

7. OBSERVING FLUCTUATIONS IN SPECTROSCOPY¹

Here we will address how fluctuations are observed in spectroscopy and how dephasing influences the absorption lineshape. Our approach will be to calculate a dipole correlation function for a dipole interacting with a fluctuating environment, and show how the time scale and amplitude of fluctuations are encoded in the lineshape. Although the description here is for the case of a spectroscopic observable, the approach can be applied to any such problems in which the deterministic motions of an object under an external potential are modulated by a random force.

We also aim to establish a connection between this picture and the Displaced Harmonic Oscillator model. Specifically, we will show that a frequency-domain representation of the coupling between a transition and a continuous distribution of harmonic modes is equivalent to a time-domain picture in which the transition energy gap fluctuates about an average frequency with a statistical time-scale and amplitude given by the distribution coupled modes.

7.1. FLUCTUATIONS AND RANDOMNESS: SOME DEFINITIONS²

“Fluctuations” is my word for the time-evolution of a randomly modulated system at or near equilibrium. You are observing an internal variable to a system under the influence of thermal agitation of the surroundings. Such processes are also commonly referred to as stochastic. A stochastic equation of motion is one in which there is both a deterministic and a random component to the time-development.

Randomness is a characteristic of all physical systems to a certain degree, even if the equations of motion that govern them are totally deterministic. This is because we generally have imperfect knowledge about all of the degrees of freedom for the system. This is the case when we look at a subset of particles which are under the influence of others that we have imperfect knowledge of. The result is that we may observe random fluctuations in our observables. This is always the case in condensed phase problems. It's unreasonable to think that you will come up with an equation of motion for the internal determinate variable, but we should be able to understand the behavior statistically and come up with equations of motion for probability distributions

¹ For readings on this topic see: Nitzan, A. *Chemical Dynamics in Condensed Phases* (Oxford University Press, New York, 2006), Chapter 7; C.H. Wang, *Spectroscopy of Condensed Media: Dynamics of Molecular Interactions*, Academic Press, Orlando, 1985.

² Nitzan, Ch. 1.5 and Ch. 7.

When we introduced correlation functions, we discussed the idea that a statistical description of a system is commonly formulated in terms of probability distribution functions P . Observables are commonly described by moments of a variable obtained by integrating over P , for instance

$$\begin{aligned}\langle x \rangle &= \int dx x P(x) \\ \langle x^2 \rangle &= \int dx x^2 P(x)\end{aligned}\tag{7.1}$$

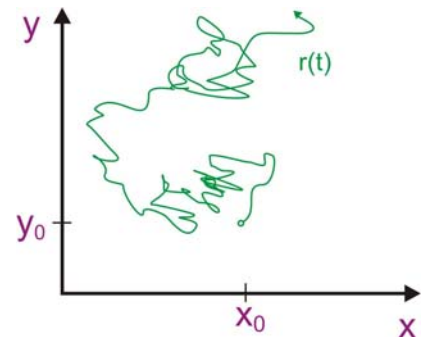
For time-dependent processes, we use a time-dependent probability distribution

$$\begin{aligned}\langle x(t) \rangle &= \int dx x(t) P(x, t) \\ \langle x^2(t) \rangle &= \int dx x^2(t) P(x, t)\end{aligned}\tag{7.2}$$

Correlation functions go a step further and depend on joint probability distributions $P(t'', A; t', B)$ that give the probability of observing a value of A at time t'' and a value of B at time t' :

$$\langle A(t'') B(t') \rangle = \int dA \int dB AB P(t'', A; t', B).\tag{7.3}$$

Random fluctuations are also described through a time-dependent probability distribution, for which we need an equation of motion. A common example of such a process is Brownian motion, the fluctuating position of a particle under the influence of a thermal environment. It's not practical to describe the absolute position of the particle, but we can formulate an equation of motion for the probability of finding the particle in time and space given that you know its initial position. This probability density obeys the well known diffusion equation, here written in one dimension:



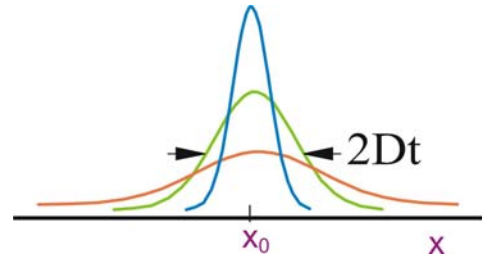
$$\frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} P(x, t)\tag{7.4}$$

Here D is the diffusion constant which sets the time-scale and spatial extent of the random motion. Note the similarity of this equation to the time-dependent Schrödinger equation for a free particle if D is taken as imaginary. Given the initial condition $P(x, t_0) = \delta(x - x_0)$, the solution is a conditional probability density

$$P(x, t | x_0, t_0) = \frac{1}{\sqrt{2\pi Dt}} \exp\left(-\frac{(x - x_0)^2}{4Dt}\right)\tag{7.5}$$

The probability distribution describes the statistics for fluctuations in the position of a particle averaged over many trajectories. Analyzing the moments of this probability density in eq. (7.2) we find that

$$\begin{aligned}\langle x \rangle &= 0 \\ \langle x^2 \rangle &= 2Dt\end{aligned}\tag{7.6}$$



So, the distribution maintains a Gaussian shape centered at x_0 , and broadening with time as $2Dt$.

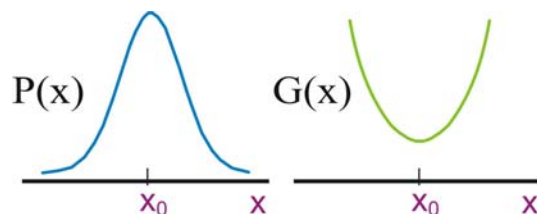
Brownian motion is an example of a Gaussian-Markovian process. Here Gaussian refers to cases in which we describe the probability distribution for a variable $P(x)$ as a Gaussian normal distribution. Here in one dimension:

$$\begin{aligned}P(x) &= A e^{-(x-x_0)^2/2\Delta^2} \\ \Delta^2 &= \langle x^2 \rangle - \langle x \rangle^2\end{aligned}\tag{7.7}$$

The Gaussian distribution is important, because the central limit theorem states that the distribution of a continuous random variable with finite variance will follow the Gaussian distribution. Gaussian distributions also are completely defined in terms of their first and second moments, meaning that a time-dependent probability density $P(x,t)$ is uniquely characterized by a mean value in the observable variable x and a correlation function that describes the fluctuations in x . Gaussian distributions for systems at thermal equilibrium are also important for the relationship between Gaussian distributions and parabolic free energy surfaces:

$$G(x) = -kT \ln P(x)\tag{7.8}$$

If the probability density is Gaussian along x , then the system's free energy projected along this coordinate (often referred to as a potential of mean force) has a harmonic shape. Thus Gaussian statistics are effective for describing fluctuations about an equilibrium mean value x_0 .



