University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 16 2/18/15
Recommended Text Reading: Atkins & DePaula: 9.6

A. Quantum Mechanical Linear Harmonic Oscillator

- A linear harmonic oscillator (LHO) has the energy equation

$$E = K + V = \frac{p^2}{2m} + \frac{\kappa x^2}{2} \tag{16.1}$$

where the frequency of the oscillator is defined by the equation $\omega = 2\pi\nu = \sqrt{\frac{\kappa}{m}}$ where κ (Greek letter kappa) is called the force constant. The amount of force required to displace a sping from its equilibrium length is proportional to the force constant.

- The time-independent Schroedinger wave equation for the LHO is developed in the same way as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{\kappa x^2}{2}\psi = E\psi \tag{16.2}$$

or $\frac{d^2\psi}{dx^2} - \frac{m\kappa x^2}{\hbar^2}\psi = -\frac{2mE}{\hbar^2}\psi$

Equation (16.2) is the wave equation for a single mass moving in a potential $V(x) = \frac{1}{2}\kappa x^2$. For a vibrating bond connecting two masses m_1 and m_2 we replace the mass in Schroedinger's equation by the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{16.3}$$

- The reduced mass has some interesting special cases.
  - Suppose $m_1 = m_2 = m \Rightarrow \mu = \frac{m^2}{m+m} = \frac{m}{2}$
  - Suppose $m_1 \gg m_2 \Rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2} \approx \frac{m_1 m_2}{m_1} = m_2$
- Using the reduced mass formalism 16.2 becomes

$$\frac{d^2\psi}{dx^2} - \frac{\mu\kappa x^2}{\hbar^2}\psi = -\frac{2\mu E}{\hbar^2}\psi \tag{16.4}$$

and by analogy the oscillation frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \tag{16.5}$$

- Equation (16.4) can be shown to be equivalent to a well-known differential equation called Hermite's equation, which can be solved to obtain:
  - The energy quantization equation: $E_n = \hbar\omega\left(n+\tfrac{1}{2}\right) = h\nu\left(n+\tfrac{1}{2}\right)$ for which n=0,1,2,3,etc. Note the ground state energy i.e. n=0 is $E_0=h\nu/2$. This is called the zero point energy $\frac{h\nu}{2}$, the existence of which is required by the Heisenberg Uncertainty Principle.

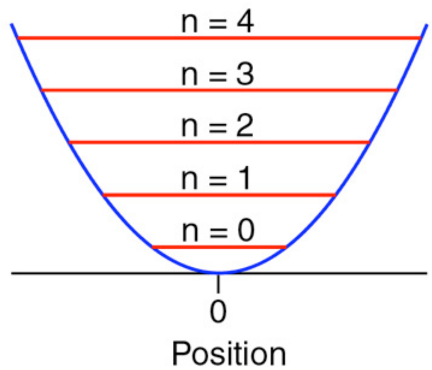

Figure 16.1: The quantized energy levels compared to the potential energy function $V(x)=\kappa x^2/2$. Note also $\Delta E = E_{n+1} - E_n = h\nu$ which means the energy levels are equally spaced for the LHO.

- The solution to Schroedinger's equation for the LHO also gives us the wave functions which have the form:

$$\psi_n(x) = A_n H_n\left(x\sqrt{\alpha}\right)e^{-\alpha x^2/2} \qquad (16.6)$$

- A_n is a constant given by:

$$A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4} \qquad (16.7)$$

and where $\alpha = \frac{\sqrt{\kappa\mu}}{\hbar}$

- For example:

$$A_0 = \left(\frac{\alpha}{\pi}\right)^{1/4};\quad A_1 = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4};\quad A_2 = \frac{1}{2\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4};\quad A_3 = \frac{1}{4\sqrt{3}}\left(\frac{\alpha}{\pi}\right)^{1/4} \qquad (16.8)$$

- $H_n(q)$ is called a Hermite polynomial of the nth order. Note $q = x\sqrt{\alpha}$
- The Hermite polynomials can be generated from the expression

$$H_n(q) = (-1)^n e^{q^2}\frac{\partial^n}{\partial q^n}\left(e^{-q^2}\right) \quad \text{where } q = x\sqrt{\alpha} \qquad (16.9)$$

- For example:

$$H_0(q) = (-1)^0 e^{q^2} \frac{\partial^0}{\partial q^0}\left(e^{-q^2}\right) = e^{q^2}\left(e^{-q^2}\right) = 1$$

$$H_1(q) = (-1)^1 e^{q^2} \frac{\partial^1}{\partial q^1}\left(e^{-q^2}\right) = -e^{q^2}\left(-2qe^{-q^2}\right) = 2q = 2x\sqrt{\alpha}$$

$$H_2(q) = (-1)^2 e^{q^2} \frac{\partial^2}{\partial q^2}\left(e^{-q^2}\right) = 4q^2 - 2 = 4\alpha x^2 - 2$$

$$H_3(q) = (-1)^3 e^{q^2} \frac{\partial^3}{\partial q^3}\left(e^{-q^2}\right) = 8q^3 - 12q = 8x^3\alpha^{3/2} - 12x\sqrt{\alpha}$$

