{C}''_{eg}(\omega_\alpha)$ is a commonly used representation. Also. from eqs. (7.72) and (7.84) we obtain the lineshape function as

$$g(t) = \int_{-\infty}^{+\infty} d\omega \, \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} \left[\exp(-i\omega t) + i\omega t - 1\right]. \tag{7.92}$$

Distribution of States: Coupling to a Harmonic Bath

More generally for condensed phase problems, the system coordinates that we observe in an experiment will interact with a continuum of nuclear motions that may reflect molecular vibrations, phonons, or intermolecular interactions. We conceive of this continuum as continuous distribution of harmonic oscillators of varying mode frequency. The Energy Gap Hamiltonian is readily generalized to the case of a continuous distribution of motions if we statistically characterize the density of states and the strength of interaction between the system and this bath. This method is also referred to as the Spin-Boson Model used for treating a spin two-level system interacting with a quantum harmonic bath.

Following our earlier discussion of the DHO model, the generalization of the EG Hamiltonian to the multimode case is

$$H_0 = \hbar\omega_{eg} + H_{eg} + H_B \tag{7.93}$$

$$H_B = \sum_\alpha \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2 \right) \tag{7.94}$$

$$H_{eg} = \sum_\alpha 2\hbar\omega_\alpha \underset{\sim}{d}_\alpha \, \underset{\sim}{q}_\alpha + \lambda \tag{7.95}$$

$$\lambda = \sum_\alpha \hbar\omega_\alpha \underset{\sim}{d}_\alpha^2 \tag{7.96}$$

Note that the time-dependence to H_{eg} results from the interaction with the bath:

$$H_{eg}(t) = e^{iH_B t/\hbar} H_{eg} e^{-iH_B t/\hbar} \tag{7.97}$$

Also, since the harmonic modes are normal to one another, the dephasing function and lineshape function are readily obtained from

$$F(t) = \prod_\alpha F_\alpha(t) \qquad g(t) = \sum_\alpha g_\alpha(t) \tag{7.98}$$

For a continuum, we assume that the number of modes are so numerous as to be continuous, and that the sums in the equations above can be replaced by integrals over a continuous distribution of states characterized by a density of states $W(\omega)$. Also the interaction with modes of a particular frequency are equal so that we can simply average over a frequency dependent coupling constant $D(\omega) = \underset{\sim}{d}^2(\omega)$. For instance, eq. (7.98) becomes
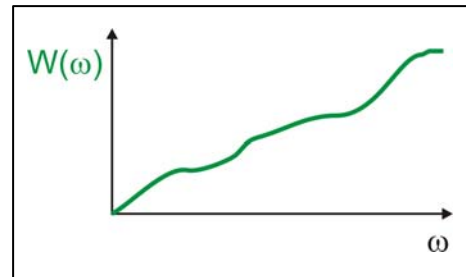
$$g(t) = \int d\omega_\alpha \, W(\omega_\alpha) g(t, \omega_\alpha) \tag{7.99}$$

Coupling to a continuum leads to dephasing that results from interactions of modes of varying frequency. This will be characterized by damping of the energy gap frequency correlation function $C_{eg}(t)$

$$C_{eg}(t) = \int d\omega_\alpha \, C_{eg}(\omega_\alpha, t) W(\omega_\alpha). \tag{7.100}$$

Here $C_{eg}(\omega_\alpha, t) = \langle \delta\omega_{eg}(\omega_\alpha, t) \delta\omega_{eg}(\omega_\alpha, 0) \rangle$ refers to the energy gap frequency correlation function for a single harmonic mode given in eq. (7.73).

While eq. (7.100) expresses the modulation of the energy gap in the time domain, we can alternatively express the continuous distribution of coupled bath modes in the frequency domain:

$$\begin{aligned}
\tilde{C}_{eg}(\omega) &= \int d\omega_\alpha \, W(\omega_\alpha) \int_{-\infty}^{+\infty} e^{i\omega t} C_{eg}(\omega_\alpha, t) dt \\
&= \int d\omega_\alpha \, W(\omega_\alpha) \tilde{C}_{eg}(\omega_\alpha)
\end{aligned} \tag{7.101}$$

