

Molecular Vibrations – Problem 4

Beyond the normal mode approximation, a very useful model for intramolecular dynamics is the Morse potential,

$$V(x) = D(e^{-2ax} - 2e^{-ax}) + D,$$

where $x = r - r_c$ is the displacement from the equilibrium configuration.

- Find the value of x at the minimum energy configuration and the potential value at this geometry.
- Find the value of the potential as $x \rightarrow \infty$, thus obtain the dissociation energy.
- Expand the potential through quadratic terms about the minimum, i.e., obtain the force constant k of the harmonic approximation to the Morse potential. Express the force constant in the usual form $k = m\omega_0^2$ (where m is the reduced mass of the diatomic molecule) and show that

$$\omega_0 = a\sqrt{\frac{2D}{m}}.$$

The eigenvalues of the Morse Hamiltonian are available. They are given by the expression

$$E_n = \hbar\omega_0 \left[\left(n + \frac{1}{2} \right) - \frac{\hbar\omega_0}{4D} \left(n + \frac{1}{2} \right)^2 \right].$$

As you can see from this, the deviations from harmonic behavior decrease as $D \gg \hbar\omega_0$.

- For $D = 5\hbar\omega_0$, calculate the energies of all the bound states of the Morse Hamiltonian. Quantify the anharmonicity by calculating the ratio of the spacing between the lowest two vibrational levels to the harmonic spacing $\hbar\omega_0$.

