University of Washington
Department of Chemistry
Chemistry 453
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Lecture 12 2/11/13

A. Particle in a Box

- Using the Schroedinger Equation we can obtain the energies and wave functions for a particle in a box. Particle-in-a-Box refers to a particle of mass m in a potential defined as:

$$V(x) = \begin{Bmatrix} 0 \;\; if \;\; 0 \le x \le a \\ \infty \;\; otherwise \end{Bmatrix} \tag{12.1}$$

.This potential constrains the particle to remain in the box.

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

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{12.2}$$

- Using equation 12.1 in 12.2...

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi(x) \; or \; \frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \tag{12.3}$$

- The general solution of equation 12.3 is:

$$\psi(x) = A\sin\frac{\sqrt{2mE}}{\hbar} + Bcos\frac{\sqrt{2mE}}{\hbar} \tag{12.4}$$

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

$$\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{a} \; or \; E_n = \frac{n^2h^2}{8ma^2} \tag{12.5}$$

- Wave functions must obey a normalization conditions like probabilities:

$$\int_0^a |\psi(x)|^2 dx = 1 \tag{12.6}$$

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

- The wave function is:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \tag{12.7}$$

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

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

B. Quantum Mechanical Expectation Values

- Although there are restrictions on what quantities can be detected and calculated in quantum mechanics (i.e. we cannot calculate an exact trajectory…as can be done classically), there are quantities that can be calculated once you know the form of the wave function. Such quantities are called observables.
- The magnitude of a wave function squared is $\psi^*(x)\psi(x) = |\psi(x)|^2$. In quantum mechanics, this denotes the probability of observing a particle at point x. 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.
- The average position of the particle is

$$\langle x \rangle = \frac{\int \psi^*(x)\, x\psi(x)\, dx}{\int \psi^*(x)\psi(x)\, dx} \tag{12.8}$$

.Note this is similar to a classical, weighted average.

  - In quantum mechanics the momentum is defined by an operator as

$$p_x = \frac{h}{2\pi i}\frac{d}{dx} \tag{12.9}$$

- The average momentum of the particle is

$$\langle p_x \rangle = \frac{\int \psi^*(x)\, p\psi(x)\, dx}{\int \psi^*(x)\psi(x)\, dx} = \frac{h}{2\pi i}\frac{\int \psi^*(x)\frac{d}{dx}\psi(x)\, dx}{\int \psi^*(x)\psi(x)\, dx}$$

C. Expectation Values: Particle in a Box

- Wave Functions: $\psi_n(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$, 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.