An integral of a single harmonic mode spectrum over a continuous density of states provides a coupling weighted density of states that reflects the action spectrum for the system-bath interaction. We evaluate this with the single harmonic mode spectrum, eq. (7.86). We see that the spectrum of the correlation function for positive frequencies is related to the product of the density of states and the frequency dependent coupling

$$\tilde{C}_{eg}(\omega) = \omega^2 D(\omega) W(\omega)(\bar{n} + 1) \tag{7.102}$$

This is an action spectrum that reflects the coupling weighted density of states of the bath that contributes to the spectrum.
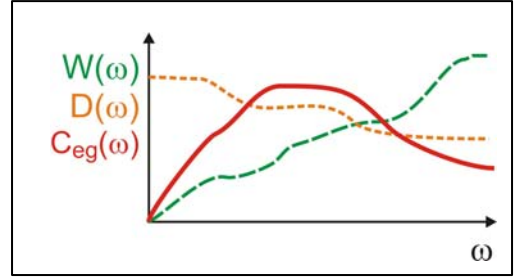
More commonly, the frequency domain representation of the coupled density of states in eq. (7.102) is expressed as a *spectral density*

$$\begin{aligned}
\rho(\omega) &\equiv \frac{\tilde{C}_{eg}''(\omega)}{\pi\omega^2} \\
&= \frac{1}{\pi} \int d\omega_\alpha \, W(\omega_\alpha) D(\omega_\alpha) \delta(\omega - \omega_\alpha) \\
&= \frac{1}{\pi} W(\omega) D(\omega)
\end{aligned} \tag{7.103}$$

From eqs. (7.72) and (7.101) we obtain the lineshape function in two forms

$$g(t) = \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} \left[\exp(-i\omega t) + i\omega t - 1 \right]$$

$$= \int_0^\infty d\omega \, \rho(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right)(1 - \cos\omega t) + i(\sin\omega t - \omega t) \right].$$

(7.104)

In this expression the temperature dependence implies that in the high temperature limit, the real part of $g(t)$ will dominate, as expected for a classical system. The reorganization energy is obtained from the first moment of the spectral density

$$\lambda = \hbar \int_0^\infty d\omega \, \omega \, \rho(\omega).$$

(7.105)

This is a perfectly general expression for the lineshape function in terms of an arbitrary spectral distribution describing the time-scale and amplitude of energy gap fluctuations. Given a spectral density $\rho(\omega)$, you can calculate spectroscopy and other time-dependent processes in a fluctuating environment.

Now, let's evaluate the lineshape function for two special cases of the spectral density. To keep things simple, we will look specifically at the high temperature limit, $kT \gg \hbar\omega$. Here $\coth(\beta\hbar\omega/2) \to 2/\beta\hbar\omega$ and we can neglect the imaginary part of the frequency correlation function and lineshape function:

1) What happens when $\tilde{C}_{eg}''(\omega)$ grows linearly with frequency? This represents a system that is coupled with equal strength to a continuum of modes. Setting $\tilde{C}_{eg}''(\omega) = \Gamma\omega$ and evaluating

$$g(t) = \int_0^{+\infty} d\omega \frac{1}{\pi\beta\hbar\omega} \frac{\tilde{C}_{eg}(\omega)}{\omega^2}(1 - \cos\omega t).$$

$$= \Gamma t$$

(7.106)

A linearly increasing spectral density leads to a homogeneous Lorentzian lineshape with width Γ. This case corresponds to a spectral density that linearly decreases with frequency, and is also referred to as the "white noise" spectrum.

2) Now take the case that we choose a Lorentzian spectral density centered at ω=0. Specifically, let's write the imaginary part of the Lorentzian lineshape in the form

$$\tilde{C}''_{eg}(\omega) = \lambda \frac{2\Lambda\omega}{\omega^2 + \Lambda^2}. \qquad (7.107)$$

Here, in the high temperature (classical) limit $kT \gg \hbar\Lambda$, neglecting the imaginary part, we find:
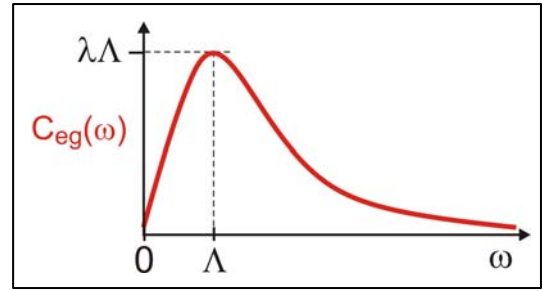
$$g(t) \approx \frac{2\lambda kT}{\hbar\Lambda^2}\left[\exp(-\Lambda t) + \Lambda t - 1\right] \qquad (7.108)$$

