

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: $z := 0, 1..2$

Lets 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 $i := 0..200$ $q_i := -5 + 0.05 \cdot i$

Set up time grid $t_i := i \cdot 0.1$

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

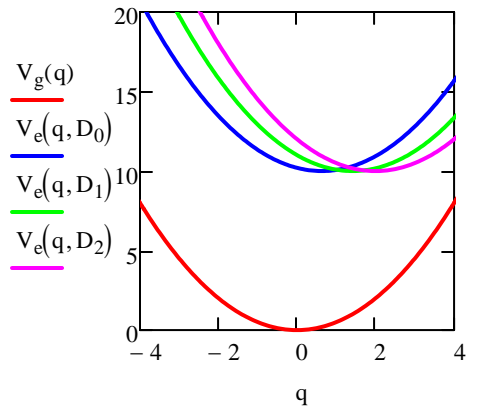
$D_z :=$

0.2
1
2

The unitless displacement of the two harmonic wells is:

Ground and excited state potential energy surfaces

$$V_g(q) := \frac{1}{2} \cdot m \cdot \omega_0^2 \cdot q^2 \quad V_e(q, D) := \omega_{eg} + \frac{1}{2} m \cdot \omega_0^2 \cdot \left(q - \sqrt{\frac{2 \cdot D \cdot \hbar}{m \cdot \omega_0}} \right)^2$$



Lineshape function, Dephasing function and dipole correlation function

$$g(t, D) := -D \cdot \left(e^{-i \cdot \omega_0 \cdot t} - 1 \right)$$

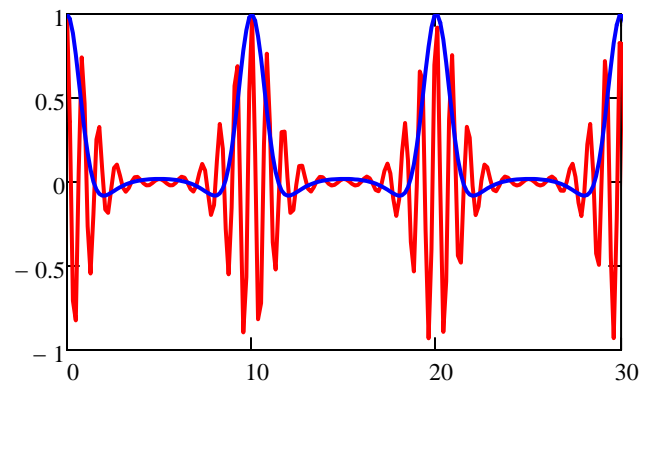
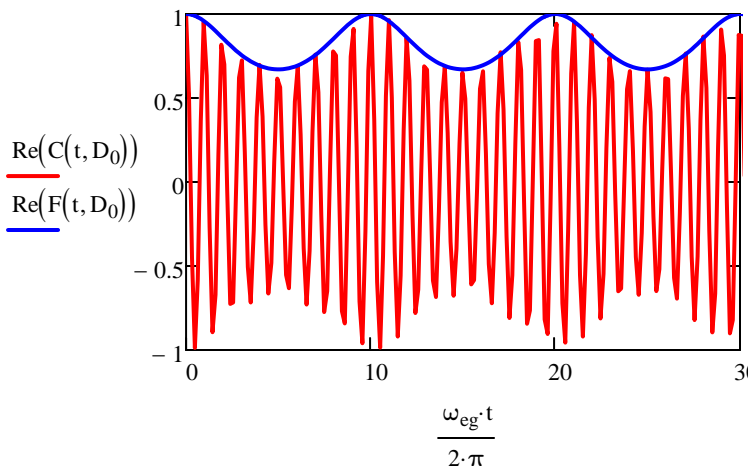
$$F(t, D) := e^{-g(t, D)}$$

$$C(t, D) := \left(|\mu_{eg}| \right)^2 \cdot e^{-i \cdot \omega_{eg} \cdot t - g(t, D)}$$

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

$D_0 = 0.2$

$D_2 = 2$



Absorption lineshape:

