Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 6
Sep 16th, 2013

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Objectives

- To learn the requirements of a wave-function to be valid and the concept of "well-behaved " function.

- To introduce the concept of expectation values show examples of how they are computed based on given wave-functions.

- To motivate the particle-in-a-box system by means of conjugated polyenes.

- To show the general strategy involved in the solution of the Schrödinger equation for a particle in a box and discuss such solution.

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Requirements for a valid wave-function

1. The wave-function must be **continuous**.

2. The wave-function must be **single-valued**.

That is, there should not be two different values of probability density for finding the particle near the same point.

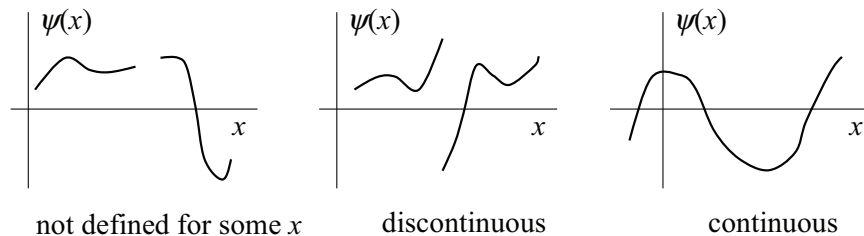**3.** The wave-function should have **continuous derivatives** everywhere

$$\frac{\partial \psi}{\partial x}, \frac{\partial^2 \psi}{\partial x^2}, \frac{\partial^3 \psi}{\partial x^3}, \ldots, \frac{\partial^n \psi}{\partial x^n}$$

except, perhaps, at certain special points (at the nuclei or physical boundaries of the system)
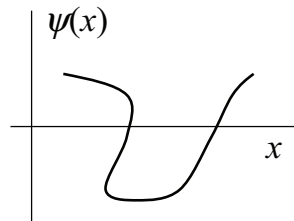
4. The wave-function should be **square-integrable**. In other words, **normalizable**

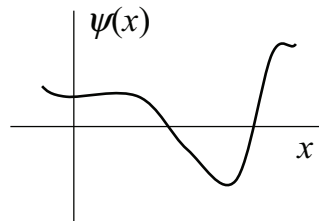Functions satisfying 1 to 3 are usually termed as **well-behaved.** 3

The wave-function must be continuous

not defined for some *x*   discontinuous   continuous

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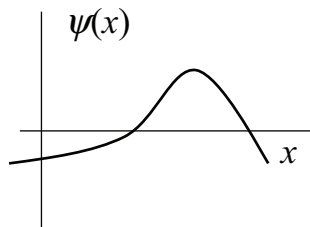# The wave-function must be single-valued
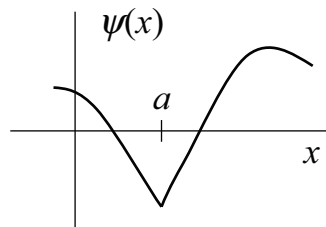

not single-valued   single-valued

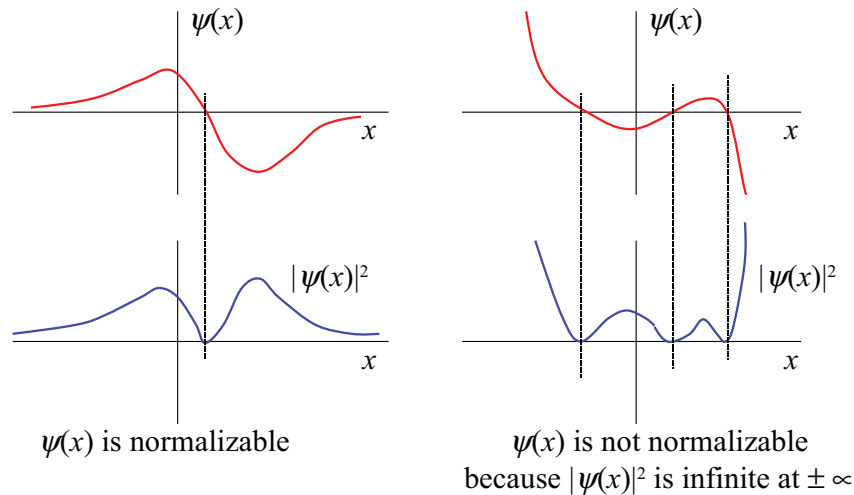# The wave-function should have continuous derivatives everywhere

$\partial\psi/\partial x$ is continuous $\partial\psi/\partial x$ is discontinuous at $x = a$

The wave-function should be square-integrable

$\psi(x)$ is normalizable

$\psi(x)$ is not normalizable
because $|\psi(x)|^2$ is infinite at $\pm\infty$

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Expectation values

- Based on the **probabilistic interpretation** of the wave-function, we introduce the **expectation value**, **expected value** or **average value**

