7.5. **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

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

(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, \( q \).

\[
H_S = |E \rangle H_E \langle E | + |G \rangle H_G \langle G |
\]

(7.124)

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

\[
H_B + H_{SB} = \sum_\alpha \left( \frac{p_a^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} \left( x_a - \frac{c_\alpha q}{m_\alpha \omega_\alpha^2} \right)^2 \right)
\]

(7.125)

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

\[
H_B = \sum_\alpha \hbar \omega_\alpha \left( p_a^2 + q_\alpha^2 \right)
\]

\[
H_{SB} = q \sum_\alpha c_\alpha x_\alpha + \lambda
\]

(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

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

(7.127)

\( \xi = 2 \hbar \omega_\gamma d \) 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:

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

(7.128)

Here \( \tilde{\gamma}(\omega) \) is the spectral distribution of couplings between our primary vibration and the bath:
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 $\gamma$ with a constant $\gamma$, the energy gap time correlation function can be obtained as

$$C_{eg}(t) = \xi \frac{\hbar}{2m} \exp(-\gamma t/2) \sin \Omega t$$

(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

$$C_{eg}(t) = \xi^2 \frac{\hbar}{2m\omega_0} \exp(-\gamma / 2) \sin \omega_0 t.$$  

(7.131)

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

$$C_{eg}(t) \propto \xi^2 \frac{\hbar}{2m\omega_0^2} \Lambda \exp(-\Lambda t)$$

(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:

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

(7.134)