Markovian means that, given the knowledge of the state of the system at time t_1 , you can exactly describe P for a later time t_2 . That is, the system has no memory of the behavior at an earlier time t_0 .

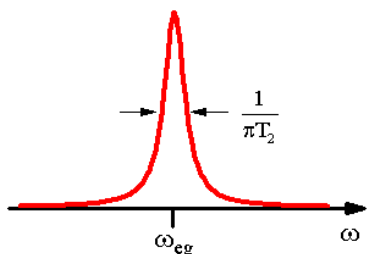
$$\begin{aligned} P(x, t_2; x, t_1; x, t_0) &= P(x, t_2; x, t_1)P(x, t_1; x, t_0) \\ P(t_2; t_1; t_0) &= P(t_2; t_1)P(t_1; t_0) \end{aligned} \tag{7.9}$$

Markovian therefore refers to a timescale long compared to correlation time for the internal variable that you care about. For instance, the diffusion equation only holds after the particle has experienced sufficient collisions with its surroundings that it has no memory of its earlier position and momentum: $t > \tau_c$.

7.2. FLUCTUATIONS IN SPECTROSCOPY: SPECTRAL DIFFUSION

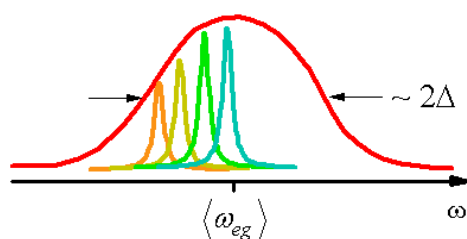
To begin our discussion about how fluctuations manifest themselves in spectroscopy, let's discuss their influence on the transition energy gap ω_{eg} for the absorption lineshape. Consider the two limiting cases of line broadening:

Homogeneous:



Here, the absorption lineshape is *dynamically* broadened by rapid variations in the amplitude, phase, or orientation of dipoles. Pure dephasing, lifetime, and rotation all contribute to an exponential decay time T_2 . For our current discussion, let's only concentrate on pure-dephasing T_2^* from rapid fluctuations in ω_{eg} .

Inhomogeneous:

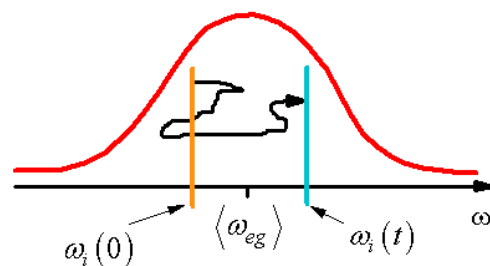


In this limit, the lineshape reflects a *static* distribution of resonance frequencies, and the width of the line represents the distribution of frequencies, which arise, for instance, from different structural environments.

Spectral Diffusion

More generally, every system lies between these limits. Imagine every molecule having a different “instantaneous frequency” $\omega_i(t)$ which evolves in time. This process is known as spectral diffusion. The homogeneous and inhomogeneous limits can be described as limiting forms for the fluctuations of a frequency $\omega_i(t)$ through a distribution of frequencies Δ .

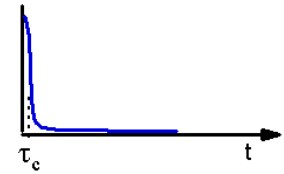
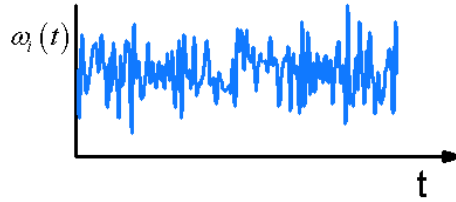
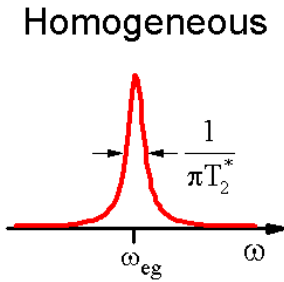
If $\omega_i(t)$ evolves rapidly relative to Δ^{-1} , the system is homogeneously broadened. If $\omega_i(t)$ evolves slowly the system is inhomogeneous. This behavior can be quantified through the transition frequency time-correlation function $C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle$. Our job will be to relate the behavior of $C_{eg}(t)$ with the correlation function that determined the lineshape, $C_{\mu\mu}(t)$.



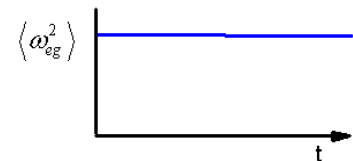
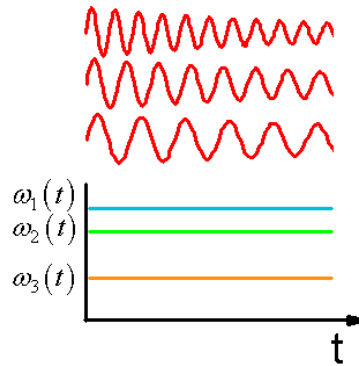
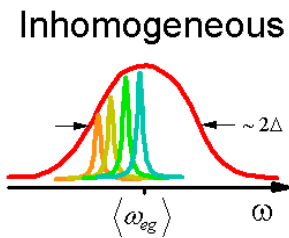
Time-domain behavior

$$C_{eg}(t) = \langle \omega_{eg}(t) \omega_{eg}(0) \rangle$$

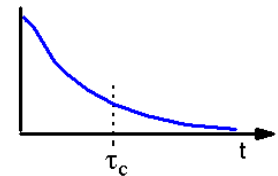
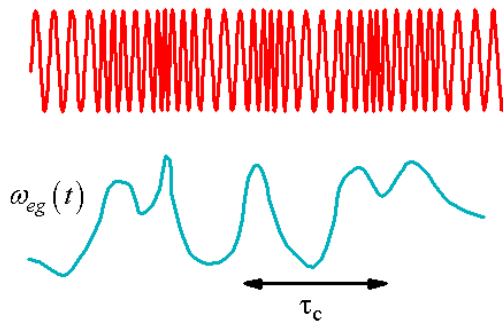
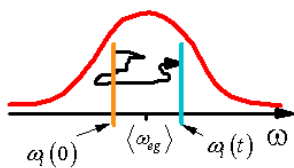
“Motionally narrowed”



