Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 7

Sep 18^{th}, 2013

Objectives

- To introduce the concept of separable Hamiltonian (operator).
- To show how the Schrödinger equation for a particle in a three-dimensional box can be solved by separation of variables.
- To introduce the concept of degenerate states (degeneracy) and apply to a particle in a three-dimensional box.
- To show a crude example of chemical bonding by means of the particle-in-a-three-dimensional-box system.

Schrödinger equation with a separable Hamiltonian

- If the Hamiltonian for a system can be expressed as

$$\hat{H}(x,y,z) = \hat{H}_X(x) + \hat{H}_Y(y) + \hat{H}_Z(z)$$

it is said to be **separable**. In such a case the solutions of the Schrödinger equation

$$\hat{H}(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

are given by

$$\boxed{\begin{aligned} &\psi(x,y,z) = \psi_X(x)\psi_Y(y)\psi_Z(z) \\ &E = E_X + E_Y + E_Z \end{aligned}}$$

- Each element of the **boxed** equations satisfy one-dimensional Schrödinger equations in the corresponding X, Y and Z axes

$$\hat{H}_X(x)\psi_X(x) = E_X\psi_X(x)$$

$$\hat{H}_Y(y)\psi_Y(y) = E_Y\psi_Y(y)$$

$$\hat{H}_Z(z)\psi_Z(z) = E_Z\psi_Z(z)$$

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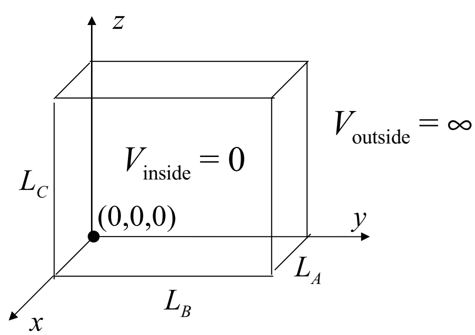
A particle in a three-dimensional box

- Let us consider a box whose dimensions are L_X by L_Y by L_Z and assume the potential *V(x,y,z)* is zero inside the box and infinity outside



- The Schrödinger equation inside the box takes the following form

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + 0\right]\psi(x,y,z) = E\psi(x,y,z)$$

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A particle in a three-dimensional box

- Based on the information presented in slide 3 of this lecture, the Hamiltonian for this system is separable

$$\hat{H}_X(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad \hat{H}_Y(y) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} \quad \hat{H}_Z(z) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$$

- This leads to three (one for each dimension) separate one-dimensional Schrödinger equations

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_X(x) = E_X\psi_X(x) \qquad \psi_X(0)=0,\ \ \psi_X(L_X)=0$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi_Y(x) = E_Y\psi_Y(y) \qquad \psi_Y(0)=0,\ \ \psi_Y(L_Y)=0$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\psi_Z(x) = E_Z\psi_Z(z) \qquad \psi_Z(0)=0,\ \ \psi_Z(L_Z)=0$$

- The **boxed conditions** are required so that the wave-function is well-behaved. They are known as **boundary conditions**.

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Solutions for a particle in a three-dimensional box

- Therefore the solutions to the three-dimensional problem (refer to slides 13-18 of lecture 6) are

$$\psi_{n_x}(x) = \sqrt{\frac{2}{L_X}}\sin\left(\frac{n_x\pi x}{L_X}\right) \quad E_{n_x} = \frac{h^2}{8mL_X^2}n_x^2,\ n_x = 1,2,3,...$$

$$\psi_{n_y}(y) = \sqrt{\frac{2}{L_Y}}\sin\left(\frac{n_y\pi y}{L_Y}\right) \quad E_{n_y} = \frac{h^2}{8mL_Y^2}n_y^2,\ n_y = 1,2,3,...$$

$$\psi_{n_z}(z) = \sqrt{\frac{2}{L_Z}}\sin\left(\frac{n_z\pi z}{L_Z}\right) \quad E_{n_z} = \frac{h^2}{8mL_Z^2}n_z^2,\ n_z = 1,2,3,...$$

- The wave-function for the three-dimensional box and its correspding energies are

$$\psi(x,y,z) = \sqrt{\frac{8}{L_XL_YL_Z}}\sin\left(\frac{n_x\pi x}{L_X}\right)\sin\left(\frac{n_y\pi y}{L_Y}\right)\sin\left(\frac{n_z\pi z}{L_Z}\right)$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_X^2}+\frac{n_y^2}{L_Y^2}+\frac{n_z^2}{L_Z^2}\right) \qquad \begin{array}{l} n_x = 1,2,3,... \\ n_y = 1,2,3,... \\ n_z = 1,2,3,... \end{array}$$

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Degeneracy of energy levels and wave-functions

Definition: Two or more wave functions of a system are said to be **degenerate** if they have the same energy.

- Degenerate states have the **same energy** but their corresponding **wave-functions are different**.