This expression looks familiar. If we equate

$$\Delta^2 = \frac{2\lambda kT}{\hbar} \qquad (7.109)$$

and

$$\tau_c = \frac{1}{\Lambda}, \qquad (7.110)$$

we obtain the same lineshape function as the classical Gaussian-stochastic model:

$$g(t) = \Delta^2 \tau_c^2 \left[\exp(-t/\tau_c) + t/\tau_c - 1\right] \qquad (7.111)$$

So, the interaction of an electronic transition with a harmonic bath leads to line broadening that is equivalent to random fluctuations of the energy gap.

Coupling to a Harmonic Bath: Correspondence to Stochastic Equation[**]

So, why does coupling to a quantum harmonic bath give the same results as the classical stochastic equations for fluctuations? Why does coupling to a continuum of bath states have the same physical meaning as random fluctuations? The answer is that in both cases, we really have imperfect knowledge of the particles of the bath, and observing a subset of those particles will have a random character that can alternatively be viewed as a correlation function or a spectral density for the time-scales of motion of the bath.

To take this discussion further, let's again consider the electronic absorption spectrum from a classical perspective. It's quite common to think that the electronic transition of interest is coupled to a particular nuclear coordinate Q which we will call a *local coordinate*. This local coordinate could be an intramolecular normal vibrational mode, a intermolecular rattling in a solvent shell, a lattice vibration, or another motion that influences the electronic transition. The idea is that we take the observed electronic transition to be linearly dependent on one or more local coordinates. Therefore describing Q allows us to describe the spectroscopy. However, since this local mode has further degrees of freedom that it may be interacting with, we are extracting a particular coordinate out or a continuum of other motions, the local mode will appear to feel a fluctuating environment—a friction.

Classically, we would describe the fluctuations in Q as Brownian motion, described by a Langevin equation. In the simplest sense this is an equation that restates Newton's equation of motion $F=ma$ for a fluctuating force acting on a harmonic coordinate Q.

$$m\ddot{Q}(t)+m\omega_0^2 Q^2 + m\gamma\dot{Q} = f(t) \tag{7.112}$$

Here the terms on the left side represent a damped harmonic oscillator. The first term is ma, the second term is the restoring force of the harmonic potential $F_{res} = \partial V/\partial Q$, and the third term allows friction γ to damp the motion of the coordinate. The motion of Q is driven by $f(t)$, a random fluctuating force. We take $f(t)$ to follow Gaussian statistics and obey the classical fluctuation-dissipation theorem:

$$\langle f(t)\rangle = 0 \tag{7.113}$$

$$\langle f(t) f(0)\rangle = 2m\gamma kT\ \delta(t) \tag{7.114}$$

[**] See: Nitzan, Ch. 8; Mukamel, Ch. 8; M. Cho and G.R. Fleming, "Chromophore-solvent dynamics," *Annu. Rev. Phys. Chem.* **47** (1996) 109.

Here the delta function indicates that we have a Markovian system – the fluctuations immediately loose all correlation on the time scale of the evolution of Q.

A more general description is the Generalized Langevin Equation, which accounts for the possibility that the damping may be time-dependent and carry memory of earlier configurations

$$m\ddot{Q}(t) + m\omega_0^2 Q^2 + m\int_0^t d\tau\, \gamma(t-\tau)\dot{Q}(\tau) = f(t). \tag{7.115}$$

$\gamma(t-\tau)$, the memory kernel, is a correlation function that describes the time-scales of the fluctuating force and obeys

$$\langle f(t)f(\tau)\rangle = 2mkT\,\gamma(t-\tau). \tag{7.116}$$

The GLE reduces to the Markovian limit eq. (7.112) for the case that $\gamma(t-\tau) = \gamma\delta(t-\tau)$.