Static distribution



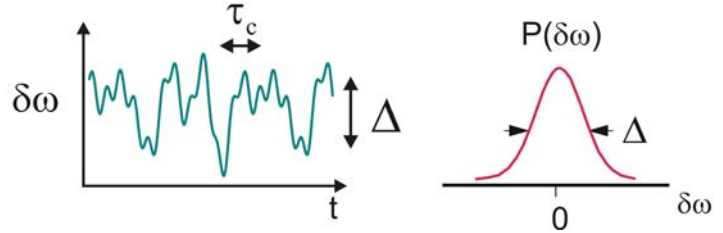
Time-varying freq.



7.3. GAUSSIAN-STOCHASTIC MODEL FOR SPECTRAL DIFFUSION

We will begin with a *classical* description of how random fluctuations in frequency influence the absorption lineshape, by calculating the dipole correlation function for the resonant transition.

This is a Gaussian stochastic model for fluctuations, meaning that we will describe the time-dependence of the transition energy as *random* fluctuations about an average value with a Gaussian statistics.



$$\omega(t) = \langle \omega \rangle + \delta\omega(t) \quad (7.10)$$

$$\langle \delta\omega(t) \rangle = 0 \quad (7.11)$$

The fluctuations in ω allow the system to explore a Gaussian distribution of transitions frequencies characterized by a variance:

$$\Delta = \langle \delta\omega^2 \rangle^{1/2}. \quad (7.12)$$

Furthermore, we will describe the time scale of the random fluctuations through a correlation time:

$$\tau_c = \frac{1}{\Delta^2} \int_0^\infty dt \langle \delta\omega(t) \delta\omega(0) \rangle. \quad (7.13)$$

Let's treat the dipole moment as a classical internal variable to the system, whose time dependence arises from a linear relationship to the frequency fluctuations $\omega(t)$

$$\frac{\partial \mu}{\partial t} = -i\omega(t)\mu \quad (7.14)$$

Although it is a classical equation, note the similarity to the quantum Heisenberg equation for the dipole operator: $\partial\mu/\partial t = i[H(t)\mu - \mu H(t)]/\hbar$. This offers some insight into how the quantum version of this problem will look. The solution to eq. (7.14) is

$$\mu(t) = \mu(0) \exp\left[-i \int_0^t d\tau \omega(\tau)\right] \quad (7.15)$$

Substituting eq. (7.10) we have

$$\mu(t) = \mu(0) \exp\left[-i \langle \omega \rangle t - i \int_0^t d\tau \delta\omega(\tau)\right]. \quad (7.16)$$

Now to evaluate the dipole correlation function we have to perform an average over an equilibrium system.

$$C_{\mu\mu}(t) = \langle \mu(t) \mu(0) \rangle = \left\langle |\mu(0)|^2 \exp \left[-i \langle \omega \rangle t - i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle \quad (7.17)$$

or making the Condon approximation

$$C_{\mu\mu}(t) = |\mu|^2 e^{-i \langle \omega \rangle t} F(t) \quad (7.18)$$

where

$$F(t) = \left\langle \exp \left[-i \int_0^t d\tau \delta\omega(\tau) \right] \right\rangle. \quad (7.19)$$

The dephasing function here is obtained by performing an equilibrium average of the exponential argument over fluctuating trajectories. For ergodic systems, this is equivalent to averaging long enough over a single trajectory.

The dephasing function is a bit of a complicated to work with as written. However, for the case of Gaussian statistics for the fluctuations, it is possible to simplify $F(t)$ by expanding it as a *cumulant expansion of averages* (see Appendix)

$$F(t) = \exp \left[-i \int_0^t d\tau' \langle \delta\omega(\tau') \rangle + \frac{i^2}{2!} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau') \delta\omega(\tau'') \rangle + \dots \right] \quad (7.20)$$

In this expression the first term is zero, and only the second term survives for a system with Gaussian statistics. We have re-written the dephasing function in terms of a correlation function that describes the fluctuating energy gap. Note that this is a classical description, so there is no time-ordering to the exponential. Now recognizing that we have a stationary system, we have

$$F(t) = \exp \left[-\frac{1}{2} \int_0^t d\tau' \int_0^t d\tau'' \langle \delta\omega(\tau' - \tau'') \delta\omega(0) \rangle \right] \quad (7.21)$$

$F(t)$ can be rewritten through a change of variables ($\tau = \tau' - \tau''$):

$$F(t) = \exp \left[-\int_0^t d\tau (t - \tau) \langle \delta\omega(\tau) \delta\omega(0) \rangle \right] \quad (7.22)$$

So the Gaussian stochastic model allows the influence of the frequency fluctuations on the lineshape to be described by a frequency correlation function that follows Gaussian statistics.

$$C_{\delta\omega\delta\omega}(t) = \langle \delta\omega(t) \delta\omega(0) \rangle \quad (7.23)$$

Note we are now dealing with two different correlation functions $C_{\delta\omega\delta\omega}$ and $C_{\mu\mu}$.

