QUANTUM MECHANICAL TREATMENT OF FLUCTUATIONS

Introduction and Preview

Now the origin of frequency fluctuations is interactions of our molecule (or more appropriately our electronic transitions) with its environment. This should have a close relationship to our Displaced Harmonic Oscillator model, which is a general approach of a transition coupled to vibrations. For that model we found that

\[
\langle \mu(t)\mu(0) \rangle = \sum_n p_n \langle n | e^{iH_0t} \mu e^{-iH_0t} \mu | n \rangle = |\mu_{eg}|^2 e^{-i\omega_{eg}t} \left\langle e^{iH_{eg}t} e^{-iH_{eg}t} \right\rangle
\]

In the case of time-dependent changes to the electronic energy gap, we can imagine writing the same problem in terms of a Hamiltonian that describes the electronic energy gap’s dependence on \( Q \) (deviation relative to \( \omega_{eg} \)):

\[
H_{eg} = H_K - H_G - \hbar \omega_{eg} = H_e - H_g \quad \text{(Energy Gap Hamiltonian)}
\]

What we will show is that when the time-dependence of the system is expressed in terms of \( H_{eg} \)

\[
C_{\mu\mu}(t) = |\mu_{eg}|^2 e^{-i\omega_{eg}t} \left\langle \exp \left( -i \int_0^t d\tau H_{eg}(\tau) \right) \right\rangle
\]

This expression is consistent with the observation of a random fluctuation of the transition energy if we equate

\[
\delta \omega_{eg}(t) \equiv \frac{\delta H_{eg}(t)}{\hbar}
\]

So, we should expect that coupling of an electronic transition to a continuous distribution of harmonic oscillators (a bath) should be mathematically equivalent to a stochastic modulation of the energy gap.

\* See Mukamel, Ch. 8 and Ch. 7
This begins to make a little more sense if we look a little closer at the Hamiltonian:

\[
H_0 = H_e + E_e + H_g + E_g = \hbar \omega_{eg} + H_{eg} + 2H_g
\]

\[
H_{eg} = H_e - H_g = \frac{1}{2} m \omega_0^2 (Q - d)^2 - \frac{1}{2} m \omega_0^2 Q^2
\]

Note that this looks identical to a Hamiltonian that describes the coupling of an electronic system to a bath [one degree of freedom here] of H.O. with a linear coupling between the two!

\[
H = H_S + H_B + H_{SB}
\]

\[
H_S = |e\rangle \langle E_e + \lambda| + |g\rangle \langle E_g| + |g\rangle \langle E_g|
\]

\[
H_B = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 Q^2
\]

\[
H_{SB} = m \omega_0^2 d \frac{Q}{\text{coupling strength}}
\]

Here we note the similarity \( H_{SB} \Leftrightarrow H_{eg} \).
**ENERGY GAP HAMILTONIAN**

Now let’s work through this more carefully. We will start by re-writing our Hamiltonian in terms of reduced coordinates

\[ H_0 = H_e + E_e + H_g + E_g \]

\[ = \hbar \omega_{eg} + H_{eg} + 2H_g \]

where \( H_{eg} = H_e - H_g \)

\[ p = \sqrt{\frac{\hbar \omega_0 m}{2}} \]

\[ q = \sqrt{\frac{m \omega_0}{2\hbar}} \]

\[ d = \sqrt{\frac{m \omega_0}{2\hbar}} \]

\[ H_e = \hbar \omega_0 \left( \frac{p^2}{2} + \left( q - \frac{d}{2} \right)^2 \right) \]

\[ H_g = \hbar \omega_0 \left( \frac{p^2}{2} + q^2 \right) \]

\[ H_{eg} = H_e - H_g = -2\hbar \omega_0 d q + \hbar \omega_0 d^2 \]

Now, the absorption lineshape is described through \( \langle \mu(t)\mu(0) \rangle \):

\[ C_{\mu\mu}(t) = \langle \mu(t)\mu(0) \rangle = \left| \mu_{eg} \right|^2 e^{-i\omega_0 t} F(t) \]

\[ F(t) = \left\langle e^{iH_e t} e^{-iH_G t} \right\rangle \]
If we want to rewrite this in terms of $H_{eg}$, we are changing the representation of the dynamics to a new Hamiltonian. Similar to the transformation to the interaction picture, we will choose to represent the time dependence of $H_{eg}$ by evolution under $H_g$