(16.10)

- Table 16.1 summarizes the quantum LHO energies and wave functions for n=0 to n=3

n	E_n (units of hv)	A_n	$H_n(x\sqrt{\alpha})$	$\psi_n(x)$
0	1/2	$\left(\frac{\alpha}{\pi}\right)^{1/4}$	1	$\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$
1	3/2	$\frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4}$	$2x\sqrt{\alpha}$	$\left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$
2	5/2	$\frac{1}{2\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4}$	$4\alpha x^2 - 2$	$\left(\frac{\alpha}{4\pi}\right)^{1/4}\left(2\alpha x^2 - 1\right)e^{-\alpha x^2/2}$
3	7/2	$\frac{1}{4\sqrt{3}}\left(\frac{\alpha}{\pi}\right)^{1/4}$	$8\alpha^{3/2}x^3 - 12x\sqrt{\alpha}$	$\left(\frac{\alpha^3}{9\pi}\right)^{1/4}\left(2\alpha x^3 - 3x\right)e^{-\alpha x^2/2}$

- The LHO energies are a ladder of equally spaced energy states where ΔE=hv.
- Note the ground state energy $E_0 = h\nu\left(0 + \frac{1}{2}\right) = \frac{h\nu}{2}$. This means the ground state energy of a quantum LHO is non-zero and the oscillator cannot exist in the classical zero ground state where the oscillator would be stationary. This is a consequence of the Heisenberg Uncertainty Principle.
- The wave functions in Table 16.1 look unfamiliar but when plotted on top of the classical potential $V(x)=\kappa x^2/2$ have a familiar appearance:

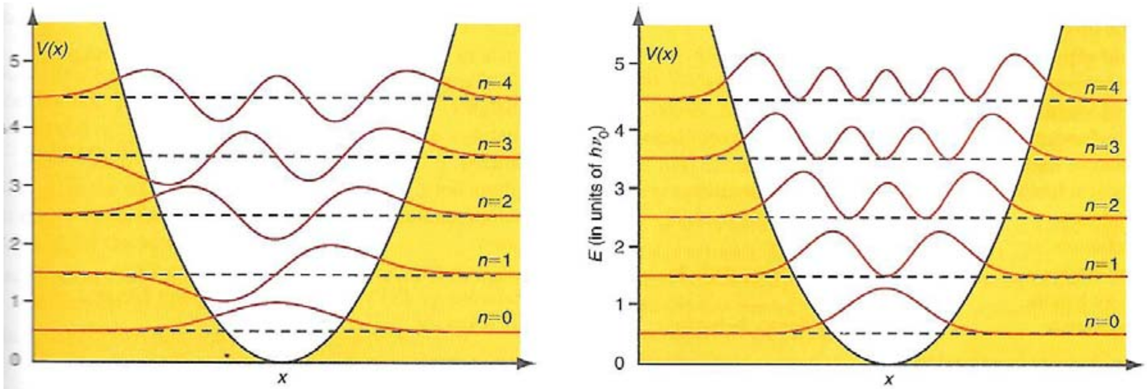

Figure 16.2: Left: First five wave functions (n=0-4) for a quantized LHO. Right: Probabilities= $|\psi(x)|^2$ for first five LHO energy states. Vertical axis is in units of hv.

- Although nodes do not occur at the classical turning points, the wave functions approach zero rapidly as x increases beyond the turning point.
- A mass oscillating classically has the greatest chance of being found at the classical turning points, where the mass stops and reverses motion. In the quantum ground state, the result is reversed. The mass has the greatest chance of being observed at x=0. But as n increases, the quantum probability at the turning points increases and decreases at x=0. This is an example of the Correspondence Principle, that classical mechanics and quantum mechanics converge at high energies or as dimensions and/or masses increase.

B. Probabilities and Expectation Values

- Like the particle in the box, the probability of find a particle in a quantized LHO between ax and x+dx is $|\psi_n(x)|^2\,dx$. The probability of finding the LHO particle in the nth energy state between x=a and x=b is

$$\Pr ob_{ab} = \int_{x=a}^{x=b} |\psi_n(x)|^2\,dx \qquad (16.11)$$

- Because the motion of the mass is symmetric about the center, defined as x=0, $\langle x_n \rangle = 0$ and $\langle p_n \rangle = 0$ for all n. A similar situation arises for particle in the box where the average position is the center of the box, defined as x=L/2, and the average momentum is zero. In that case $\langle x_n \rangle = \frac{L}{2}$ and $\langle p_n \rangle = 0$ for all n.
- We also have the averages:

$$\langle x_n^2 \rangle = \int_{-\infty}^{\infty} \psi_n(x)\,x^2\psi_n(x)\,dx = \frac{h\nu}{\kappa}\left(n+\tfrac{1}{2}\right) \qquad (16.12)$$

$$\langle p_n^2 \rangle = \int_{-\infty}^{+\infty} \psi_n(x)\left[-\hbar^2\,\frac{d^2\psi_n(x)}{dx^2}\right]dx = h\nu\mu\left(n+\tfrac{1}{2}\right) \qquad (16.13)$$

