University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 14. 02/11/15
Recommended Text Reading: Atkins DePaula: 9.1, 9.2, 9.3

A. The Equipartition Principle & Energy Quantization

- The Equipartion Principle is a direct consequence of representing the partition function as an integral. When we do that we assume we may vary the energy continuously by varying the coordinates and momenta continuously. Energy levels are therefore continuous and the gap between adjacent energy levels is infinitely small for translations, rotations, and vibrations.
- When the gap between energy levels is small heat will always be absorbed by the motions of the molecules and so energy is equally partitioned between these motions.
- So long as the energy is a sum of squares of momenta and coordinates, the partition function will depend on the same standard integral expression $\int_0^{\infty} e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$ and a factor of $\sqrt{T}$ will be generated for each occurrence of this integral in q. This is the mathematical origin of the Equipartition Principle.
- The only trouble is...this does not work a lot of the time. As outlined in the last lecture, the Equipartition Principle (EP)fails to predict thermodynamic properties of systems related to vibrational and rotational motions. at low temperatures . As a result heat capacities and other physical properties with their origins in atomic vibrational motions in crystals and ideal diatomic gases are inaccurately predicted.
- A clue as to what is going wrong here is afforded by the vibrational and rotational absorption spectra of diatomic molecules in the gas phase. Figure 11.1 is a spectrum of the frequencies of radiation absorbed by the vibrational and rotational motions of the HCl molecule:

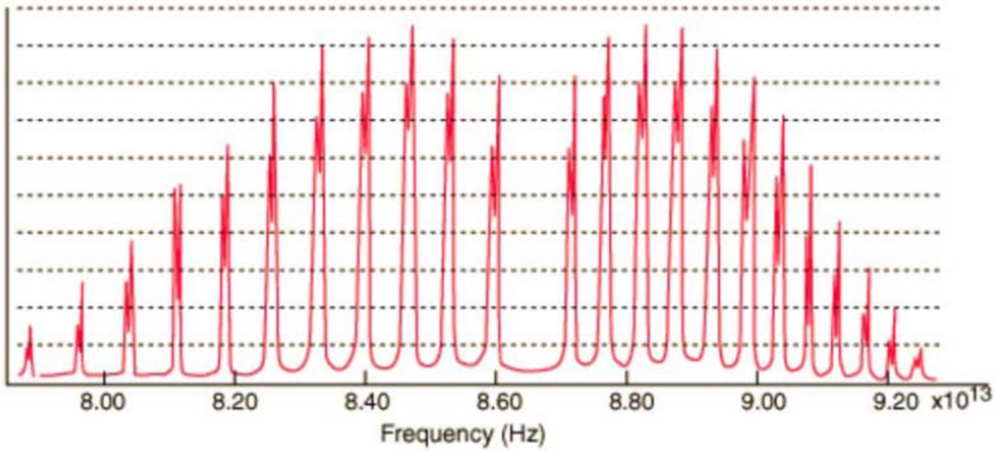


Figure 14.1: The spectrum of frequncies absorbed by the vibrational and rotational motions of HCl in the gas phase. The fact that discrete frequencies are absorbed implies that energy levels for these motions are discontinuous.

- The spectrum in Figure 14.1 is explained if we assume the rotational and vibrational energies are discreetly spaced as shown in Figure 11.2

