

# Perturbation Theory

We will be interested in the effect on molecules of weak interactions such as electric or magnetic fields. Moreover, Almost any process that is considered forbidden in quantum mechanics can be observed due to some higher order effect. In all of these cases we treat the effect of a small perturbation on the system using Perturbation Theory.

The hamiltonian  $H^{(0)}$  is modified by a perturbative term  $H'$  :

$$H = H^{(0)} + \lambda H'$$

We assume that we know the zero-order (0) eigenfunctions and energies:

$$H^{(0)}\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(0)}$$

# Perturbed Energy and Wave Function

The lamda,  $\lambda$  is just a number. It can be used to “turn on” the Perturbation. If  $\lambda = 0$  then the perturbation is not present. If  $\lambda = 1$  then the perturbation is present. This method is convenient so we can keep track of any changes. We can Also consider various orders or perturbation, first order,  $\lambda$ , second order,  $\lambda^2$  etc.

$$\Psi_i = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \dots$$

We say the  $\Psi^{(1)}$  is first order correction to the wave function. Similarly, the energies can be written:

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

Convergence requires the  $E^{(1)} \ll E^{(0)}$  etc.

# Perturbed Energy and Wave Function

If the states are not degenerate then we find that:

$$E_i^{(1)} = \langle \Psi_i^{(0)} | H' | \Psi_i^{(0)} \rangle \equiv H'_{ii}$$

$$\Psi_i^{(1)} = \sum_{j \neq i} \frac{\langle \Psi_j^{(0)} | H' | \Psi_i^{(0)} \rangle}{E_i^{(0)} - E_j^{(0)}} \Psi_j^{(0)} = \sum_{j \neq i} \frac{H'_{ij}}{E_i^{(0)} - E_j^{(0)}} \Psi_j^{(0)}$$

The perturbed wave function is composed of a linear combination of terms derived from the zero-order wave function.

$$\Psi_i^{(1)} = \sum_{j \neq i} c_{ji} \Psi_j^{(0)}$$

The prerequisite for the existence of a perturbed wave function is that the matrix elements  $\langle \Psi_j | H' | \Psi_i \rangle$  are not zero.

$$\Psi_n^{(1)} = \sum_{m=1}^{\infty} c_{mn} \Psi_m^{(0)} \text{ where } c_{mn} = \langle \Psi_n^{(1)} | \Psi_m^{(0)} \rangle$$

and

$$\Phi = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)}$$

$$\left( H^{(0)} + \lambda H' \right) \left( \Psi_n^{(0)} + \lambda \Psi_n^{(1)} \right) = \left( E_n^{(0)} + \lambda E_n^{(1)} \right) \left( \Psi_n^{(0)} + \lambda \Psi_n^{(1)} \right)$$

$$H^{(0)} \Psi_n^{(0)} + \lambda H' \Psi_n^{(0)} + \lambda H^{(0)} \Psi_n^{(1)} = E_n^{(0)} \Psi_n^{(0)} + \lambda E_n^{(1)} \Psi_n^{(0)} + \lambda E_n^{(0)} \Psi_n^{(1)}$$

$$\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle + \langle \Psi_m^{(0)} | H^{(0)} | \Psi_n^{(1)} \rangle = E_n^{(1)} \langle \Psi_m^{(0)} | \Psi_n^{(0)} \rangle + E_n^{(0)} \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle$$

$$\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle + E_m^{(0)} \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle = E_n^{(0)} \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle$$

$$\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle = \left( E_n^{(0)} - E_m^{(0)} \right) \langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle$$

$$\langle \Psi_m^{(0)} | \Psi_n^{(1)} \rangle = \frac{\langle \Psi_m^{(0)} | H' | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

# The Anharmonic Oscillator

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} \chi_v + \frac{k}{2} Q^2 \chi_v = E_v \chi_v$$

$$H^{(0)} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} + \frac{k}{2} Q^2$$

$$H^{(1)} = \frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4$$

$$\chi_0^{(0)}(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}$$

$$\chi_1^{(0)}(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} Q e^{-\alpha Q^2/2}$$

$$E_n^{(1)} = \int_{-\infty}^{\infty} dQ \chi_n^{(0)*}(Q) \left( \frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4 \right) \chi_n^{(0)}(Q)$$

$$E_0^{(1)} = \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dQ e^{-\alpha Q^2} \left( \frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4 \right)$$

$$= \frac{\gamma}{24} \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dQ e^{-\alpha Q^2} Q^4$$