Now, we will calculate the lineshape assuming that $C_{\delta\omega\delta\omega}$ takes on an exponential form

$$C_{\delta\omega\delta\omega}(t) = \Delta^2 \exp[-t/\tau_c] \quad (7.24)$$

Then eq. (7.22) gives

$$F(t) = \exp\left[-\Delta^2 \tau_c^2 \left(\exp(-t/\tau_c) + t/\tau_c - 1\right)\right]. \quad (7.25)$$

Or given $F(t) = \exp(-g(t))$

$$g(t) = \Delta^2 \tau_c^2 \left(\exp(-t/\tau_c) + t/\tau_c - 1\right) \quad (7.26)$$

Let's look at the limiting forms of $g(t)$:

- 1) **Long correlation times** (or short t): $t \ll \tau_c$. This corresponds to the inhomogeneous case where $C_{\delta\omega\delta\omega}(t) = \Delta^2$, a constant. For $t \ll \tau_c$ we can perform a short time expansion of exponential

$$e^{-t/\tau_c} \approx 1 - \frac{t}{\tau_c} + \frac{t^2}{2\tau_c^2} + \dots \quad (7.27)$$

and from eq. (7.26) we obtain

$$g(t) = \Delta^2 t^2 / 2 \quad (7.28)$$

At short times, our dipole correlation function will have a Gaussian decay with a rate given by Δ^2 : $F(t) = \exp(-\Delta^2 t^2 / 2)$. This has the proper behavior for a classical correlation function, i.e. even in time $C_{\mu\mu}(t) = C_{\mu\mu}(-t)$.

In this limit, the absorption lineshape is:

$$\begin{aligned} \sigma(\omega) &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-i\langle\omega\rangle t - g(t)} \\ &= |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle\omega\rangle)t} e^{-\Delta^2 t^2 / 2} \\ &= \sqrt{\pi} |\mu|^2 \exp\left(-\frac{(\omega - \langle\omega\rangle)^2}{2\Delta^2}\right) \end{aligned} \quad (7.29)$$

We obtain a Gaussian inhomogeneous lineshape centered at the mean frequency with a width dictated by the frequency distribution.

- 2) **Short correlation times**: $t \gg \tau_c$. This corresponds to the homogeneous limit in which you can approximate $C_{\delta\omega\delta\omega}(t) = \Delta^2 \delta(t)$. For $t \gg \tau_c$ we set $e^{-t/\tau_c} \approx 0$, $t/\tau_c \gg 1$ and eq. (7.26) gives

$$g(t) = -\Delta^2 \tau_c t \quad (7.30)$$

If we define the constant

$$\Delta^2 \tau_c \equiv \Gamma = \frac{1}{T_2} \quad (7.31)$$

we see that the dephasing function has an exponential decay!

$$F(t) = \exp[-t/T_2] \quad (7.32)$$

The lineshape for short correlation times (or fast fluctuations) takes on a Lorentzian shape

$$\sigma(\omega) = |\mu|^2 \int_{-\infty}^{+\infty} dt e^{i(\omega - \langle \omega \rangle)t} e^{-t/T_2}$$

$$\text{Re } \sigma(\omega) \propto \frac{1}{(\omega - \langle \omega \rangle)^2 + \frac{1}{T_2^2}} \quad (7.33)$$

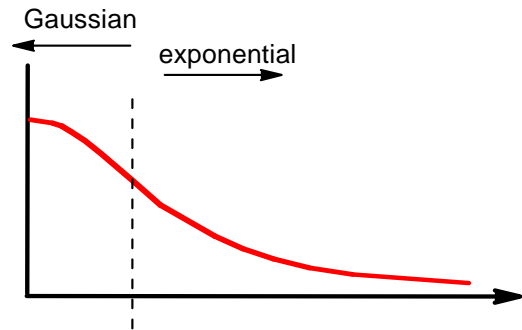
This represents the homogeneous limit! Even with a broad distribution of accessible frequencies, if the system explores all of these frequencies on a time scale fast compared to the inverse of the distribution ($\Delta \tau_c > 1$), then the resonance will be “motionally narrowed” into a Lorentzian line.

General Behavior

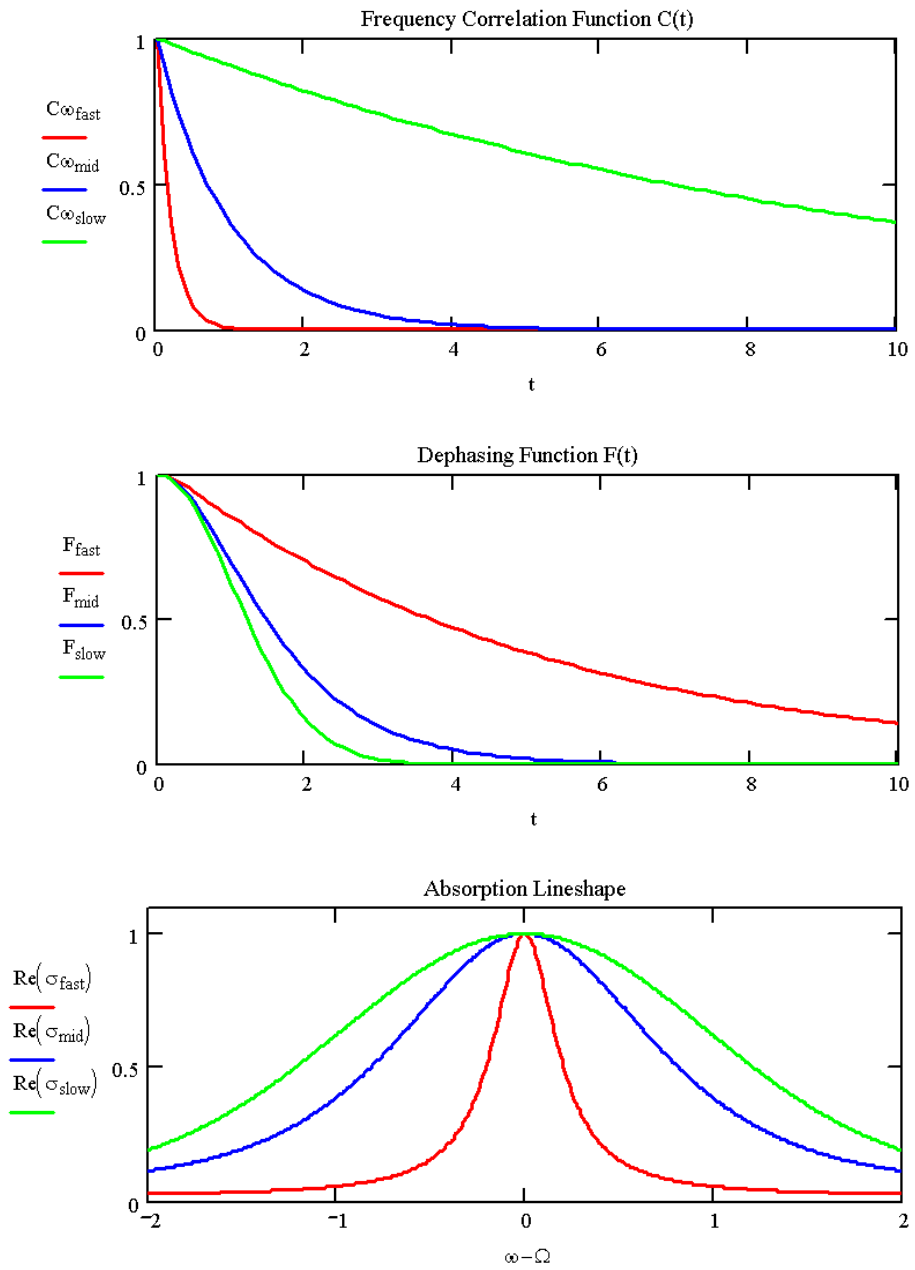
More generally, the envelope of the dipole correlation function will look Gaussian at short times and exponential at long times. The correlation time is the separation between these regimes. The behavior for varying time scales of the dynamics (τ_c) are best characterized with respect to the distribution of accessible frequencies (Δ). So we can define a factor