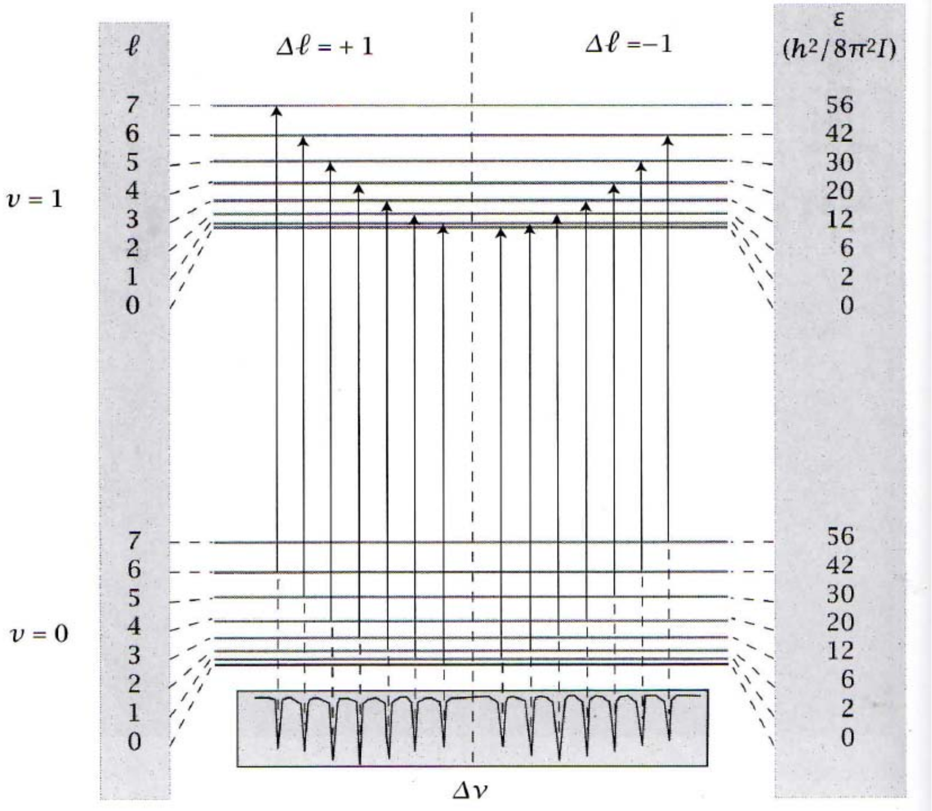


Figure 14.2 Vibrational energies and rotational energies are not a continuum, but rather are quantized. So energy transitions that occur upon the absorption of radiation produce discrete transitions, indicated by the arrows, and which correspond to the absorption lines that we observe in the vibrational spectrum of HCl.

B. Some Basic Quantum Mechanical Postulates

- To calculate macroscopic properties like U, S, A, P, etc. we require energies for atomic translations, vibrations, rotations, as well as electronic energies. These energies are summed into partition functions which in turn generate the macroscopic properties that we want.
- Although the energies we have for translational motions of gases seem to produce correct results when subjected to this process, vibrational and rotational energies are not distributed in a continuum and when that is assumed we get results for

heat capacities etc. which are especially inaccurate at low temperatures. Moreover, data like Figure 14.1 indicate the energy continuum idea is not applicable to all motions and especially not to atomic vibrations and molecular rotations.

- Quantum mechanics is a theory which produces discrete or “quantized” energy values for motions of atoms, molecules, electrons, etc. The physical basis for discrete energy levels can be mostly easily explained for systems that display periodic motions.