The Langevin equation can be used to describe the correlation function for the time dependence of Q. For the Markovian case, eq. (7.112),

$$C_{QQ}(t) = \frac{kT}{m\omega_0^2}\left(\cos\Omega t + \frac{\gamma}{2\Omega}\sin\Omega t\right)e^{-\gamma t/2} \tag{7.117}$$

where the reduced frequency $\Omega = \sqrt{\omega_0^2 - \gamma^2/4}$. The frequency domain expression is

$$\tilde{C}_{QQ}(\omega) = \frac{\gamma kT}{m\pi}\frac{1}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\gamma^2}. \tag{7.118}$$

In the case of the GLE, similar expression are obtained, although now the damping constant is replaced by $\tilde{\gamma}(\omega)$, which is the frequency spectrum of the correlation function for the fluctuating force on the oscillator. This coordinate correlation function is just what we need for describing lineshapes. Note the quantum mechanical energy gap correlation function was

$$C_{eg}(t) = \langle\delta H_{eg}(t)\delta H_{eg}(0)\rangle = \hbar^2\omega_0^2 d^2\langle \underset{\sim}{q}(t)\underset{\sim}{q}(0)\rangle \tag{7.119}$$

We can get obtain exactly the same behavior as the classical GLE by solving the quantum mechanical problem by coupling to a bath of N harmonic oscillators, specified by coordinates q.

$$H_{nuc} = \sum_{\alpha=1}^{N}\hbar\omega_\alpha\left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2\right) \tag{7.120}$$

With this Hamiltonian, we can construct N harmonic coordinates any way we like with the appropriate unitary transformation. Specifically, we want to transform to a frame of reference

that includes our local mode Q and $N-1$ other linearly coupled normal modes, X_i. Given the transformation:

$$\underset{\sim}{U} \underset{\sim}{x} = \begin{pmatrix} Q \\ X_1 \\ X_2 \\ \vdots \\ X_{n-1} \end{pmatrix} \tag{7.121}$$

we can write

$$H_{nuc} = \hbar\omega_0 \left(\underset{\sim}{p}^2 + \underset{\sim}{Q}^2 \right) + \sum_{\alpha=1}^{N-1} \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{X}_\alpha^2 \right) + 2\underset{\sim}{Q}\sum_\alpha c_\alpha X_\alpha \tag{7.122}$$

Here we have expressed the Hamiltonian as a primary local mode Q linearly coupled to the remaining degrees of freedom with a strength c. In the following section, we describe how the correlation function for the coordinate Q in a Hamiltonian of this form is the same as the classical GLE, and reflects the fluctuating force acting on Q.

Electronic transition, ω_{eg} $\longleftrightarrow$ Primary coordinate, Q $\longleftrightarrow$ Bath of H.O.s, X_α
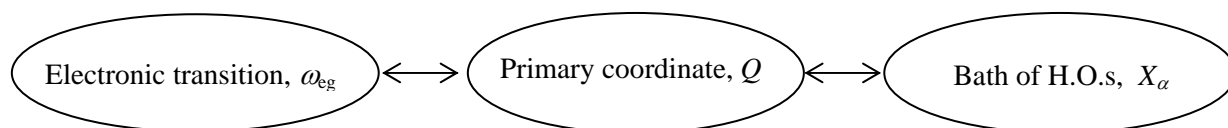
Therefore, a harmonic bath can be used to construct the behavior corresponding to random fluctuations. The important thing to remember when using a harmonic bath is that it is an abstract entity and does not have a clear physical interpretation in and of itself. If the spectral density has a peak at a frequency that corresponds to a known vibration of the molecule, it is reasonable to assume that the electronic transition is coupled to this motion. On the other hand if the spectral density is broad and featureless, as is common for low frequency intermolecular motions in condensed phases, then it is difficult to ascribe a clear microscopic origin to the motion. It is challenging to evaluate and understand both the frequency dependent density of states and the frequency dependent coupling, making is that much more challenging to assign the spectral density. Strategies that are meant to decompose and assign these effects remain an active area of research.

The Brownian Oscillator

Now we do back to our energy gap Hamiltonian and express it in a form that describes the energy gap dependence on one primary vibration which is linearly coupled to the remaining modes of a quantum bath. This formulation is known as the Brownian oscillator model.

