QUANTUM MECHANICAL TREATMENT OF FLUCTUATIONS*

Introduction and Preview

Now the origin of frequency fluctuations is expected to be interactions of our molecule (or more appropriately our electronic transitions) with its environment. This we can treat with our D.H.O. model, which is a general approach to coupling to nuclear vibrations.

We found that

$$\langle \mu(t)\mu(0)\rangle = \sum_n p_n \langle n | e^{iH_0 t}\,\bar{\mu}\, e^{-iH_0 t}\,\bar{\mu} | n\rangle$$

$$= |\mu_{eg}|^2 e^{-i\omega_{eg}t}\left\langle e^{H_g t}\, e^{-iH_e t}\right\rangle$$

We can write this in terms of the Hamiltonian that describes the electronic energy gap's dependence on Q (deviation relative to ω_{eg}):

$$H_{eg} = H_e^{TOT} - H_g^{TOT} - \hbar\omega_{eg} = H_e - H_g \qquad \text{(Energy Gap Hamiltonian)}$$

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

Now if we believe there are interactions that lead to fluctuations in the energy group—variations in d or ω_0, then our H_{eg} is now time-dependent!

$$C_{\mu\mu}(t) = e^{-i\langle\omega_{eg}\rangle t}\left\langle exp_+ \frac{-i}{\hbar}\int_0^t d\tau\, H_{eg}(\tau)\right\rangle$$

Performing the cumulant expansion:

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

* See Mukamel, Ch. 8 and Ch. 7

Defining $\delta\omega_{eg}(t) \equiv \frac{H_{eg}(t)}{\hbar}$

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

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

So we have an expression for how the time-dependence of the energy gap Hamiltonian leads to the lineshape.

Also note:

$$H_0 = H_e + E_e + H_g + E_g$$

$$= \hbar\omega_{eg} + H_{eg} + 2H_g \qquad H_g = \frac{p^2}{2m} + \tfrac{1}{2} m\omega_D^2 Q^2$$

$$H_{eg} = H_e - H_g = \tfrac{1}{2} m\omega_0^2 (Q-d)^2 - \tfrac{1}{2} m\omega_0^2 Q^2$$

$$= \underbrace{-m\omega_0^2 d\, Q}_{\text{linear in } Q} + \underbrace{\tfrac{1}{2} m\omega_0^2 d^2}_{\text{const}}$$

Note that this looks very much like 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!

$$H = H_S + H_B + H_{SB}$$

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

$$H_B = \frac{p^2}{2m} + \tfrac{1}{2} m\omega_0^2 Q^2$$

$$H_{SB} \left(\cong H_{eg}\right) = \underbrace{m\omega_0^2 d^2}_{\text{coupling strength}}\ Q$$

Fluctuations in coupling to bath could lead to line broadening! Equivalently, coupling to a bath of many harmonic oscillators should lead to line-broadening.

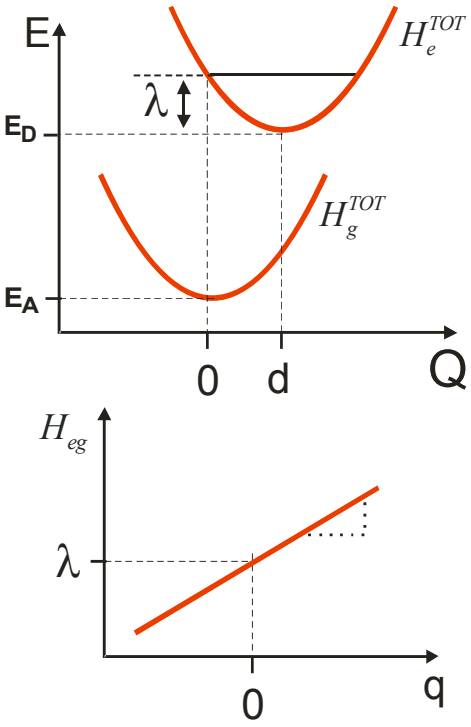
Time-Dependent Energy Gap Hamiltonian

Let's work through this more carefully. Start by defining reduced coordinates

$$\underset{\sim}{p} = \sqrt{\frac{\hbar\omega_0 m}{2}}\, p$$

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

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



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

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

$$H_{eg} = H_e - H_g = 2\hbar\omega_0 \underset{\sim}{d}\,\underset{\sim}{q} + \underbrace{\hbar\omega_0 \underset{\sim}{d}^2}_{\lambda}$$

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

$$C_{\mu\mu}(t) = \langle \mu(t)\mu(0) \rangle = |\mu_{eg}|^2 \, e^{-i\omega_{eg}t} \, F(t)$$

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

If we want to rewrite this in terms of H_{eg}, we are changing representation to a new Hamiltonian. Similar to the transformation to the interaction picture, we will choose a new frame of reference: the ground state H_g and the dynamics of the excited state will be represented in reference to the ground state through H_{eg}:

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

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

$$where \;\; H_{eg}(\tau) = e^{iH_g t} \, H_{eg} \, e^{-iH_g t}$$

This equation implies:

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

The cumulant expansion to second order says:

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

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

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

$$\delta\omega_{eg} = \frac{\delta H_{eg}}{\hbar}$$

Now note the way we defined H_{eg} means that

$$\left\langle H_{eg} \right\rangle = \hbar\omega_0\, \underset{\sim}{d}^2 = \lambda$$

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

So we have

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

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

Now, evaluating $C_{eg}(t) = \left\langle H_{eg}(t) H_{eg}(0) \right\rangle$ for one harmonic oscillator

$$C_{eg}(t) = \sum_n p_n \left\langle n \left| H_{eg}(t)\, H_{eg}(0) \right| n \right\rangle$$

$$= \omega_0^2\, D\left[\left(\overline{n} + 1 \right) e^{-i\omega_0 t} + \overline{n}\, e^{+i\omega_0 t} \right] \qquad D = \underset{\sim}{d}^2$$

and

$$g(t) = D\left[coth(\beta\hbar\omega_0 / 2)(1 - cos\,\omega_0 t) + i(sin\,\omega_0 t - \omega_0 t) \right]$$

$$= g' + ig''$$

Note we now have damped $(g')$and oscillating (g'')contributions to $F(t)$.