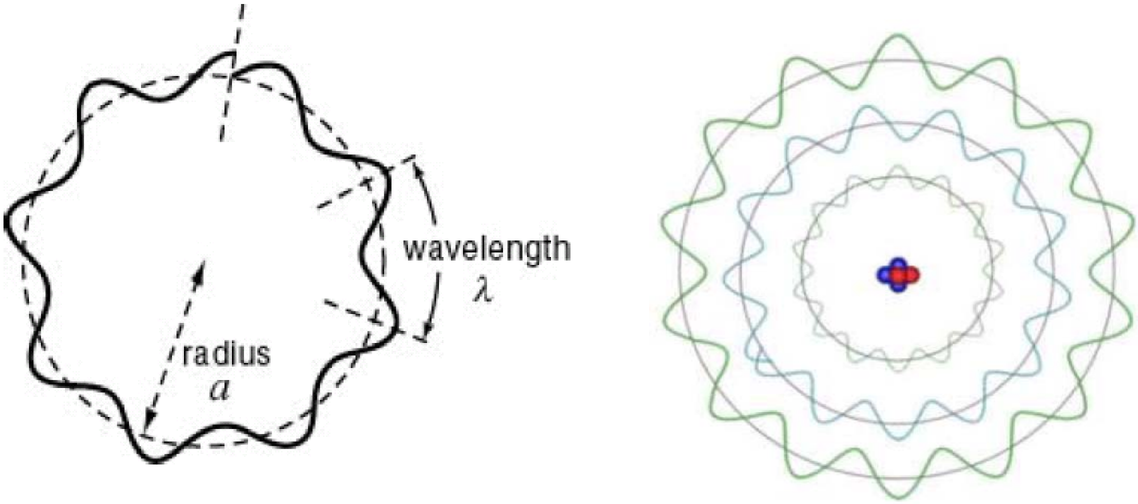


Figure 14.3: A simple view of how the wave length of a particle wave must be matched to the length of the orbit. In the case of a circular orbit of radius a, the length of the orbit must accommodate an integral number of wavelengths:

- A particle whose properties are governed by quantum mechanics has associated with it a wavelength that is related to its momentum by deBroglie’s equation

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad (14.1)$$

  where h=Planck’s constant=6.62x10^{-34}Js

- If the particle is bound in space its orbit must be compatible with its wavelength, else the wave will interfere with itself as shown in Figure 14.3
- Because the energies of mechanical motions at the atomic level are quantized, energy can only be absorbed or emitted in discrete quantum called photons.If a quantum of energy or photon is quantified by is hν, where ν is the frequency of the energy, and the difference between adjacent energy levels is ΔE, then for absorption or emission of energy to occur

$$\Delta E = h\nu \qquad (14.2)$$

- The wave nature of a particle is quantified by a wave function. The energies of the particle's quantized motion are E_n , where n is a positive integer. Corresponding to each energy is a particle wave function for one dimensional motion is ψ(x,). How do we obtain this wave function? A form for the quantum mechanical wave equation is found as follows.
- In classical mechanics we solve Newton's equation F=Ma to obtain a particles position and momentum as a function of time. These quantities may be obtained with arbitrarily high precision. The energy is explicitly a function of position and momentum by

$$E = \frac{p^2}{2m} + V(x) \tag{14.3}$$

- It is assumed that in quantum mechanics equation 14.3 still holds. However when we combine equation 14.1 with equation 14.3 we obtain

$$\frac{h^2}{2m\lambda^2} + V(x) = E \tag{14.4}$$

- In quantum mechanics we assume the wave equation must agree with equation 14.4 and like other wave equations it must be linear. This means it must contain the wave function only to the first power. This means the wave equation must have the form:

$$\frac{h^2}{2m\lambda^2}\psi(x) + V(x)\psi(x) = E\psi(x) \tag{14.5}$$

- In other wave problems, a plausible form for the wave function is

$$\psi(x) = A\sin\left(\frac{2\pi x}{\lambda}\right) + B\cos\left(\frac{2\pi x}{\lambda}\right) \tag{14.6}$$

- A one dimensional wave equation that is consistent with 14.5 and 14.6 is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \tag{14.7}$$

where $\hbar = \frac{h}{2\pi} = 1.05\times10^{-34}\,Js$

- Equation 14.7 is the one dimensional, stationary Schroedinger equation.
- The values and form for the potential energy V depends upon the nature of the problem. For some types of motion like electronic motion or molecular rotations, Schrodinger's equation is transformed from Cartesian coordinates to spherical coordinates.
- The physical meaning of the wave function was not at first agreed upon. The wave function is now interpreted as a probability, i.e. the probability of observing a particle between x and x+dx is $\psi^*(x)\psi(x)dx$ and the probability of finding a particle between x=a and x=b is $\int_a^b \psi^*(x)\psi(x)dx$. The superscript * denotes a complex conjugate. Wave functions can be complex numbers. But the probability is a real number. Multiplying a complex number a+ib by its complex conjugate a-ib assures the product is real.

- Unlike classical mechanics where the momenta and coordinates of a particle can be determined to arbitrarily high precision for all time, in quantum mechanics the momentum and position of a particle cannot be simultaneously determined with arbitrary precision. The uncertainties of position Δx and momentum Δp are intertwined by the Heisenberg Uncertainty Principle:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{14.7}$$

- In quantum mechanics knowledge of the wave function allows us to calculate a particle's average position and average momentum. These quantities are called expectation values in quantum mechanics.
- In the next 3 lectures we will explore the properties of quantized translations, vibrations, and rotations.