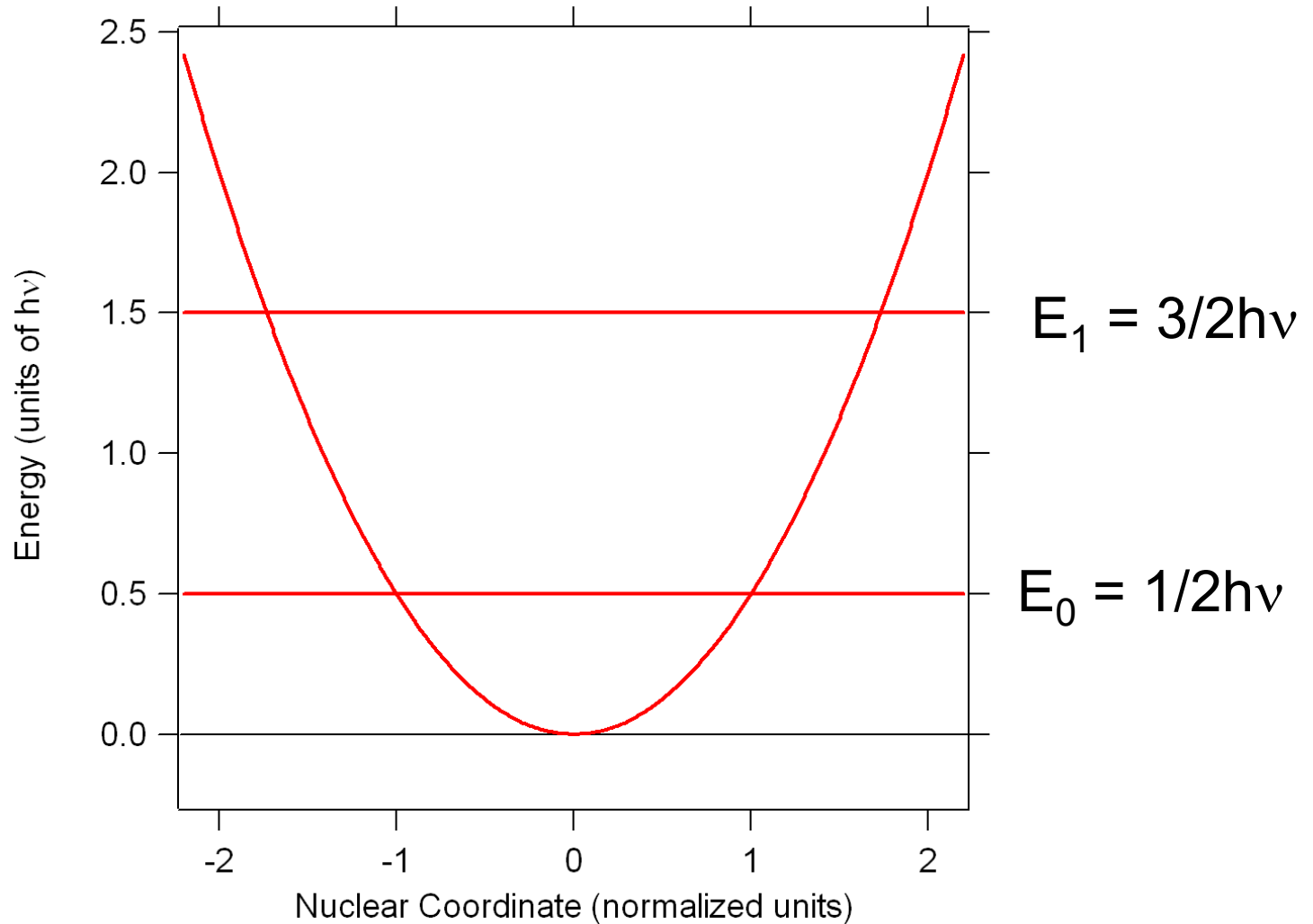
$$= \frac{\gamma}{32\alpha^2}$$

$$E_1^{(1)} = 2 \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dQ \alpha Q^2 e^{-\alpha Q^2} \left( \frac{\beta}{6} Q^3 + \frac{\gamma}{24} Q^4 \right)$$