We begin by writing

$$H = H_S + H_B + H_{SB} \tag{7.123}$$

where the system Hamiltonian is the full Hamiltonian for a displaced harmonic oscillator Hamiltonian which described the coupling of the electronic energy gap to a local mode, q.

$$H_S = |E\rangle H_E \langle E| + |G\rangle H_G \langle G| \tag{7.124}$$

The remaining terms describe the interaction of the primary oscillator q with the remaining coordinates of the bath x_a

$$H_B + H_{SB} = \sum_\alpha \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} \left(x_\alpha - \frac{c_\alpha q}{m_\alpha \omega_\alpha^2} \right)^2 \right) \tag{7.125}$$

Note here each of the bath oscillators is expressed as a displaced harmonic oscillator to the primary mode. Here c_α is the coupling strength. This can be expressed in a somewhat more familiar form by separating

$$H_B = \sum_\alpha \hbar \omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{q}_\alpha^2 \right)$$
$$H_{SB} = q \sum_\alpha c_\alpha x_\alpha \ + \ \lambda \tag{7.126}$$

The Brownian Oscillator Hamiltonian can now be used to solve for the modulation of the electronic energy gap induced by the bath. We start with

$$C_{eg}(t) = \langle \delta H_{eg}(t) \delta H_{eg}(0) \rangle = \xi^2 \langle \underset{\sim}{q}(t) \underset{\sim}{q}(0) \rangle \tag{7.127}$$

$\xi = 2\hbar \omega_0 \underset{\sim}{d}$ is the measure of the coupling of our primary oscillator to the electronic transition. The correlation functions for q are complicated to solve for, but can be done analytically:

$$\tilde{C}_{eg}''(\omega) = \xi \frac{\hbar}{2m} \frac{\omega \tilde{\gamma}(\omega)}{\left(\omega_0^2 - \omega^2 \right)^2 + \omega^2 \tilde{\gamma}^2(\omega)} . \tag{7.128}$$

Here $\tilde{\gamma}(\omega)$ is the spectral distribution of couplings between our primary vibration and the bath:

$$\tilde{\gamma}(\omega) = \pi \sum_{\alpha} \frac{c_{\alpha}^2}{2m_{\alpha}\omega_{\alpha}^2} \delta(\omega - \omega_{\alpha}) \qquad (7.129)$$

Here we see that the correlation function for the motion of the Brownian oscillator primary coordinate is equivalent to the randomly fluctuation coordinate described by the GLE, where the friction spectrum is described the magnitude of couplings between the primary and bath oscillators.

For the case that we can replace $\tilde{\gamma}(\omega)$ with a constant γ, the energy gap time correlation function can be obtained as

$$C_{eg}''(t) = \xi \frac{\hbar}{2m} \frac{1}{\Omega} \exp(-\gamma t/2) \sin \Omega t \qquad (7.130)$$

where $\Omega = \sqrt{\omega_0^2 - \gamma^2/4}$ is the reduced frequency. Using this model to describe the energy gap correlation function allows one to vary the parameters to interpolates smoothly between the coherent undamped limit and the overdamped Gaussian stochastic limit. Consider the following:

1) If we set $\gamma \to 0$, we recover our earlier result for $C_{eg}(t)$ and $g(t)$ for coupling to a single undamped nuclear coordinates and leads to fine structure on the electronic spectrum

2) For weak damping $\gamma << \omega$, eq. (7.130) becomes

$$C_{eg}''(t) = \xi^2 \frac{\hbar}{2m\omega_0} \exp(-\gamma/2) \sin \omega_0 t . \qquad (7.131)$$

3) For strong damping $\gamma >> 2\omega_i$, Ω is imaginary and we can re-write the expression in an overdamped form

$$C_{eg}''(t) \propto \xi^2 \frac{\hbar}{2m\omega_0^2} \Lambda \exp(-\Lambda t) \qquad (7.132)$$

where
$$\Lambda = \frac{\omega_0^2}{\gamma} . \qquad (7.133)$$

This is the correlation function for the Gaussian-stochastic model.

Absorption lineshapes are calculated as before, by calculating the lineshape function from the spectral density above. This model allows a bath to be constructed with all possible time scales,

by summing over many nuclear degrees of freedom, each of which may be under- or over-damped. In the frequency domain:

$$\tilde{C}''_{eg}(\omega) = \sum_i \tilde{C}''_{eg,i}(\omega) = \sum_i \xi_i \frac{\hbar}{2m} \frac{\omega\gamma(\omega)}{\left(\omega_i^2 - \omega^2\right)^2 + \omega^2\,\gamma_i^2(\omega)}. \tag{7.134}$$

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