C. Particle in a Box; Simple Approach

- A particle with potential energy V(x)=0 for 0<x<L and V(x) infinite otherwise, see Figure 14.4, is referred to as a particle in a box.

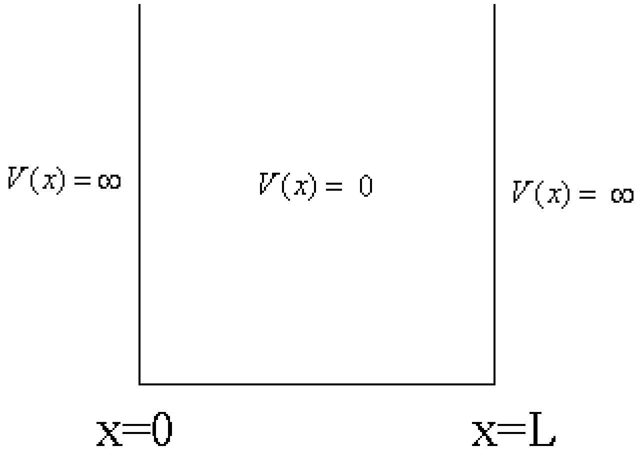


Figure 14.4: Potential energy profile for a particle in a box.

- In such a potential defined as

$$V(x) = \left\{ \begin{matrix} 0 \ \ if \ \ 0 \leq x \leq a \\ \infty \ \ otherwise \end{matrix} \right\} \tag{14.8}$$

the particle must stay between x=0 and x=L because it would need an infinite amount of energy to escape from this region. As long as the particle remains within the box it can go anywhere in the box and will have any energy $E = K = \frac{1}{2}mv^2$.

- Quantum mechanics produces a different outcome, which we can obtain simply as follows. The particle is associated with a wave where the wave must have nodes at x=0 and x=L. This means the particle can have any wavelength

$$\lambda_n = \frac{2L}{n}; n = 1, 2, 3, 4\ldots \qquad (14.9)$$

  - Putting equations 14.6 into 14.1:

$$\lambda_n = \frac{2L}{n} = \frac{h}{p_n} \qquad (14.10)$$

  - Equation 14.7 leads to an expression for the linetic energy of a particle that can have only certain values:

$$E_n = \tfrac{1}{2}mv_n^2 = \frac{p_n^2}{2m} = \frac{1}{2m}\left(\frac{h}{\lambda_n}\right)^2 = \frac{n^2h^2}{8mL^2} \qquad (14.11)$$

D. Particle-in-a Box: Schroedinger's Equation

- The simple use of the debroglie equation (i.e. equation 14.1) and the intuitive treatment of the particle waves presented in the prior section can be made more rigorous by solving Schroedinger's equation for the particle-in-the-box.
- The simple approach gave us an expression for the energy of the particle but gave no expression for the particle's wave form. Using the Schroedinger Equation we can obtain the energies and wave functions for a particle in a box, which is a model for quantized translations.

- The wave function $\psi(x)$ is determined from the time-independent Schroedinger equation:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad (14.12)$$

- Using the potential V(x)=0 for the particle within the box equation 14.13 becomes

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi(x) \; or \; \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \qquad (14.13)$$

where $\hbar = \frac{h}{2\pi} = 1.05\times10^{-34}\,Js$

- The general solution of equation 14.14 is:

$$\psi(x) = A\sin\left(\frac{\sqrt{2mE}}{h}x\right) + Bcos\left(\frac{\sqrt{2mE}}{h}x\right) \qquad (14.14)$$

- With the boundary conditions: $\psi(0) = \psi(L) = 0$ we get B=0 and the quantization condition:

$$\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{L} \; or \; E_n = \frac{n^2h^2}{8mL^2} \qquad (14.15)$$

- Wave functions must obey a normalization conditions like probabilities:

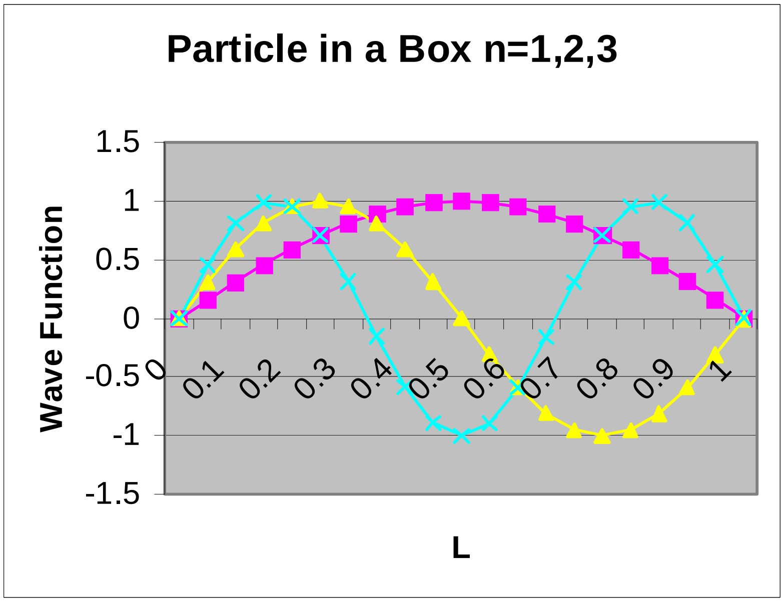
$$\int_0^a |\psi(x)|^2 dx = 1 \qquad (14.16)$$

which gives us $A = \sqrt{\frac{2}{L}}$

  - The wave function is:

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \tag{14.17}$$

Figure 14.5: Particle in Box Wave functions for n=1,2,3



The probability that the particle in energy state n is at position x is

$$P_n(x) = \psi_n^*(x)\psi_n(x) = \left|\psi_n(x)\right|^2 = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$

C. How to “Find” a Particle in a Box

- Wave Functions: $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$, n=1, 2, 3are picture below.
- Note the x points where the wave function is zero. These points are called nodes.
- The number of nodes increases with n.

- The probability of finding a particle in the nth energy at a point x is $\psi_n^2(x) = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)$. Plots of particle probabilities for n=1,2,3 are displayed below.

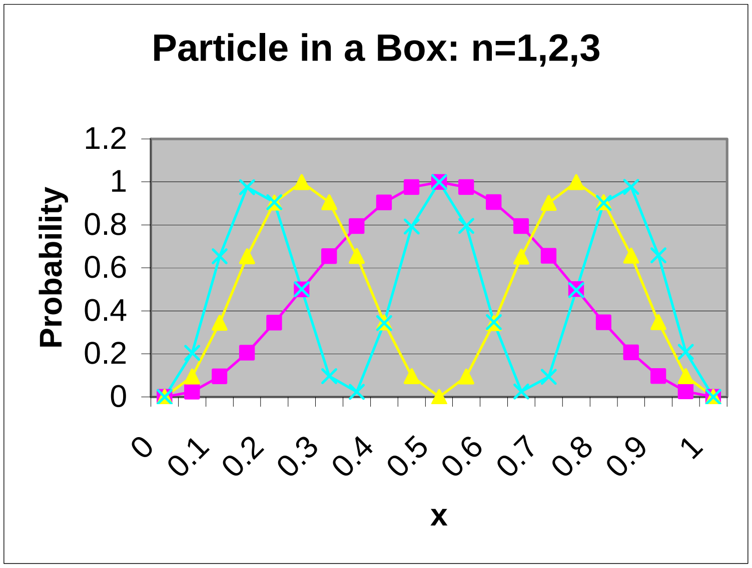


Figure 14.6: Particle in Box probabilities for n=1,2,3

- Therefore for any n the probability of finding the particle between any two points is

$$P_{a-b}^{n} = \int_{x=a}^{x=b} \psi_n^2(x)\,dx = \frac{2}{L}\int_{x=a}^{x=b} dx \sin^2\left(\frac{n\pi x}{L}\right) \tag{14.18}$$