$$\kappa = \Delta \cdot \tau_c \quad (7.34)$$

$\kappa \ll 1$ is the fast modulation limit and $\kappa \gg 1$ is the slow modulation limit. Let's look at how $C_{\delta\omega\delta\omega}$, $F(t)$, and $\sigma_{abs}(\omega)$ change as a function of κ .

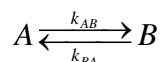


$$\Delta = 1 \quad \tau_c = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \quad \kappa = \begin{pmatrix} 0.2 \\ 1 \\ 10 \end{pmatrix} \quad \begin{array}{l} \text{fast} \\ \text{mid} \\ \text{slow} \end{array}$$

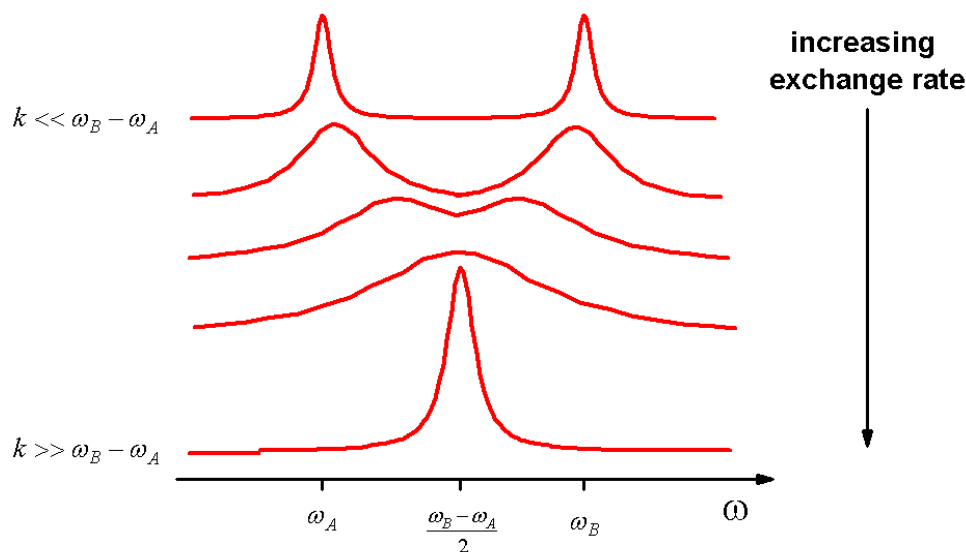


We see that for a fixed distribution of frequencies Δ the effect of increasing the time scale of fluctuations through this distribution (decreasing τ_c) is to gradually narrow the observed lineshape from a Gaussian distribution of static frequencies with width (FWHM) of $2.35 \cdot \Delta$ to a motionally narrowed Lorentzian lineshape with width (FWHM) of $\Delta^2 \tau_c / \pi = \Delta \cdot \kappa / \pi$.

This is analogous to the motional narrowing effect first described in the case of temperature dependent NMR spectra of two exchanging species. Assume we have two resonances at ω_A and ω_B associated with two chemical species that are exchanging at a rate k_{AB}



If the rate of exchange is slow relative to the frequency splitting, $k_{AB} \ll \omega_A - \omega_B$, then we expect two resonances, each with a linewidth dictated by the molecular relaxation processes (T_2) and transfer rate of each species. On the other hand, when the rate of exchange between the two species becomes faster than the energy splitting, then the two resonances narrow together to form one resonance at the mean frequency.³



³ Anderson, P. W. A mathematical model for the narrowing of spectral lines by exchange or motion. *J. Phys. Soc. Japan* **9**, 316 (1954).; Kubo, R. in *Fluctuation, Relaxation, and Resonance in Magnetic Systems* (ed. Ter Haar, D.) (Oliver and Boyd, London, 1962).

APPENDIX: THE CUMULANT EXPANSION

For a statistical description of the random variable x , we wish to characterize the moments of x : $\langle x \rangle, \langle x^2 \rangle, \dots$. Then the average of an exponential in x can be expressed as an expansion in moments

$$\langle e^{ikx} \rangle = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle \quad (7.35)$$

An alternate way of expressing this expansion is in terms of cumulants $c_n(x)$

$$\langle e^{ikx} \rangle = \exp \left(\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} c_n(x) \right), \quad (7.36)$$

where the first few cumulants are:

$$c_1(x) = \langle x \rangle \quad \text{mean} \quad (7.37)$$

$$c_2(x) = \langle x^2 \rangle - \langle x \rangle^2 \quad \text{variance} \quad (7.38)$$

$$c_3(x) = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + 2\langle x \rangle^3 \quad \text{skewness} \quad (7.39)$$

An expansion in cumulants converges much more rapidly than an expansion in moments, particularly when you consider that x may be a time-dependent variable. For a system that obeys Gaussian statistics, all cumulants with $n > 2$ vanish!