C. Vibrational Partition Function:

- Quantum mechanics shows us the a harmonic oscillator is simply a ladder of equally spaced energies $E_n = h\nu\left(n+\frac{1}{2}\right)$, and the lowest energy is n=0 for which $E_0 = h\nu/2$.
- The partition function is calculated exactly as was the energy ladder...correcting for the lowest energy:

$$q_{vib} = \sum_{n=0}^{\infty} e^{-E_n/k_BT} = \sum_{n=0}^{\infty} e^{-h\nu\left(n+\frac{1}{2}\right)/k_BT} = e^{-h\nu/2k_BT}\sum_{n=0}^{\infty} e^{-nh\nu/k_BT} \qquad (16.14)$$

- Now we treat the series using the same power series approach as in the energy ladder:

$$q = e^{-h\nu/2k_BT}\sum_{n=0}^{\infty} e^{-nh\nu/k_BT} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} \qquad (16.15)$$

- The internal vibrational energy is as usual:

$$\begin{aligned} U_{vib} &= Nk_BT^2\frac{\partial \ln q}{\partial T} = \frac{Nk_BT^2}{q}\frac{\partial q}{\partial T} = \frac{Nk_BT^2}{q}\frac{\partial}{\partial T}\left(e^{-h\nu/2k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-1}\right) \\ &= \frac{Nk_BT^2}{q}\left(\frac{h\nu}{2k_BT^2}e^{-h\nu/2k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-1} + \frac{h\nu}{k_BT^2}e^{-h\nu/2k_BT}e^{-h\nu/k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-2}\right) \\ &= Nk_BT^2\left(\frac{h\nu}{2k_BT^2}+\frac{h\nu}{k_BT^2}e^{-h\nu/k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-1}\right) = N\left(\frac{h\nu}{2}+h\nu e^{-h\nu/k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-1}\right) \\ &= Nh\nu\left(\frac{1}{2}+e^{-h\nu/k_BT}\left(1-e^{-h\nu/k_BT}\right)^{-1}\right) = Nh\nu\left(\frac{1}{2}+\left(e^{h\nu/k_BT}-1\right)^{-1}\right) \end{aligned} \qquad (16.16)$$

- Note this is almost exactly the energy ladder internal energy: $U = \dfrac{N\varepsilon}{1-e^{-\varepsilon/k_BT}}$ where ε=hν and the factor of ½ accounts for the lowest energy value (i.e. n=0).
- Note: At T=0K the vibrational internal energy is predicted to be $U_{vib} = Nh\nu\left(\frac{1}{2}+\left(e^{h\nu/k_B0}-1\right)^{-1}\right) = \frac{Nh\nu}{2}$. At absolute zero quantum particles possess non-zero vibrational energy.
- The heat capacity is basically identical to the energy ladder heat capacity with the substitution ε=hν:

$$C_{V,vib} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[Nh\nu\left(\frac{1}{2}+\left(e^{h\nu/k_BT}-1\right)^{-1}\right)\right] = Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT}-1\right)^2} \qquad (16.17)$$

- Note the heat capacity approaches zero as T approaches zero. Entropy is found from

$$S = \frac{U}{T} + Nk_B \ln q \tag{16.18}$$

- Note the particles are in a solid and thus assumed to be distinguishable i.e. $Q=q^N$.\
- Suppose we assume that the rungs of the LHO energy ladder were very close together so that $k_BT >> \Delta E = h\nu$. Then equation 16.16 becomes

$$\begin{aligned} q_{vib} &= \sum_{n=0}^{\infty} e^{-h\nu\left(n+\frac{1}{2}\right)/k_BT} \approx \int_0^{\infty} e^{-h\nu\left(n+\frac{1}{2}\right)/k_BT} dn \\ &= e^{-h\nu/2k_BT} \int_0^{\infty} e^{-nh\nu/k_BT} dn = \frac{k_BT}{h\nu} e^{-h\nu/2k_BT} \end{aligned} \tag{16.19}$$

- This "high temperature limit" partition function can be used to find the vibrational internal energy:

$$\begin{aligned} U_{vib} &= Nk_BT^2 \frac{\partial \ln q}{\partial T} = Nk_BT^2 \frac{\partial}{\partial T} \ln\left(\frac{k_BT}{h\nu} e^{-h\nu/2k_BT}\right) \\ &= Nk_BT^2 \frac{\partial}{\partial T}\left[-\frac{h\nu}{2k_BT} + \ln\left(\frac{k_BT}{h\nu}\right)\right] = \frac{Nh\nu}{2} + Nk_BT^2 \frac{h\nu}{k_BT} \frac{\partial}{\partial T}\left(\frac{k_BT}{h\nu}\right) = \frac{Nh\nu}{2} + Nk_BT \end{aligned} \tag{16.20}$$

- In this limit the heat capacity goes back to being a constant:

$$C_{V,vib} = \left(\frac{\partial U_{vib}}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{Nh\nu}{2} + Nk_BT\right) = Nk_B \tag{16.21}$$