Absorption Lineshape for the Displaced Harmonic Oscillator Model

Investigate the low temperature lineshape for electronic transition coupled to a single harmonic mode.

We will perform calculations for three couplings: weak medium, and strong: \( z := 0, 1, .. 2 \)

Let's work in units of \( \hbar := 1 \) \( \mu_{eg} := 1 \) \( m := 1 \)

Define the frequency of the electronic transition: \( \omega_{eg} := 10 \)

and the vibrational frequency: \( \omega_0 := 1 \)

Set up displacement grid \( i := 0 \ldots 200 \)

\( q_i := -5 + 0.05 \cdot i \)

Set up time grid \( t_i := i \cdot 0.1 \)

Set up frequency grid: \( \omega_i := -4 + \omega_{eg} + 0.05 \cdot i \)

The unitless displacement of the two harmonic wells is:

\[
\begin{array}{c|c|c}
\hline
D & 0.2 & 1 \\
\hline
\end{array}
\]

Ground and excited state potential energy surfaces

\[
V_g(qx) := \frac{1}{2} m \cdot \omega_0^2 \cdot qx^2 \\
V_d(q, D) := \omega_{eg} + \frac{1}{2} m \cdot \omega_0^2 \left( q - \sqrt{\frac{2 \cdot D \cdot \hbar}{m \cdot \omega_0}} \right)^2
\]

Lineshape function, Dephasing function and dipole correlation function

\[
g(t, D) := -D \left( e^{-i \cdot \omega_0 t} - 1 \right) \\
F(t, D) := e^{-gt(D)} \\
C(t, D) := \left( \mu_{eg} \right)^2 \cdot e^{-i \cdot \omega_{eg} \cdot t - g(t, D)}
\]

Plot the correlation function and dephasing function for low and high coupling

\[
D_0 = 0.2 \\
D_2 = 2
\]
Absorption lineshape:

\[ \delta(g) := \text{if}(g = 0, 1, 0) \]

\[ \sigma(\omega, D) := \left( |\mu_{eq}| \right)^2 e^{-D \cdot \sum_{J=0}^{10} \frac{D^J}{J!} \left( \delta(\omega - \omega_{eq} - J \cdot \omega_0) \right)} \]

Envelope of vibronic progression:

\[ \text{Env}(\omega, D) := \frac{\pi}{\sqrt{D \cdot \omega_0^2}} \cdot 0.25 \left( |\mu_{eq}| \right)^2 \cdot \exp \left[ \frac{-(\omega - \omega_{eq} - D \cdot \omega_0)^2}{2 \cdot D \cdot \omega_0^2} \right] \]

Plot lineshapes for low, mid and high coupling.

(a) \( D_0 = 0.2 \)

(b) \( D_1 = 1 \)

(c) \( D_2 = 2 \)
\[ D = \begin{pmatrix} 0.2 \\ 1 \\ 2 \end{pmatrix} \quad \omega_0 = 1 \]

\[ \sigma(\omega_i, D_2) \]
\[ \sigma(\omega_i, D_1 + 0.4) \]
\[ \sigma(\omega_i, D_0 + 0.8) \]