

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 23: The harmonic oscillator

References

1. Levine, *Physical Chemistry*, Chapter 17.12

Key Concepts

- Recall our initial assumption about the energies of molecules: the various energies can be considered independently, namely:

$$E_{total} = E_{elec} + E_{vib} + E_{rot} + E_{nuclear} + E_{other} + \dots$$

and the total wave function that describes a molecular system can be expressed as the product of individual wave functions.

- We now need to model the vibrations of molecules to understand the energetics of molecular vibration. A good place to start is diatomic molecules.
- The bonding curve (potential energy versus atomic separation) exhibits a minimum at the equilibrium separation (R_e) with an associated energy, which we called D_e .
- To understand vibrations, we need to model the energy of the system when there is a displacement from the equilibrium separation. As you can see from a typical bonding curve, pushing the atoms together or pulling them apart results in a higher energy. There is a force trying to *restore* the system back to R_e the system will try and return to the equilibrium separation.
- We can approximate the energy associated with displacements from this equilibrium position using a Taylor expansion:

$$E(R) = \underbrace{E(R_e)}_{D_e} + \left(\frac{dE}{dR}\right)_{R=R_e} (R - R_e) + \frac{1}{2} \left(\frac{d^2E}{dR^2}\right)_{R=R_e} (R - R_e)^2 + \frac{1}{3!} \left(\frac{d^3E}{dR^3}\right)_{R=R_e} (R - R_e)^3 + \dots$$

The second term is always equal to zero since R_e is a minimum and the first derivative of $E(R)$ would be zero.

- The “simplest” model for this system would be to only consider the terms up to $(R - R_e)^2$ resulting in:

$$E(R) = \frac{1}{2} \left(\frac{d^2E}{dR^2}\right)_{R=R_e} (R - R_e)^2$$

where we can substitute a single variable $x = R - R_e$:

$$E = \frac{1}{2} \left(\frac{d^2E}{dR^2}\right) x^2 = \frac{1}{2} kx^2$$

where we have defined the zero of energy (which is an arbitrary) to D_e so the constant term can be omitted. Here x represents the displacement from the equilibrium position, which results in an increase in potential energy when $x \neq 0$.

- The above expression is the same one you arrived at in physics when considering the potential energy of a stretched spring (harmonic oscillator) using Hooke’s law. The constant k is the force constant which in classical spring physics describes the stiffness of the spring.

- Remember our goal in quantum mechanics is to determine the wave functions that describe the system and the allowed energies associated with those wave functions. To do this, we need the Schrödinger Equation. For the case of vibrational energy of a diatomic molecule we need to make two adjustments: (1) replace the m for mass with the reduced mass of the diatomic system ($\mu = \frac{M_1 M_2}{M_1 + M_2}$) and (2) insert $\frac{1}{2}kx^2$ for the potential energy.

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E_{vib}\psi$$

- Solving the above expression is hard, but solutions do exist. Not surprisingly, the allowed energy levels of the quantum mechanical harmonic oscillator (QMHO) are quantized:

$$E_{vib} = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) \quad v = 0, 1, 2, 3, 4, \dots$$

where v is the vibrational quantum number. An alternate expression is:

$$E_{vib} = h\nu_e \left(v + \frac{1}{2} \right)$$

where ν_e is the fundamental vibrational frequency of a given bond (with a certain value of k). As you can see, ν_e and k are related:

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- An important result is the so-called zero-point energy: the lowest available vibrational energy state does not have $E = 0$, but is non-zero, $E(v = 0) = \frac{1}{2}h\nu_e$.
- The harmonic oscillator can be used to understand the origin of IR spectra. Absorption of IR radiation occurs when the energy of vibrational transition equals the energy of the radiation: $\Delta E_{transition} = h\nu_{obs}$, where ν_{obs} is the observed frequency of absorption.
- Vibrational transitions are limited by selection rules, which for the QMHO says that $\Delta v = \pm 1$, where v is the vibrational quantum number. Therefore, only transitions to adjacent vibrational states are observed. Also, to absorb IR radiation a molecule must have a dipole moment (permanent or transient).
- So since $\Delta v = +1$ for pure vibrational spectroscopy, we can write the following relation:

$$\nu_{obs} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \nu_e \quad \text{or} \quad \bar{\nu}_{obs} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \bar{\nu}_e$$