Alternately we can write this as $g(t) = D\left[\bar{n}\left(\underline{e^{-i\omega_0 t} - 1} + \underline{e^{+i\omega_0 t} - 1} \right) + \left(e^{-i\omega_0 t} - 1 \right) \right] - iD\omega_0 t$.

At low t, $\coth(x) \to 1$ and

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

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

combining with

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

we have our old result:

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

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 oscillatory $C_{eg}(\omega_0, t)$:

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

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

Alternatively in the frequency domain:

$$\tilde{C}_{eg}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t}\, C_{eg}(t)\, dt$$

$$= \int d\omega_0\, W(\omega_0) \underbrace{\int_{-\infty}^{+\infty} e^{i\omega t}\, C_{eg}(\omega_0, t)\, dt}_{C_{eg}(\omega_0)}$$

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

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

We define a <u>spectral density</u> or coupling-weighted density of states:

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

This leads to:

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

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

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

Now take the case

$$C''_{eg}(\omega) = 2\lambda\Lambda \frac{\omega}{\omega^2 + \Lambda^2} \qquad \textit{Lorentzian distribution}$$

In the high temperature limit $\frac{kT}{\hbar} >> \Lambda$ we get:

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

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

$$\Delta^2 = \frac{2\lambda kT}{\hbar} \qquad \tau_c = \frac{1}{\Lambda}$$

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:

$$\underbrace{m\ddot{Q}(t) + m\omega_0^2 Q^2}_{H.O.} + \underbrace{m\int_0^t d\tau\,\gamma(t-\tau)\dot{Q}(\tau)}_{damping,\ for\ no\ memory\ \Rightarrow m\gamma\dot{Q}} = f(t) + F(t)$$

$F(t)$: random force

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

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

$$\langle f(t)f(\tau)\rangle = 2mkT\,\gamma(t-\tau)$$

This oscillator has a correlation function described by

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

Looks similar to a damped H.O.

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

$$C_{eg}(t) = \left\langle H_{eg}(t) H_{eg}(0) \right\rangle = \hbar^2 \omega_0^2 \, \underset{\sim}{d}^2 \left\langle \underset{\sim}{q}(t) \underset{\sim}{q}(0) \right\rangle$$

We can get exactly the same behavior as the classical GLE by coupling to a bath of harmonic oscillators (normal modes, x). For

$$h_{nuc} = \sum_{\alpha=1}^{N} \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{x}_\alpha^2 \right) \qquad \text{where } \underset{\sim}{x} \Leftrightarrow \underset{\sim}{q}$$

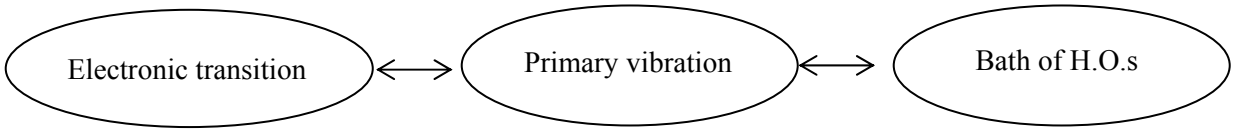
With this Hamiltonian, we can construct N harmonic coordinates any way we like with the appropriate unitary transformation. We want to transform to our local mode Q:

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

Now:

$$h_{nuc} = \underbrace{\hbar\omega_0 \left(\underset{\sim}{p}^2 + \underset{\sim}{Q}^2 \right)}_{\textit{system}} + \underbrace{\sum_{\alpha=1}^{N-1} \hbar\omega_\alpha \left(\underset{\sim}{p}_\alpha^2 + \underset{\sim}{X}_\alpha^2 \right)}_{\textit{bath}} + \underbrace{2Q \sum_{\alpha} c_\alpha X_\alpha}_{\substack{\textit{system-bath} \\ \textit{interaction}}}$$

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:



Brownian Oscillator Hamiltonian (Spin-Boson Hamiltonian)

$$H = H_s + H_B + H_{SB}$$

$$H_S = |e\rangle H_e^{TOT} \langle e| + |g\rangle H_g^{TOT} \langle g|$$

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

$$H_{SB} = 2 \underset{\sim}{q} \sum_\alpha \underset{\sim}{c}_\alpha \underset{\sim}{x}_\alpha \qquad\qquad \underset{\sim}{c}_\alpha : coupling$$

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

Here $\xi = 2\hbar\omega_0 \underset{\sim}{d}$ 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 analyically:

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

where γ is the spectral distribution of couplings between our primary vibration and the bath

$$\gamma(\omega) = \pi \sum_\alpha \underset{\sim}{c}_\alpha^2 \delta(\omega - \omega_\alpha)$$

For a constant γ, $\gamma(\omega) \to \gamma$:

$$C''_{eg}(t) = \xi \frac{\hbar}{2m} \frac{1}{\Omega} exp(-\gamma t/2) sin\,\Omega t$$

$$\Omega = \sqrt{\omega_0^2 - \gamma^2/4} \qquad reduced\ frequency$$

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 $\gamma << \omega$

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

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

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

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.

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