1 Taylor expansion of the Morse oscillator

The Taylor expansion of $U(x)$ to fourth order is

$$U(x) = D\beta^2 x^2 - D\beta^3 x^3 + \frac{7}{12} D\beta^4 x^4 + \mathcal{O}(x^5).$$

The leading term is $D\beta^2 x^2$, and for small values of $x$ (which represents the deviation of the bond length from the minimum of the well), this term will dominate.

2 First-order perturbation theory applied to the Morse oscillator

a)

We can write

$$\hat{H}_{MO} = \hat{T} + V_{MO}(x) = \hat{T} + V_{MO}(x) + V_{HO}(x) - V_{HO}(x) = (\hat{T} + V_{HO}(x)) + (V_{MO}(x) - V_{HO}(x)) = \hat{H}_{HO} + V'(x)$$

where $\hat{T} = -\frac{h^2}{2\mu} \frac{d^2}{dx^2}$, $V_{HO}(x) = \frac{1}{2} k x^2$, $V_{MO}(x) = D \left[ 1 - e^{-\beta x} \right]^2$, $\hat{H}_{HO}$ is the harmonic oscillator Hamiltonian, and the perturbing potential $V'(x)$ is given by

$$V'(x) = (V_{MO} - V_{HO}) = D \left[ 1 - e^{-\beta x} \right]^2 - \frac{1}{2} k x^2$$

The best choice of $k$ is one that minimizes the magnitude of $V'(x)$ near $x = 0$, which we take as the $\mathcal{O}(x^2)$ term from the Taylor expansion in part (1):

$$D\beta^2 x^2 = \frac{1}{2} k x^2$$

$$k = 2D\beta^2$$

And our perturbing potential is therefore

$$V'(x) = D \left[ 1 - e^{-\beta x} \right]^2 - D\beta^2 x^2.$$  

b) The zero-order eigenenergy is simply the ground-state energy of the harmonic oscillator.

We first compute the reduced mass:

$$\mu = (m_{H}^{-1} + m_{Cl}^{-1})^{-1} = (1 + \frac{1}{17})^{-1} \text{amu} = 0.944 \text{amu}$$
Now, we compute the energies

\[
E_0 = \frac{\hbar}{2} \left( \frac{k}{\mu} \right)^{1/2} = \frac{\hbar}{2} \left( \frac{2D\beta^2}{\mu} \right)^{1/2}
\]

\[
= \frac{1.05 \cdot 10^{-34} \text{J s}}{2} \left[ \frac{2}{\mu} \cdot 7.31 \cdot 10^{-19} \text{J} \left( \frac{1.82 \cdot 10^{10}}{\text{m}} \right)^2 \frac{0.944 \text{amu}}{\text{g}} \right]^{1/2}
\]

\[
= \frac{1.05 \cdot 10^{-34} \text{J s}^2}{2} \left[ \frac{2}{\mu} \cdot 7.31 \cdot 10^{-19} \text{kg m}^2 \left( \frac{1.82 \cdot 10^{10}}{\text{m}} \right)^2 \frac{0.944 \text{amu}}{\text{g}} \right]^{1/2}
\]

\[
= \frac{1.05 \cdot 10^{-34} \text{J s}^2}{2} \left[ \frac{2}{\mu} \cdot 7.31 \cdot 10^{-19} \text{kg m}^2 \cdot 602 \cdot 10^{23} \frac{\text{amu}}{\text{mol}} \cdot 6.02 \cdot 10^{23} \frac{\text{mol}}{\text{kg}} \cdot \frac{1000 \text{g}}{\text{kg}} \cdot \frac{6.02 \cdot 10^{23}}{\text{mol}} \right]^{1/2}
\]

\[
= \frac{5.25 \cdot 10^{-35} \text{J s}^2}{2} \left[ \frac{3.08 \cdot 10^{29}}{\text{s}^2} \right]^{1/2}
\]

\[
= \frac{5.25 \cdot 10^{-35} \text{J s}^2}{2} \left[ \frac{5.55 \cdot 10^{14}}{\text{s}^2} \right]^{1/2}
\]

\[
= \frac{2.91 \cdot 10^{-20} \text{J}}{2} \cdot \frac{6.02 \cdot 10^{23}}{\text{mol}} \cdot \frac{23}{4184 \text{J}}
\]

\[
= 4.19 \text{kcal mol}^{-1}
\]

I don’t bother plugging in constants to \( \psi_0(x) \) because the result is rather meaningless.

c) The first-order perturbation theory correction is given by

\[
E' = \langle \psi_0 | V' | \psi_0 \rangle
\]

\[
= \int_{-\infty}^{+\infty} dx \psi_0^*(x) V'(x) \psi_0(x)
\]

\[
= \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} dx e^{-\alpha x^2} \left\{ D \left[ 1 - e^{-\beta x} \right]^2 - \frac{1}{2} k x^2 \right\}
\]

\[
= \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} dx e^{-\alpha x^2} \left\{ D \left[ 1 - e^{-\beta x} \right]^2 - D \beta^2 x^2 \right\}
\]

\[
= D \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} dx e^{-\alpha x^2} \left\{ \left[ 1 - e^{-\beta x} \right]^2 - \beta^2 x^2 \right\}
\]