We obtain the cumulants above by comparing terms in powers of x in eq. (7.35) and (7.36). We start by postulating that instead of expanding the exponential directly, we can instead expand the exponential argument in powers of an operator or variable H

$$F = \exp[c] = 1 + c + \frac{1}{2}c^2 + \dots \quad (7.40)$$

$$c = c_1 H + \frac{1}{2}c_2 H^2 + \dots \quad (7.41)$$

Inserting eq. (7.41) into eq. (7.40) and collecting terms in orders of H gives

$$\begin{aligned} F &= 1 + \left(c_1 H + \frac{1}{2}c_2 H^2 + \dots \right) + \frac{1}{2} \left(c_1 H + \frac{1}{2}c_2 H^2 + \dots \right)^2 + \dots \\ &= 1 + (c_1)H + \frac{1}{2}(c_2 + c_1^2)H^2 + \dots \end{aligned} \quad (7.42)$$

Now comparing this with the expansion of the exponential

$$\begin{aligned} F &= \exp[fH] \\ &= 1 + f_1 H + \frac{1}{2}f_2 H^2 + \dots \end{aligned} \quad (7.43)$$

allows one to see that

$$\begin{aligned}
 c_1 &= f_1 \\
 c_2 &= f_2 - f_1^2
 \end{aligned}
 \tag{7.44}$$

The cumulant expansion can also be applied to time-correlations. Applying this to the time-ordered exponential operator we obtain:

$$\begin{aligned}
 F(t) &= \left\langle \exp_+ \left[-i \int_0^t dt \omega(t) \right] \right\rangle \\
 &\approx \exp \left[c_1(t) + c_2(t) \right]
 \end{aligned}
 \tag{7.45}$$

$$c_1 = -i \int_0^t d\tau \langle \omega(\tau) \rangle
 \tag{7.46}$$

$$\begin{aligned}
 c_2 &= -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \omega(\tau_2) \omega(\tau_1) \rangle - \langle \omega(\tau_2) \rangle \langle \omega(\tau_1) \rangle \\
 &= -i \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega(\tau_2) \delta\omega(\tau_1) \rangle
 \end{aligned}
 \tag{7.47}$$

For Gaussian statistics, all higher cumulants vanish.

7.4. QUANTUM MECHANICAL TREATMENT OF FLUCTUATIONS: THE ENERGY GAP HAMILTONIAN[§]

Introduction

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.

Energy Gap Hamiltonian

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

$$H_0 = H_e + E_e + H_g + E_g \quad (7.48)$$

$$H_0 = \hbar\omega_{eg} + H_{eg} + 2H_g \quad (7.49)$$

where the Energy Gap Hamiltonian is

$$H_{eg} = H_e - H_g. \quad (7.50)$$

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:

$$H_0 = H_S + H_{SB} + H_B \quad (7.51)$$

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

$$\tilde{p} = \sqrt{\frac{2}{\hbar\omega_0 m}} \hat{p}. \quad (7.52)$$

[§] See Mukamel, Ch. 8 and Ch. 7.

$$\underline{q} = \sqrt{\frac{m\omega_0}{2\hbar}} \hat{q} \quad (7.53)$$

$$\underline{d} = \sqrt{\frac{m\omega_0}{2\hbar}} d \quad (7.54)$$

$$H_e = \hbar\omega_0 \left(\underline{p}^2 + (\underline{q} - \underline{d})^2 \right) \quad (7.55)$$

$$H_g = \hbar\omega_0 (\underline{p}^2 + \underline{q}^2)$$

From (7.50) we have

$$\begin{aligned} H_{eg} &= -2\hbar\omega_0 \underline{d} \underline{q} + \hbar\omega_0 \underline{d}^2 \\ &= -2\hbar\omega_0 \underline{d} \underline{q} + \lambda \end{aligned} \quad (7.56)$$

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.

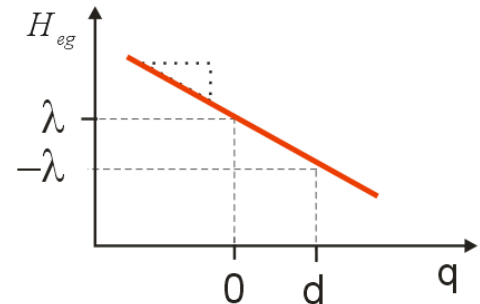
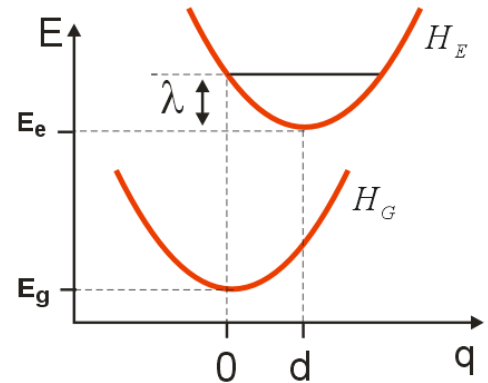
$$C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} F(t) \quad (7.57)$$

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

We now want to rewrite the dephasing function in terms of the time dependence to the energy gap H_{eg} ; that is, if $F(t) = \langle U_{eg} \rangle$, 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

$$H_e = H_g + H_{eg} \quad \Leftrightarrow \quad H = H_0 + V \quad (7.59)$$

Then we see that we can represent the time dependence of H_{eg} by evolution under H_g . The time-propagators are



$$e^{-iH_e t/\hbar} = e^{-iH_g t/\hbar} \exp_+ \left[\frac{-i}{\hbar} \int_0^t d\tau H_{eg}(\tau) \right] \quad (7.60)$$

$$U_e = U_g U_{eg}$$

and

$$\begin{aligned} H_{eg}(t) &= e^{iH_g t/\hbar} H_{eg} e^{-iH_g t/\hbar} \\ &= U_g^\dagger H_{eg} U_g \end{aligned} \quad (7.61)$$

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

$$U_{eg}(\tau) = \exp_+ \left[\frac{-i}{\hbar} \int_0^\tau d\tau' H_{eg}(\tau') \right] \quad (7.62)$$

$$F(t) = \left\langle e^{iH_g t} e^{-iH_e t} \right\rangle = \left\langle \exp_+ \left[\frac{-i}{\hbar} \int_0^t d\tau H_{eg}(\tau) \right] \right\rangle \quad (7.63)$$

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 $H_{BA}(\tau) = e^{+iH_A \tau} H_{BA} e^{-iH_A \tau}$. 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