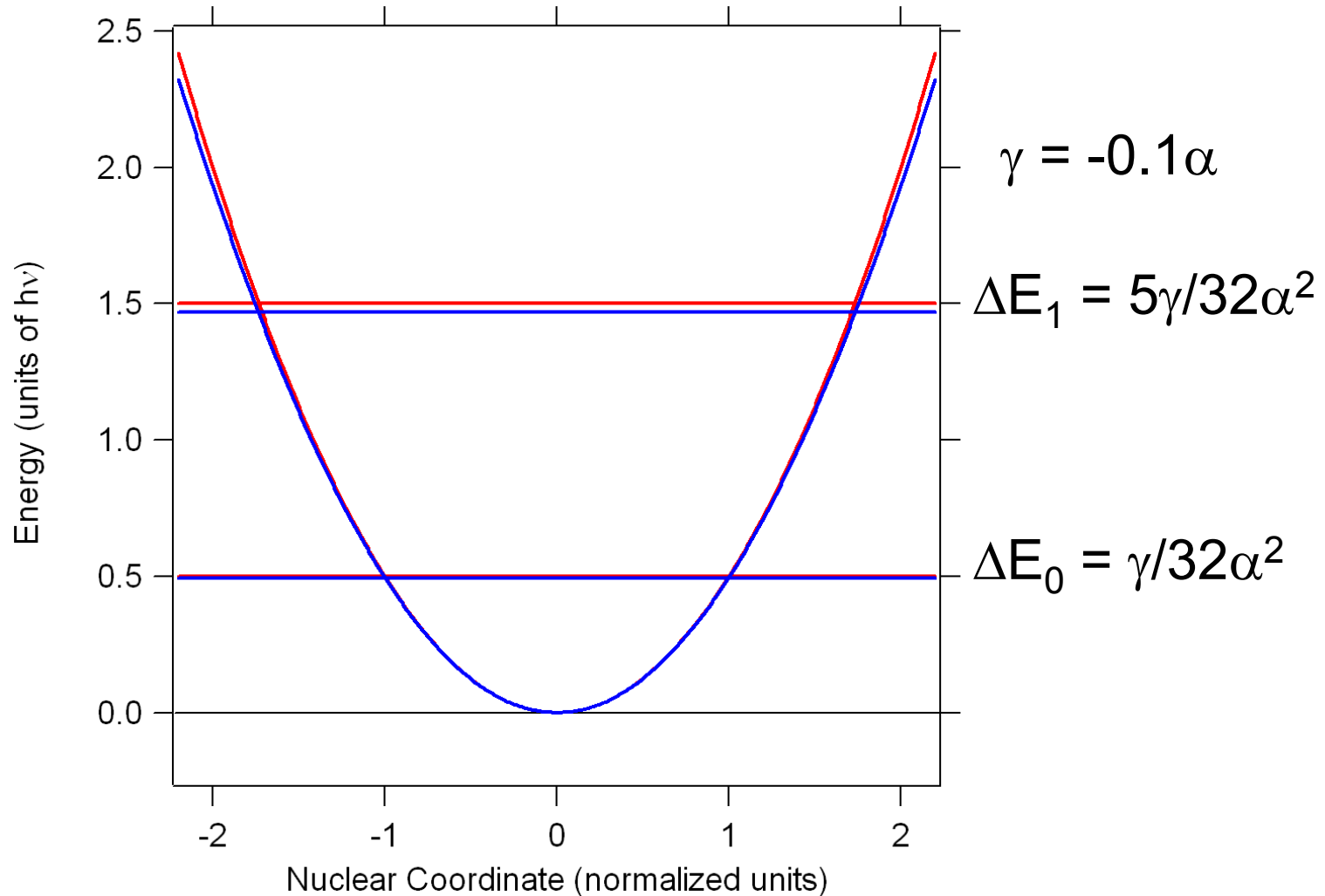
$$= \frac{\gamma \alpha}{12} \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} dQ e^{-\alpha Q^2} Q^6$$

$$= \frac{5\gamma}{32\alpha^2}$$

# Zeroth Order Energies



# First Order Corrections



In this example the anharmonic correction is a little more than 1%