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

$$e^{-iH_g t/\hbar} = e^{-iH_{eg} t/\hbar} \exp \left[ \frac{-i}{\hbar} \int_0^t d\tau H_{eg} (\tau) \right]$$

$$U_e = U_g U_{eg}$$

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

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

This implies:

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

**Note: Transformation to a new Hamiltonian**

If we have

$$e^{iH_{eg} t} A e^{-iH_{eg} t}$$

and we want to express this in terms of

$$A e^{-i(H_{eg} - H_{eg})} = A e^{-iH_{eg} t}$$

we will now be evolving the system under a different Hamiltonian $H_{BA}$, and we must perform a transformation into this new frame of reference. In general if you want to change to a new Hamiltonian, you need to perform a unitary transformation under the reference Hamiltonian:

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

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

$$e^{-iH_B \tau} = e^{-iH_{BA} \tau} \exp \left[ -\frac{i}{\hbar} \int_0^\tau dt H_{BA}(\tau) \right]$$

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

$$e^{+iH_B \tau} e^{-iH_{BA} \tau} = \exp \left[ -\frac{i}{\hbar} \int_0^\tau dt H_{BA}(\tau) \right]$$

The cumulant expansion to second order says:

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

$$= \exp \left[ -\frac{i}{\hbar} \lambda t + \left( -\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 C_{eg}(\tau_2, \tau_1) + \ldots \right]$$

Note time ordering now.

Here, we noted that the way we defined $H_{eg}$ means that

$$\langle H_{eg} \rangle = \hbar \omega_0 \delta^2 = \lambda$$

(The energy gap could also be defined relative to the energy gap at $Q = 0$: $H_{eg}' = H_e - H_g - \lambda$.)

Also, we defined

$$C_{eg}(\tau_2, \tau_1) = \langle H_{eg}(\tau_2) H_{eg}(\tau_1) \rangle - \langle H_{eg}(\tau_2) \rangle \langle H_{eg}(\tau_1) \rangle$$

$$= \langle \delta H_{eg}(\tau_2) \delta H_{eg}(\tau_1) \rangle \quad \Rightarrow \quad \langle \delta \omega_{eg}(\tau_2) \delta \omega_{eg}(\tau_1) \rangle$$

$$\delta \omega_{eg} = \frac{\delta H_{eg}}{\hbar} = \frac{H_{eg} - \langle H_{eg} \rangle}{\hbar}$$
So we have
\[
C_{\mu\nu}(t) = |\mu_{eg}|^2 e^{-\frac{\hbar g(t)}{\lambda}} e^{-\frac{\hbar}{\lambda}}
\]

\[
g(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta\omega_{eg}(\tau_1) \delta\omega_{eg}(0) \rangle
\]

This is the correlation function expression that determines the absorption lineshape for a time-dependent energy gap.

Now, evaluating \( C_{eg}(t) = \langle \delta\omega_{eg}(t) \delta\omega_{eg}(0) \rangle \) for one harmonic oscillator

\[
C_{eg}(t) = \sum_n p_n \langle n | \delta\omega_{eg}(t) \delta\omega_{eg}(0) | n \rangle
\]

\[
= \frac{1}{\hbar^2} \sum_n P_n \langle n | e^{iH_{eg}t/\hbar} \delta H_{eg} e^{-iH_{eg}t/\hbar} \delta H_{eg} | n \rangle
\]

\[
= \omega_0^2 D (\bar{n} + 1) e^{-i\omega_0 t} + \bar{n} e^{+i\omega_0 t}
\]

Again \( \bar{n} \) is the thermally averaged occupation number. Also

\[
g(t) = D \left[ \text{coth} \left( \beta \omega_0 / 2 \right) (1 - \cos \omega_0 t) + i \left( \sin \omega_0 t - \omega_0 t \right) \right]
\]

\[
coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}}
\]

\[
g(t) = g' + ig''
\]

Note we now have real \((g')\) and imaginary \((g'')\) contributions to \( F(t) \).