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

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}

$$\langle H_{eg} \rangle = \hbar \omega_0 d^2 = \lambda \quad (7.65)$$

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

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

where

$$\delta H_{eg} = H_{eg} - \langle H_{eg} \rangle. \quad (7.67)$$

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

$$\delta\omega_{eg} \equiv \frac{\delta H_{eg}}{\hbar} \quad (7.68)$$

we obtain

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

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

So, the dipole correlation function can be expressed as

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

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

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

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

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

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

Note that C_{eg} is a complex quantity with

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

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

Here $\coth(x) = (e^x + e^{-x}) / (e^x - e^{-x})$. As the temperature is raised well beyond the frequency of the oscillator, C_{eg} becomes real, $|C_{eg}'| \gg |C_{eg}''|$, 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

$$\begin{aligned} g(t) &= D \left[\coth(\beta \hbar \omega_0 / 2) (1 - \cos \omega_0 t) + i(\sin \omega_0 t - \omega_0 t) \right] \\ &= g' + i g'' \end{aligned} \quad (7.77)$$

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

$$\begin{aligned} g(t) &= D \left[\bar{n} (e^{-i\omega_0 t} - 1 + e^{+i\omega_0 t} - 1) + (e^{-i\omega_0 t} - 1) \right] - iD\omega_0 t \\ &= D \left[(\bar{n} + 1) (e^{-i\omega_0 t} - 1) + \bar{n} (e^{+i\omega_0 t} - 1) \right] - iD\omega_0 t \end{aligned} \quad (7.78)$$

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, $\coth(\beta \hbar \omega_0 / 2) \rightarrow 1$ and $\bar{n} \rightarrow 0$, we have

$$\begin{aligned} g(t) &= D [1 - \cos \omega_0 t + i \sin \omega_0 t - i \omega_0 t] \\ &= D [1 - e^{-i\omega_0 t} - i \omega_0 t] \end{aligned} \quad (7.79)$$

Combining with

$$F(t) = e^{-i\lambda t / \hbar - g(t)} = e^{-iD\omega_0 t - g(t)} \quad (7.80)$$

we have our old result:

$$F(t) = \exp \left[D (e^{-i\omega_0 t} - 1) \right]. \quad (7.81)$$

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

$$\begin{aligned} F(t) &= \exp \left[\frac{-2D}{\beta \hbar \omega_0} (1 - \cos(\omega_0 t)) \right] \\ &= e^{-2DkT / \hbar \omega_0} \sum_{j=0}^{\infty} \frac{1}{j!} \left(\frac{2DkT}{\hbar \omega_0} \right)^j \cos^j(\omega_0 t) \end{aligned} \quad (7.82)$$

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:

$$\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} C_{eg}(t) dt = 2 \operatorname{Re} \int_0^{+\infty} e^{i\omega t} C_{eg}(t) dt. \quad (7.83)$$

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

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

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

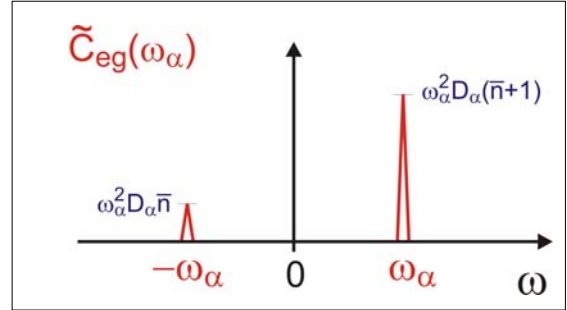
Where $\tilde{C}'_{eg}(\omega)$ and $\tilde{C}''_{eg}(\omega)$ are the Fourier transforms of the real and imaginary components of $C_{eg}(t)$, respectively. Note that $\tilde{C}_{eg}(\omega)$ is an entirely real quantity.

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)):

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

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

$$\tilde{C}(-\omega) = e^{-\beta\hbar\omega} \tilde{C}(\omega). \quad (7.87)$$



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

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

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

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:

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

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

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

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

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

$$H_0 = \hbar\omega_{eg} + H_{eg} + H_B \quad (7.93)$$

$$H_B = \sum_{\alpha} \hbar\omega_{\alpha} (\underline{p}_{\alpha}^2 + \underline{q}_{\alpha}^2) \quad (7.94)$$

$$H_{eg} = \sum_{\alpha} 2\hbar\omega_{\alpha} \underline{d}_{\alpha} \underline{q}_{\alpha} + \lambda \quad (7.95)$$

$$\lambda = \sum_{\alpha} \hbar\omega_{\alpha} \underline{d}_{\alpha}^2 \quad (7.96)$$

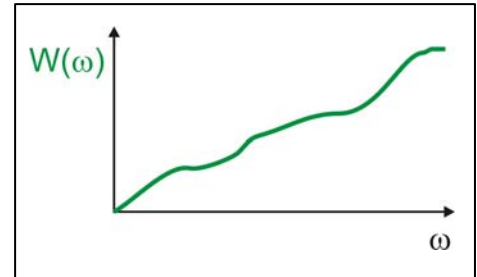
Note that the time-dependence to H_{eg} results from the interaction with the bath:

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

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

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

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 $D(\omega) = \underline{d}^2(\omega)$. For instance, eq. (7.98) becomes



$$g(t) = \int d\omega_\alpha W(\omega_\alpha) g(t, \omega_\alpha) \quad (7.99)$$

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 $C_{eg}(t)$

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

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).