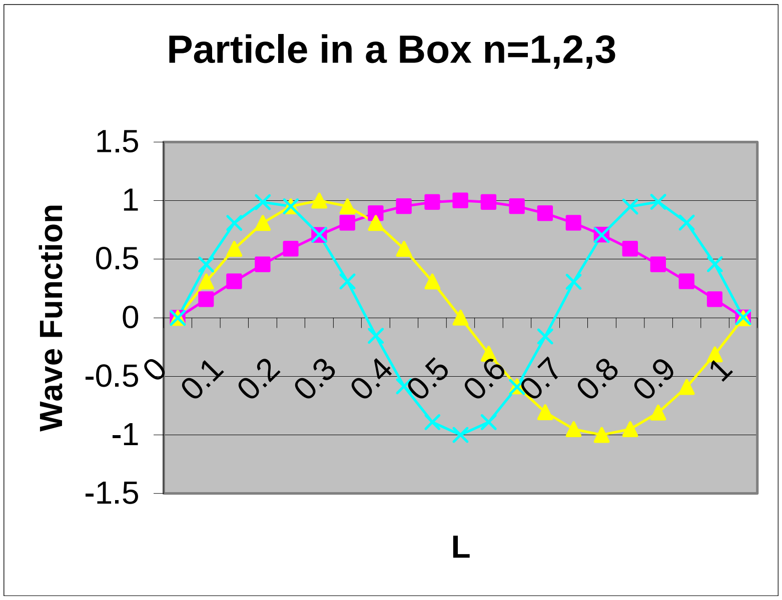


Figure 12.1: Particle in Box Wave functions for n=1,2,3

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

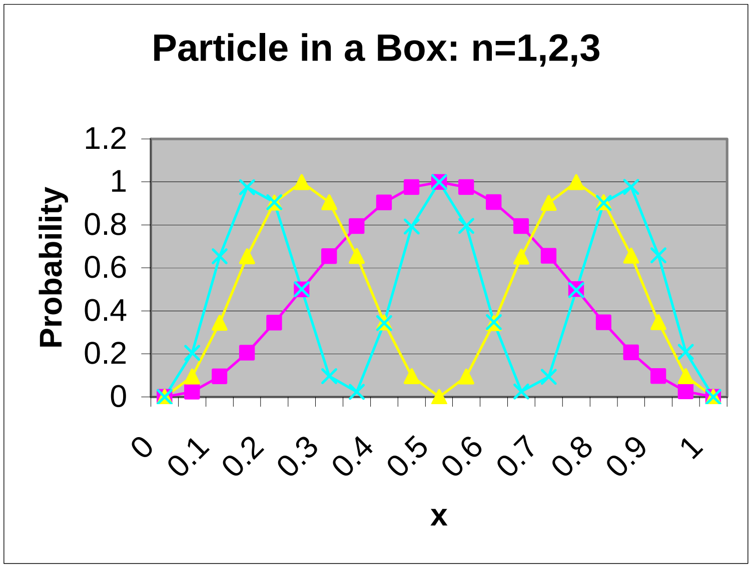


Figure 12.2: Particle in Box probabilities for n=1,2,3

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

$$P_{a-b}^{n} = \int_{x=a}^{x=b} \psi_n^2(x)\,dx = \frac{2}{L}\int_{x=a}^{x=b} dx \sin^2\left(\frac{n\pi x}{L}\right) \qquad (12.10)$$

C. Two and Three Dimensions

- Electronic energies in cyclic systems like benzene and cyclobutadiene may be approximated with two dimensional particle-in-a-box.
- For a two dimensional box with side a, b, length the energy is a sum of two terms:

$$E = E_x + E_y = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right) \qquad (12.11)$$

the wave function is a product of two terms:

$$\Psi_{n_x,n_y}(x,y) = \psi_{n_x}(x)\psi_{n_y}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right) \qquad (12.12)$$

where $n_{x,y}=1,2,3,4\ldots$

- Note equations 12.11 and 12.12 indicate occurrence of degeneracy: different wave functions with the same energy. For example, the energies

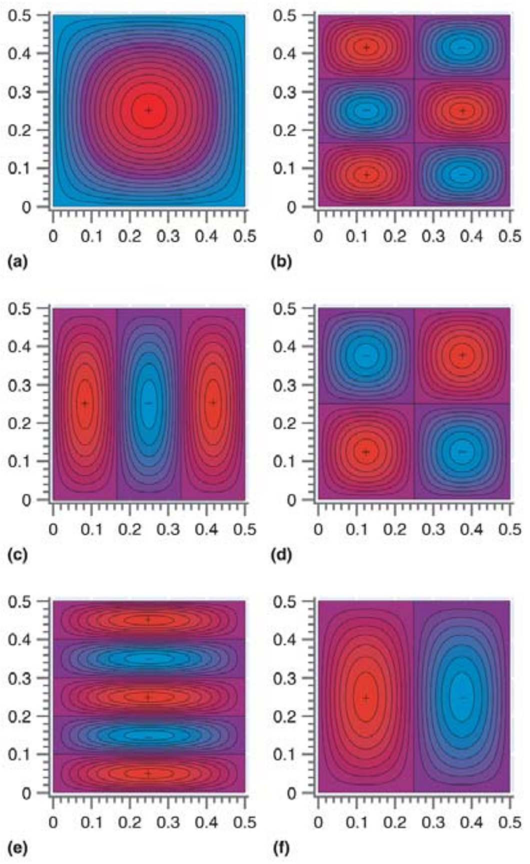
$$E(1,2) = \frac{h^2}{8m}\left(\frac{1^2}{a^2} + \frac{2^2}{b^2}\right) \text{ and } E(2,1) = \frac{h^2}{8m}\left(\frac{2^2}{a^2} + \frac{1^2}{b^2}\right) \qquad (12.13)$$

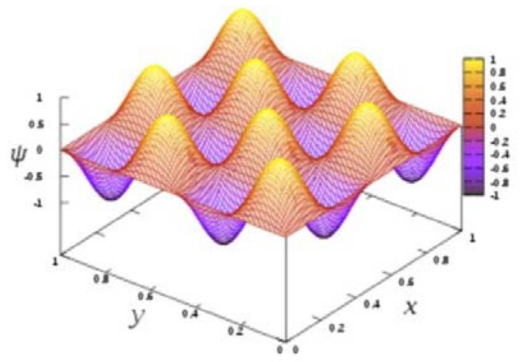
- The wave functions differ in their spatial distribution of density

$$\psi_{n_x=1}(x)\psi_{n_y=2}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{b}\right) \text{ versus } \psi_{n_x=2}(x)\psi_{n_y=1}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{b}\right)$$

(12.14)