Alternatively, we can write this as

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

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

Vibrational progression  Hot bands \( \lambda / \hbar \)

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At low T, $coth(\beta \hbar\omega_0 / 2) \rightarrow 1$ and $\bar{n} \rightarrow 0$

$$g(t) = D [1 - \cos \omega_0 t + i \sin \omega_0 t - i \omega_0 t]$$

$$= D [1 - e^{-i\omega_0 t} - i \omega_0 t]$$

Combining with

$$F(t) = e^{iD_{\omega_0 t - g(t)}}$$

We have our old result:

$$F(t) = \exp \left[ D (e^{-i\omega_0 t} - 1) \right]$$
**Distribution of Nuclear States**

Coupling to a distribution of states characterized by a density of states \( W(\omega_D) \). As discussed before, we expect

\[
F(t) = \exp \left[ -\int d\omega_0 \, W(\omega_0) \, g(t, \omega_0) \right]
\]

Coupling to a continuum will induce irreversible relaxation, which will be characterized by damping of \( C_{eg}(t) \). This is achieved by summing over a distribution of \( C_{eg}(\omega_0, t) \):

\[
C_{eg}(t) = \int d\omega_0 \, C_{eg}(\omega_0, t) W(\omega_0)
\]

Alternatively in the frequency domain:

\[
\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{\text{int}} \, C_{eg}(t) \, dt
\]

\[
= \int d\omega_0 \, W(\omega_0) \int_{-\infty}^{+\infty} e^{\text{int}} C_{eg}(\omega_0, t) \, dt
\]

\[
\tilde{C}_{eg}(\omega_0) = \omega_0^2 D(\omega_0) \left[ (\pi + 1) \delta(\omega + \omega_0) + \pi \delta(\omega - \omega_0) \right]
\]

\[
C''_{eg}(\omega_0) = \omega_0^2 D \left[ \delta(\omega - \omega_0) + \delta(\omega + \omega_0) \right]
\]

We define a spectral density or coupling-weighted density of states:

\[
\rho(\omega) = \frac{C''_{eg}(\omega)}{2\pi \omega^2} = \int d\omega_0 \, W(\omega_0) D(\omega_0) \delta(\omega - \omega_0) = W(\omega) D(\omega)
\]

This leads to:

\[
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\]

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

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

\[ \lambda = \hbar \int_{0}^{\infty} d\omega \ \omega \rho(\omega) \]

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.

**Special case:** Now take the specific case that we choose a Lorentzian spectral density centered at \( \omega = 0 \):

\[ C_{eg}''(\omega) = 2\lambda \Lambda \frac{\omega}{\omega^2 + \Lambda^2} \]

In the high temperature limit \( \frac{kT}{\hbar} \gg \Lambda \) we get:

\[ g(t) = \frac{2\lambda kT}{\hbar \Lambda^2} \left[ \exp(-\Lambda t) + \Lambda t - 1 \right] - i \frac{\Lambda}{\hbar} \left[ \exp(-\Lambda t) + \Lambda t - 1 \right] \]

So if we ignore the imaginary part of \( g(t) \), and we equate

\[ \Delta^2 = \frac{2\lambda kT}{\hbar \omega_c} \quad \tau_c = \frac{1}{\Lambda} \]

we have our stochastic model:

\[ g(t) = \Delta^2 \tau_c^2 \left[ \exp(-t / \tau_c) + t / \tau_c - 1 \right] \]
So, the interaction of an electronic transition with a frequency distribution of nuclear coordinates
(a bath) leads to line broadening and irreversible relaxation. The effect is to damp the nuclear
oscillations on electronic states.

More commonly we would think of our electronic transition coupled to a particular nuclear
coordinate $Q$ which may be a local mode, but the local mode feels a fluctuating environment—a
friction.

**Classically**, we would understand the fluctuations as Brownian motion, described by a
generalized Langevin equation:

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

For a random force:  \( \langle f(t) \rangle = 0 \)

For no memory:  \( \gamma(t - \tau) = \gamma \delta(t - \tau) \)

This oscillator has a correlation function described by

$$C_{\varphi\varphi}(\omega) \propto \frac{1}{-\omega^2 + \omega_0^2 - i\omega \gamma(\omega)}$$

Looks similar to a damped H.O.