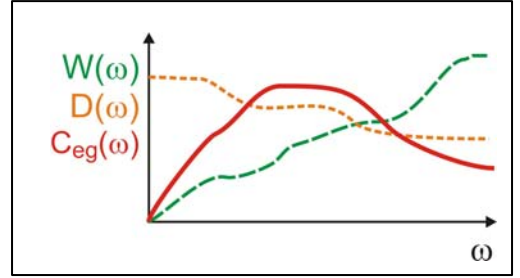
While eq. (7.100) expresses the modulation of the energy gap in the time domain, we can alternatively express the continuous distribution of coupled bath modes in the frequency domain:

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

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

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

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*

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

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

$$\begin{aligned}
g(t) &= \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} [\exp(-i\omega t) + i\omega t - 1] \\
&= \int_0^{\infty} d\omega \rho(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) (1 - \cos \omega t) + i(\sin \omega t - \omega t) \right].
\end{aligned} \tag{7.104}$$

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

$$\lambda = \hbar \int_0^{\infty} d\omega \omega \rho(\omega). \tag{7.105}$$

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 $\coth(\beta\hbar\omega/2) \rightarrow 2/\beta\hbar\omega$ 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

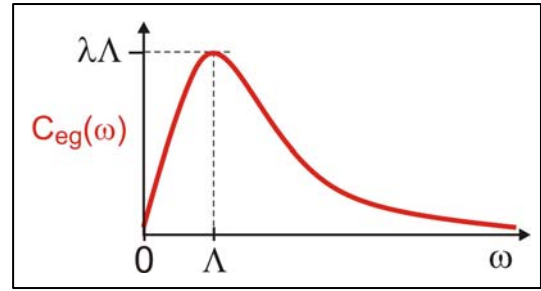
$$\begin{aligned}
g(t) &= \int_0^{+\infty} d\omega \frac{1}{\pi\beta\hbar\omega} \frac{\tilde{C}_{eg}(\omega)}{\omega^2} (1 - \cos \omega t) \\
&= \Gamma t
\end{aligned} \tag{7.106}$$

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 $\omega=0$. Specifically, let's write the imaginary part of the Lorentzian lineshape in the form

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

Here, in the high temperature (classical) limit $kT \gg \hbar\Lambda$, neglecting the imaginary part, we find:



$$g(t) \approx \frac{2\lambda kT}{\hbar\Lambda^2} [\exp(-\Lambda t) + \Lambda t - 1] \quad (7.108)$$

This expression looks familiar. If we equate

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

and

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

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

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

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.

7.5. CORRESPONDENCE OF HARMONIC BATH AND STOCHASTIC EQUATIONS**

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 of 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 .

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

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:

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

$$\langle f(t) \rangle = 0 \quad (7.113)$$

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

Here the delta function indicates that we have a Markovian system – the fluctuations immediately lose 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

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

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

$$\langle f(t) f(\tau) \rangle = 2mkT \gamma(t-\tau). \quad (7.116)$$

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),

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

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

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

In the case of the GLE, similar expressions 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

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

We can 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 .

$$H_{mc} = \sum_{\alpha=1}^N \hbar \omega_{\alpha} \left(p_{\alpha}^2 + q_{\alpha}^2 \right) \quad (7.120)$$

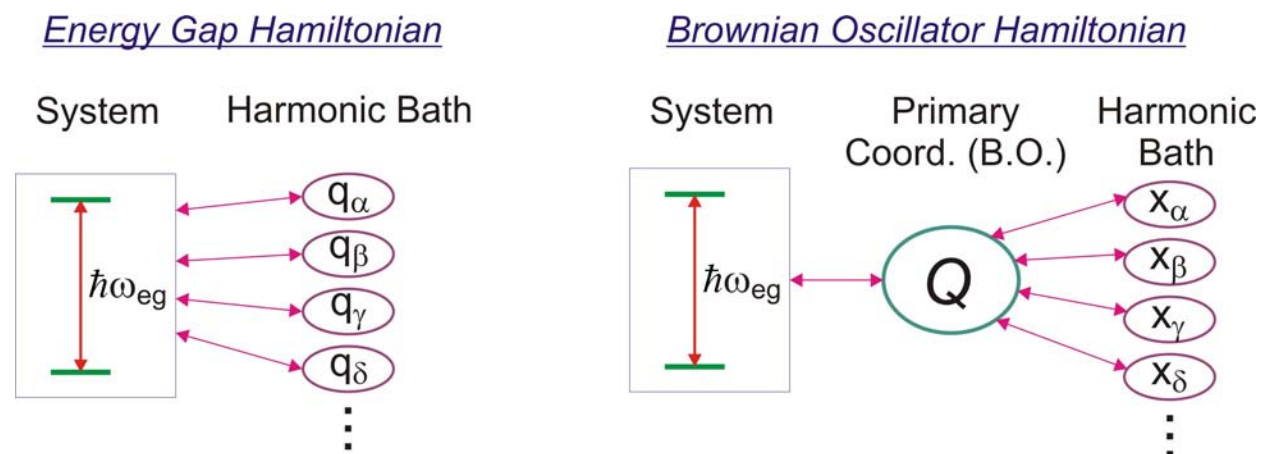
With this Hamiltonian, we can construct N harmonic coordinates any way we like with the appropriate unitary transformation. Specifically, we want to transform to a frame of reference that includes our local mode Q and $N-1$ other linearly coupled normal modes, X_i . Given the transformation:

$$\underline{\tilde{x}} = \begin{pmatrix} Q \\ X_1 \\ X_2 \\ \vdots \\ X_{n-1} \end{pmatrix} \quad (7.121)$$

we can write

$$H_{mic} = \hbar\omega_0 \left(\underline{\tilde{p}}^2 + \underline{\tilde{Q}}^2 \right) + \sum_{\alpha=1}^{N-1} \hbar\omega_{\alpha} \left(\underline{\tilde{p}}_{\alpha}^2 + \underline{\tilde{X}}_{\alpha}^2 \right) + 2\underline{\tilde{Q}} \sum_{\alpha} c_{\alpha} X_{\alpha} \quad (7.122)$$

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 (the Brownian Oscillator) is the same as the classical GLE, and reflects the fluctuating force acting on Q .



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 molecular 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 it 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.

7.6. THE BROWNIAN OSCILLATOR HAMILTONIAN

Let's go 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

$$H = H_S + H_B + H_{SB} \quad (7.123)$$

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 .

$$H_S = |E\rangle H_E \langle E| + |G\rangle H_G \langle G| \quad (7.124)$$

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

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

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

$$\begin{aligned} H_B &= \sum_\alpha \hbar \omega_\alpha \left(p_\alpha^2 + q_\alpha^2 \right) \\ H_{SB} &= q \sum_\alpha c_\alpha x_\alpha + \lambda \end{aligned} \quad (7.126)$$

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

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

$\xi = 2\hbar\omega_0 d$ 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:

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

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

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

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

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

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 $\gamma \rightarrow 0$, 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 $\gamma \ll \omega$, eq. (7.130) becomes

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

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

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

where $\Lambda = \frac{\omega_0^2}{\gamma}$. (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:

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