

13.2: Complex Potential Energy Surfaces- Vibration

We now take our first step into non-flat potential surfaces by studying the quantum mechanics of springs; this is called the harmonic oscillator problem. Incidentally, chemical bonds work just like springs. Two atoms form a bond along the “x” direction, with an equilibrium bond distance of x_0 . Any displacement from equilibrium results in a linear restoring force: $F = -\frac{\partial V}{\partial x} = -k_f(x - x_0)$, the strength of which is dictated by the spring constant k_f . Since we want to know the potential energy V as a function of the position we note that $\frac{\partial V}{\partial x} = -F(x)$ and integrate as follows:

$$\int \partial V = V(x) = - \int -k_f(x - x_0) \partial x = \frac{1}{2} k_f (x - x_0)^2$$

To place this in a quantum mechanical context we simply insert the position operator \hat{x} as so: $\hat{V} = \frac{1}{2} k_f (\hat{x} - x_0)^2$, which likewise makes the potential energy an operator. And while we are ready to put this into the Schrödinger equation, however, before we do so there is a very small change that significantly simplifies everything. This is to simply drop the equilibrium distance x_0 from the potential energy operator as shown here:

$$\hat{V} = \frac{1}{2} k_f (\hat{x} - x_0)^2 \rightarrow \frac{1}{2} k_f \hat{x}^2$$

The implication is that the position operator \hat{x} is now interpreted as the bond’s displacement *away* from equilibrium. Thus, a positive $\langle \hat{x} \rangle$ means that the bond is stretched and a negative $\langle \hat{x} \rangle$ means compressed. There is one more issue to examine, which is the fact that the kinetic energy operator $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ has the familiar factor of mass. However, when describing vibrational motion between two bonded atoms then it is no longer clear which atom’s mass should be used. The solution is to use the reduced mass: $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$, where m_1 and m_2 are the masses of atoms 1 and 2, respectively.

13.2.1.1 Wavefunctions

With knowledge of the Schrödinger equation:

v	H_v	There is an interesting mathematical relationship that can be demonstrated with Hermite polynomials: $H_{v+1} = \frac{2x}{\alpha} \cdot H_v - 2v \cdot H_{v-1}$ This is called a recursion and allows all the Hermite polynomials to be determined with just the first one: $H_{v=0} = 1$.
0	1	
1	$\frac{2x}{\alpha}$	
2	$\frac{4x^2}{\alpha^2} - 2$	
3	$\frac{8x^3}{\alpha^3} - \frac{12x}{\alpha}$	

Table 13.1 Hermite polynomials.

$\frac{1}{\sqrt{2\mu}} \frac{d}{dx} \left(\frac{1}{\sqrt{2\mu}} \frac{d\psi}{dx} \right) + (E - V)\psi = 0$

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we are ready to solve for the wavefunction ψ . This effort is somewhat complex; as such, we will simply assure you that the mathematics are tractable and that the wavefunctions are as shown in Figure 13.8. These solutions can be succinctly described using the following formula:

$$\psi_v(x) = N_v H_v e^{-\frac{x^2}{2\alpha^2}}$$

where $\alpha = \left(\frac{\hbar^2}{\mu k_f}\right)^{\frac{1}{4}}$, $v \rightarrow 0, 1, 2 \dots$ is the principal quantum number, $N_v = \left(\frac{1}{v! 2^v \alpha \sqrt{\pi}}\right)^{\frac{1}{2}}$ is the normalization constant, and H_v are the Hermite polynomials listed in Table 13.1.

Let's turn our attention to the ground state wavefunction which has a bell-shape as shown in Figure 13.8. Subsequent excited states have additional nodes due to the Hermite polynomials; these increase the curvature and thus the kinetic energy of each state. Note how, in calculus, the double derivative found in the kinetic energy operator is called the "curvature" of a function! The Hermite polynomials also assures that the wavefunctions are orthogonal to each other.

There are many other quantum mechanical properties to examine, including the fact that $\langle \hat{x} \rangle = \int \psi_v^* \cdot x \cdot \psi_v dx = 0$ regardless of the state. From this we learn that the bond is on average at the equilibrium bond length, even in highly excited states. Calculation of the energy E as a function of principle quantum number v reveals the relationship: $E(v) = (v + \frac{1}{2}) \hbar \omega$, where ω is the angular frequency: $\omega = \left(\frac{k_f}{mass}\right)^{\frac{1}{2}}$. An important implication is the fact that the ground state has energy is finite: $E_{v=0} = \frac{1}{2} \hbar \omega$. Like the particle in a box this is the zero-point energy, and it means that the atoms are always vibrating. There are other interesting analogies to the particle in a box problem; the wavefunctions look surprisingly similar including the way they pick up additional nodes in each excited state. One significant difference is that the harmonic oscillator energies are linear with the principal quantum number, $E \propto v$, whereas the particle in a box is quadratic in proportion to its principal quantum number, $E \propto n^2$.

13.2.1.2 Kinetic Isotope Effect and Turning Points. An interesting implication of the zero-point energy is that it is inversely proportional to the reduced mass. This has an effect on the rate of a chemical reaction as dictated by the ΔG^* barrier. Take for example the breaking of a carbon-hydrogen (R_3C-H) bond. Given that the reduced mass is less for a C-H bond vs. the deuterated analog C-D, there is a smaller barrier for the C-H bond to break as shown in Figure 13.9 A. As a reaction rate is proportional to the barrier $k \sim e^{-\Delta G^*}$ (like the Arrhenius equation), the relative rates of reaction involving a proton are generally faster to the same with deuterium according to the formula:

$$\frac{k_{CH}}{k_{CD}} \sim \frac{e^{-\Delta G_{CH}^*}}{e^{-\Delta G_{CD}^*}}$$

While this ratio can be as high as $8\times$, in reality there are many other factors in play and as such the kinetic enhancement can be less. Regardless, the kinetic isotope effect is quite useful because it gives organic chemists a method to investigate which bonds break in a reaction. Thus, it is often used for mechanistic analysis.

The wavefunction shown in Figure 13.8 are for a carbon monoxide molecule, which has a high spring constant $k_f=1860$ N/m. As such, the bond doesn't stretch far as evident from the fact that the wavefunctions do not have significant amplitude past $\sim 1/2$ Bohr, where a Bohr is a unit of length and is equal to 0.53 \AA . In contrast, I_2 has a very weak bond as evident from a $k_f=170$ N/m, and as such it can stretch almost twice as much as CO. Regardless of how strong a bond is, the atoms have a way of stretching further than they should as revealed by the vibrational potential energy surface and ground state wavefunction shown in Figure 13.9 B. The point where the total energy is equal to the potential, where there must be no more kinetic energy:

$$\frac{1}{2} \hbar \omega = \frac{1}{2} k_f \cdot x_{tp}^2 \rightarrow x_{tp} = \pm \sqrt{\frac{\hbar \omega}{k_f}}$$

This is marked in the figure as the turning point (x_{tp}), which is where a normal spring would stretch to the point where it stops and starts to compress back. However, this isn't true for the quantum mechanical spring, as the wavefunction has some finite value for any x . As a result:

$$\int_{x_{tp}}^{\infty} |\psi_{v=0}|^2 dx = 0.078$$

Consequently, there is $\sim 8\%$ chance that a bond will stretch past the point of having no kinetic energy, which is analogous to tunneling discussed previously. Does this mean that the kinetic energy is in fact negative? What does negative kinetic energy motion look like? This is one of the wonders of quantum mechanics as there is no analogy to our everyday experiences that would help describe this.

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