This coordinate correlation function is just what we need for describing lineshapes. Note:

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

We can get exactly the same behavior as the classical GLE by coupling to a bath of harmonic
oscillators (normal modes, $x$). For
\[ h_{\text{mic}} = \sum_{\alpha=1}^{N} \hbar \omega_{\alpha} \left( p_{\alpha}^{2} + x_{\alpha}^{2} \right) \]

where \( x \Leftrightarrow q \)

With this Hamiltonian, we can construct \( N \) harmonic coordinates any way we like with the appropriate unitary transformation. We want to transform to our local mode \( Q \):

\[
U x = \begin{pmatrix}
Q \\
X_{1} \\
X_{2} \\
\vdots \\
X_{n-1}
\end{pmatrix}
\]

Now:

\[
h_{\text{mic}} = \hbar \omega_{0} \left( p_{-}^{2} + Q_{-}^{2} \right) + \sum_{\alpha=1}^{N-1} \hbar \omega_{\alpha} \left( p_{\alpha}^{2} + X_{\alpha}^{2} \right) + 2Q \sum_{\alpha} c_{\alpha} X_{\alpha}
\]

So, going back to our displaced H.O. problem, we can rewrite our Hamiltonian to include the interaction of one primary vibration with a bath, which leads to damping:

Electronic transition \( \leftrightarrow \) Primary vibration \( \leftrightarrow \) Bath of H.O.s
Brownian Oscillator Hamiltonian (Spin-Boson Hamiltonian)

The formulation of the energy gap Hamiltonian in which we assume that the electronic distribution is coupled to nuclear coordinates described by a distribution of harmonic oscillators is known as the Brownian oscillator model (popularized by Mukamel). It is obtained as follows:

\[ H = H_s + H_B + H_{SB} \]

\[ H_s = \langle e \rangle H_e^{TOT} \langle e \rangle + \langle g \rangle H_g^{TOT} \langle g \rangle \]

\[ H_B = \sum \hbar \omega \alpha \left( p^2 + x^2 \right) \]

\[ H_{SB} = 2 \gamma \sum \alpha \gamma \alpha c_\alpha x_\alpha \quad c_\alpha : coupling \]

\[ C_{eg} (t) = \langle \delta H_{eg} (t) \delta H_{eg} (0) \rangle = \xi^2 \left\langle q(t)q(0) \right\rangle \]

Here \( \xi = 2\hbar \omega_0 d \) 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:

\[ \tilde{C}_{eg}^\omega (\omega) = \frac{\xi}{2 \gamma} \frac{\hbar}{2m} \frac{\omega \gamma(\omega)}{\left( \omega_0^2 - \omega^2 \right)^2 + \omega^2 \gamma^2(\omega)} \]

where \( \gamma \) is the spectral distribution of couplings between our primary vibration and the bath

\[ \gamma(\omega) = \pi \sum \alpha \gamma \alpha \delta(\omega - \omega_\alpha) \]

For a constant \( \gamma \), \( \gamma(\omega) \rightarrow \gamma \):

\[ C_{eg}^\omega (t) = \frac{\xi}{2 \gamma} \frac{1}{2 \hbar m \Omega} \exp \left( -\gamma t / 2 \right) \sin \Omega t \]

\[ \Omega = \sqrt{\omega_0^2 - \gamma^2 / 4} \quad reduced \ frequency \]
This model interpolates between the coherent undamped limit and the overdamped stochastic limit.

If we set $\gamma \to 0$, we recover our earlier result for $C_{eg}(t)$ and $g(t)$ for coupling to undamped nuclear coordinates.

For weak damping $\gamma << \omega$

$$C''_{eg}(t) \propto \xi \frac{1}{\omega_0} \exp\left(-\gamma/2\right) \sin \omega_0 t$$

For strong damping $\gamma >> 2\omega_i$, $\Omega$ is imaginary and

$$C''_{eg}(t) \propto \xi \Lambda \exp(-\Lambda t) \quad \Lambda = \frac{\omega_D^2}{\gamma}$$

which is the 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.

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