Figure 12.3: Wave functions for particle in a Square Box: a=b. Bottom left: three dimensional perspective for wave function $n_x=n_y=4$. Bottom right shows contour plots for
a) $n_x=n_y=1$; b) $n_x=2$, $n_y=3$
c) $n_x=3$, $n_y=1$; d) $n_x=n_y=2$
e) $n_x=1$; $n_y=5$; f) $n_x=2$, $n_y=1$





- For a three dimensional box with sides a, b, c in length the energy is a sum of three terms:

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad (12.15)$$

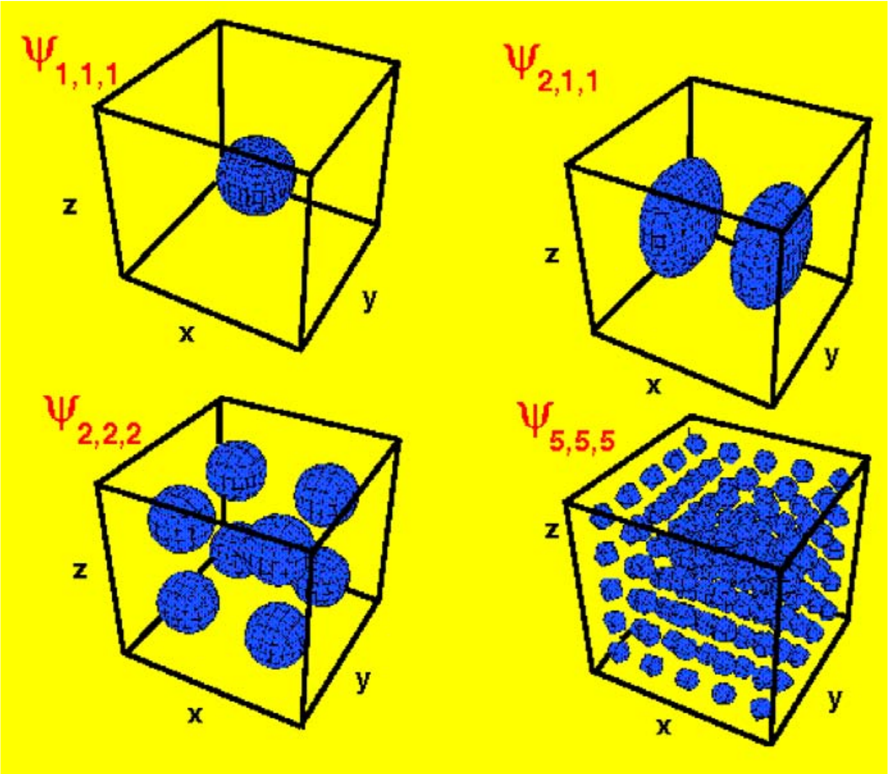
the wave function is a product of two terms:

$$\Psi_{n_x,n_y,n_z}(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi y}{c}\right)$$

(12.16)

where $n_{x,y,z}$=1,2,3,4…

Figure 12.4: $\Psi_{n_x,n_y,n_z}(x,y,z)$ for a particle in a cubic box.



D. The Quantum Translational Partition Function

- Particle-in-Box energies can be used to calculate thermodynamic properties for ideal monatomic gases, and other quantum particles undergoing translation. Use particle-in-a-3D-box energies in a single particle partition function expression:

$$q_{trans} = \sum_{n_{x,y,z}=1}^{\infty} e^{-\varepsilon(n_x,n_y,n_z)/k_BT} = \sum_{n=1}^{\infty}\exp\left[-\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right] \qquad (12.17)$$

- Now assume it is a big box so that $\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}$ <<1. Then we can

  replace the triple summation with a triple integral

$$
\begin{aligned}
q_{trans} &\approx \int_1^\infty dn_x \int_1^\infty dn_y \int_1^\infty dn_z \exp\left[-\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right] \\
&\approx \int_0^\infty dn_x \exp\left[-\left(\frac{n_x^2}{a^2}\right)\frac{h^2}{8mk_BT}\right]\int_0^\infty dn_y \exp\left[-\left(\frac{n_y^2}{b^2}\right)\frac{h^2}{8mk_BT}\right]\int_0^\infty dn_z \exp\left[-\left(\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right] \quad (12.18) \\
&= \frac{abc}{h^3}\left(2\pi mk_BT\right)^{3/2} = \frac{V}{h^3}\left(2\pi mk_BT\right)^{3/2}
\end{aligned}
$$

- Note this is the same result as obtained with the classical translational partition function. We expect this result because in changing from a summation to an integral we assumed the energy level spacing $\Delta E \ll k_B T$.