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

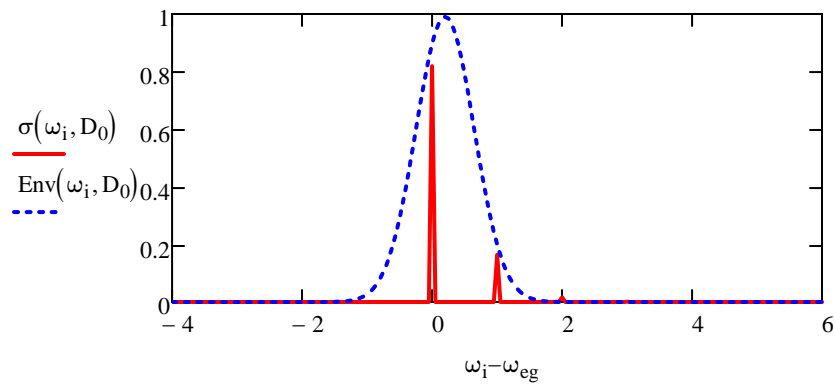
$$\sigma(\omega, D) := (|\mu_{eg}|)^2 \cdot e^{-D} \cdot \sum_{J=0}^{10} \left[\frac{D^J}{J!} \cdot (\delta(\omega - \omega_{eg} - J \cdot \omega_0)) \right]$$

Envelope of vibronic progression:

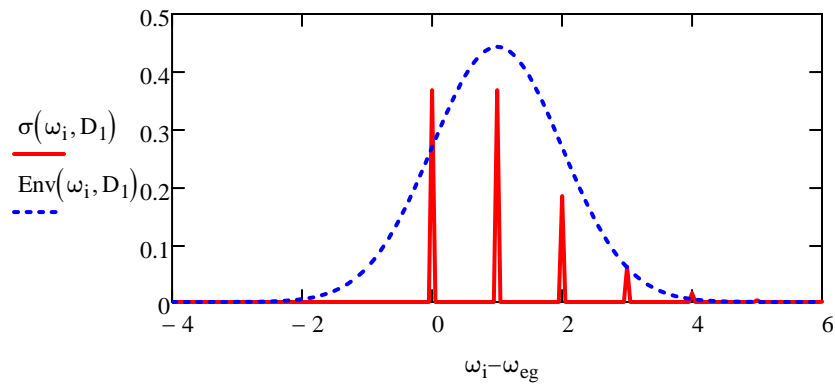
$$\text{Env}(\omega, D) := \sqrt{\frac{\pi}{D \cdot \omega_0^2}} \cdot 0.25 \cdot (|\mu_{eg}|)^2 \cdot \exp\left[\frac{-(\omega - \omega_{eg} - D \cdot \omega_0)^2}{2 \cdot D \cdot \omega_0^2} \right]$$

Plot lineshapes for low, mid and high coupling.

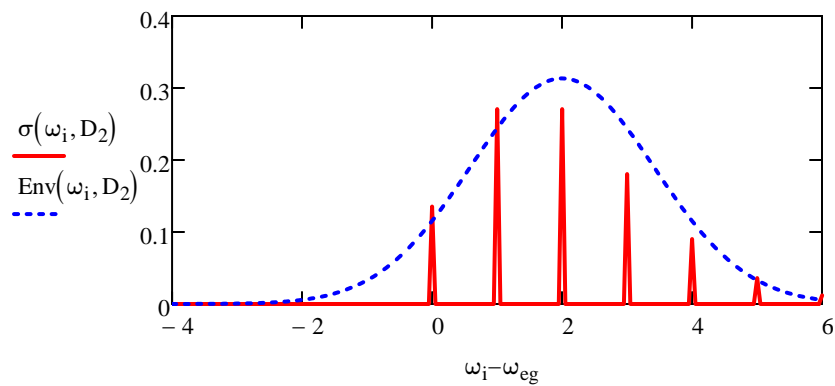
(a) $D_0 = 0.2$



(b) $D_1 = 1$



(c) $D_2 = 2$



$$D = \begin{pmatrix} 0.2 \\ 1 \\ 2 \end{pmatrix} \quad \omega_0 = 1$$