Because \( \alpha \) appears in an exponent multiplied by \( x^2 \), it must be in units of inverse-distance-squared, and the unit chosen for distance must be the same as \( \beta \), which represents an inverse-distance. We will choose to use Angstroms as our unit of distance:

\[
\alpha = \sqrt{\frac{k \mu}{\hbar^2}} = \left[ \frac{2D\beta^2 \mu}{\hbar^2} \right]^{1/2}
\]

\[
= \left[ \frac{2}{\mu} \cdot 7.31 \cdot 10^{-19} \text{J} \left( \frac{1.82 \cdot 10^{10}}{\text{m}} \right)^2 \frac{0.944 \text{amu}}{\text{g}} \cdot \frac{g}{\text{amu mol}} \cdot \frac{\text{mol}}{6.02 \cdot 10^{23}} \cdot \frac{\text{kg}}{1000 \text{g}} \cdot \frac{1000 \text{g}}{\text{kg}} \cdot \frac{6.02 \cdot 10^{23}}{\text{mol}} \right]^{1/2}
\]

\[
= \frac{8.30 \cdot 10^{21}}{\text{m}^2} \left( \frac{\text{m}}{10^{10} \text{A}} \right)^2
\]

\[
= 83.0 \text{A}^{-2}
\]

Note that the squared ground-state wavefunction gives the probability amplitude:

\[
\psi_0^2(x) = \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha x^2}
\]
has the form of a Gaussian distribution
\[ p(x) \sim e^{-\frac{x^2}{2\sigma^2}} \]
with standard deviation \( \sigma = (2\alpha)^{-1/2} = 7.76 \cdot 10^{-2} \text{Å} \).

Now to get \( \beta \) into distance units of \( \text{Å} \):
\[ \beta = \frac{1.82 \cdot 10^{10}}{m} \cdot \frac{m}{10^{10} \text{Å}} \]
\[ = \frac{1.82}{\text{Å}} \]

We also put \( D \) into units of kcal/mol:
\[ D = \frac{7.31 \cdot 10^{-19} \text{J}}{\text{kcal}} \cdot \frac{6.02 \cdot 10^{23} \text{J}}{\text{mol}} \]
\[ = \frac{105 \text{kcal}}{\text{mol}} \]

We can now easily do the integral with Mathematica’s `Integrate[]` function:
\[ E' = \langle \psi_0 | V' | \psi_0 \rangle \]
\[ = \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{+\infty} dx \, e^{-\alpha x^2} \left\{ D \left[ 1 - e^{-\beta x} \right]^2 - D \beta^2 x^2 \right\} \]
\[ = \frac{0.0744 \text{kcal}}{\text{mol}} \]

This is a rather small difference!

### 3 The variational method

The variational method requires we compute elements of the Hamiltonian matrix:
\[
H = \begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix}
\]
where
\[ H_{ij} = \langle \psi_i | \hat{H}_{\text{MO}} | \psi_j \rangle \]

State energies can be found by zeros of the secular determinant
\[
\det(H - E \mathbf{I}) = 0
\]
\[
(H_{00} - E)(H_{11} - E) - H_{01} H_{10} = 0
\]
\[
E^2 - (H_{00} + H_{11})E + (H_{00} H_{11} - H_{01} H_{10}) = 0
\]

The solution to this is simply given by the quadratic formula
\[
E = \frac{-(H_{00} + H_{11}) \pm \left[ (H_{00} + H_{11})^2 - 4(H_{00} H_{11} - H_{01} H_{10}) \right]^{1/2}}{2}
\]

We can now attempt to calculate the elements \( H_{ij} \):
\[
H_{ij} = \langle \psi_i | \hat{H}_{\text{MO}} | \psi_j \rangle
\]
\[
= \langle \psi_i | \hat{H}_{\text{HO}} + V' | \psi_j \rangle
\]
\[
= \langle \psi_i | \hat{H}_{\text{HO}} | \psi_j \rangle + \langle \psi_i | V' | \psi_j \rangle
\]
\[
= \delta_{ij} E_i + \langle \psi_i | V' | \psi_j \rangle
\]
where we have used the orthonormality of the harmonic oscillator wavefunctions as well as the fact that $\hat{H}_{\text{HO}}|\psi_i\rangle = E_i$ in the last step.

So we must compute the first excited state energy

$$E_1 = \frac{3\hbar}{2} \left( \frac{k}{\mu} \right)^{1/2} = \frac{3\hbar}{2} \left( \frac{2D^2}{\mu} \right)^{1/2} = \frac{3}{2} \cdot \frac{1.05 \cdot 10^{-34} \text{ J s}}{5.55 \cdot 10^{14} \text{ s}} \cdot \frac{5.55 \cdot 10^{14} \text{ kcal}}{4184 \text{ J mol}} = \frac{12.6 \text{ kcal}}{\text{ mol}}$$

and three unique integrals:

$$\langle \psi_0 | V' | \psi_0 \rangle = \int_{-\infty}^{+\infty} dx \, \psi_0^*(x) V'(x) \psi_0(x)$$

$$\langle \psi_1 | V' | \psi_1 \rangle = \int_{-\infty}^{+\infty} dx \, \psi_1^*(x) V'(x) \psi_1(x)$$

$$\langle \psi_0 | V' | \psi_1 \rangle = \langle \psi_1 | V' | \psi_0 \rangle = \int_{-\infty}^{+\infty} dx \, \psi_0^*(x) V'(x) \psi_1(x)$$

We have already computed the first one, so we simply need to compute the second and third. We compute the rest by Mathematica, to obtain

$$\mathbf{H} = \begin{bmatrix} -4.19 & -0.912 \\ -0.912 & 12.6 \end{bmatrix}$$

where all energies are given in kcal/mol.

Solving for the ground-state energy and subtracting off $E_0$, the ground-state energy of the harmonic oscillator, gives:

$$E' = -0.0203 \text{ kcal} \frac{\text{mol}}{\text{mol}}$$