- For instance, for a three-dimensional cubic box (all dimensions of the box are equal to *L*), there are **three** distinct states that have the **same energy**

$$E_{2,1,1} = \frac{h^2}{8mL^2}\left(2^2 + 1^2 + 1^2\right) = \frac{6h^2}{8mL^2} = 6\varepsilon_0 = E_{1,2,1} = E_{1,1,2}$$

- The ground state of the particle in a cubic box is **non-degenerate**

$$E_{1,1,1} = \frac{3h^2}{8mL^2} = 3\varepsilon_0$$

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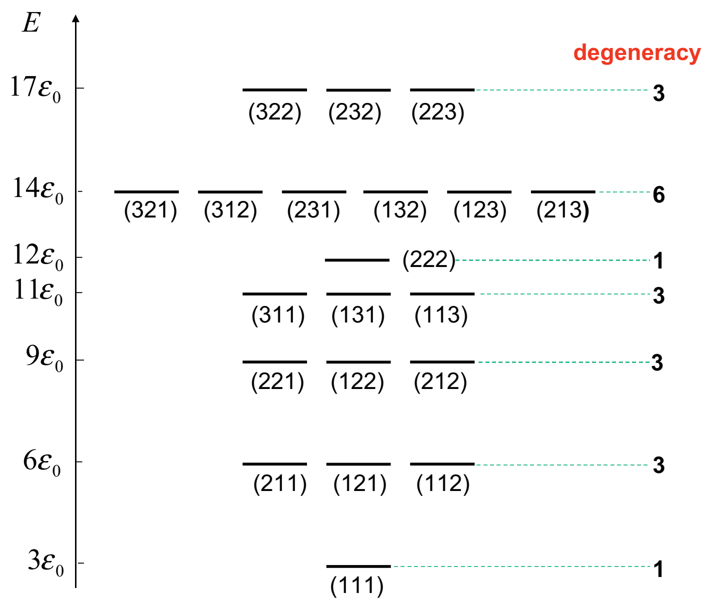
Energy levels for a particle in a cubic box



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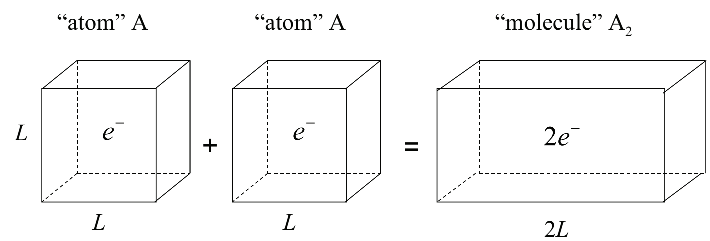
Rectangular-box model for chemical bonding

- Let us consider the following "primitive" model of **chemical bonding**.
- Two cubic boxes with side *L* contain one electron each. The boxes are combined to a form a rectangular box which represents the molecule



- We proceed to compute the change energy of this reaction

Rectangular-box model for chemical bonding

- The ground-state energy of each "atom" is

$$E_A = E_{1,1,1} = \frac{h^2}{8m}\left(\frac{1}{L^2} + \frac{1}{L^2} + \frac{1}{L^2}\right) = 3\varepsilon_0$$

- The ground-state energy for the **two-electron** "molecule" is

$$E_{\text{molec}} = 2\left(\frac{h^2}{8m}\right)\left(\frac{1}{(2L)^2} + \frac{1}{L^2} + \frac{1}{L^2}\right) = 2\left(\frac{1}{4} + 1 + 1\right)\frac{h^2}{8mL^2} = \frac{9}{2}\varepsilon_0$$

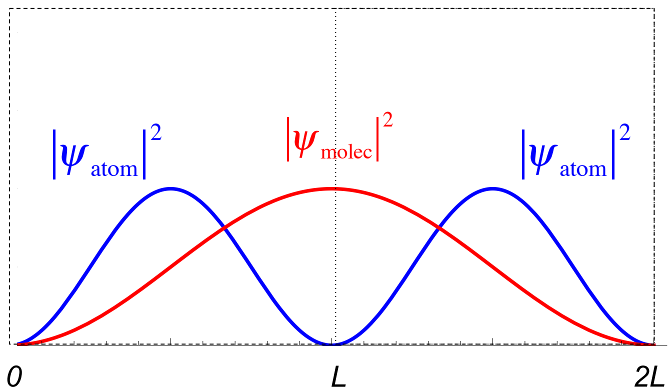
- The energy formation of this "molecule" is

$$\Delta E = E_{\text{molec}} - 2E_A = -\frac{3}{2}\varepsilon_0 < 0 \quad \text{(exothermic)}$$

Rectangular-box model for chemical bonding

- Based on the calculation shown before we conclude that the cubic boxes are effectively "bonded"

- Electron delocalization is the main cause of such a bonding



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