- The **average value** of an observable *A*, when the system is an state is given by

$$\langle A \rangle_\varphi (t) = \frac{\int\limits_{-\infty}^{\infty} \varphi^*(x,t)\hat{A}(x,t)\varphi(x,t)\,dx}{\int\limits_{-\infty}^{\infty} \varphi^*(x,t)\varphi(x,t)\,dx}$$
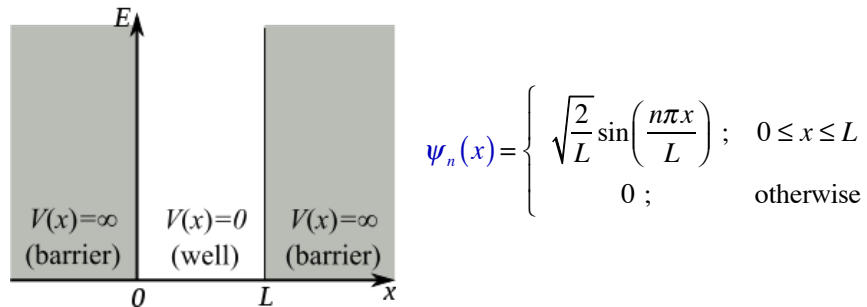
where *A* is the operator representing the observable A.

- The **average value** depends on the state, and in general depends on time

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Example of expectation values

- Later we will see that the **nth state** of the **particle-in-a-box** system represented by the following wave-function

$$\psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi x}{L}\right) ; & 0 \le x \le L \\ 0 ; & \text{otherwise} \end{cases}$$

E

$V(x)=\infty$ (barrier) | $V(x)=0$ (well) | $V(x)=\infty$ (barrier)

0 L x

- The **average position** of the particle, when at the **nth state** is given by

$$\langle x \rangle_{\psi_n} = \frac{\displaystyle\int_0^L \psi_n^*(x)\,\hat{x}\,\psi_n(x)}{\displaystyle\int_0^L \psi_n^*(x)\psi_n(x)} = \frac{L}{2}$$

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Example of expectation values

- The **average linear momentum** of the particle, when at the **nth state**, is given by

$$\langle p \rangle_{\psi_n} = \frac{\displaystyle\int_0^L \psi_n^*(x)\,\hat{p}\,\psi_n(x)}{\displaystyle\int_0^L \psi_n^*(x)\psi_n(x)} = 0$$

- Therefore the particle in a box **is on average** at the middle point of the box and **has on average** zero linear momentum.

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Application problem No.1: Conjugated poleyenes

- A system of $\pi-$electrons in a linear conjugated poleyne can be thought of as a system of non-interacting electrons in a one-dimensional box

1,3-butadiene

$V = \infty$ $V = \infty$

$x=0$ $x=L$
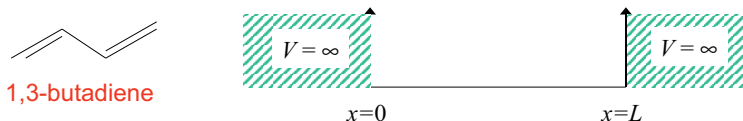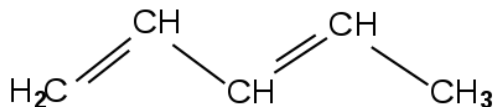
- **Assumption 1.** The $\pi-$ electrons do not interact with one another, but they obey the Pauli exclusion principle.

- **Assumption 2.** The length L of the "box" is equal to the total length of the poleyne chain plus two radii of an sp^2 C atom

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Example of the 1,3-butadine molecule

1.34Å   1.54Å   1.34Å
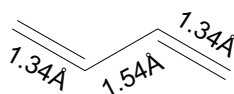
From standard reference tables:

$$R(C–C) = 1.54 \text{ Å}$$
$$R(C=C) = 1.34 \text{ Å}$$
$$r(sp^2 C) = 0.73 \text{ Å}$$

Using these values we find

$$L = 0.73 + 1.34 + 1.54 + 1.34 + 0.73 = 5.68 \text{ Å}$$

$$V(x) = \begin{cases} 0 \; ; & 0 \leq x \leq L \\ +\infty \; ; & \text{otherwise} \end{cases}$$

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Solving the Schrödinger equation for a particle in a box

- The potential for the system under discussion is given by

$$V(x) = \begin{cases} 0 \; ; & 0 \leq x \leq L \\ +\infty \; ; & \text{otherwise} \end{cases}$$

- Due to the piece-wise nature of the potential, the Schrödinger equation associated to this potential can be studied in three regions.

- Region I : $-\infty < x < 0 \quad \rightarrow \quad \psi_1(x)$

  Region II : $0 \leq x \leq L \quad \rightarrow \quad \psi_2(x)$

  Region III : $L < x < +\infty \quad \rightarrow \quad \psi_3(x)$

- In regions I and III the potential is "infinitely high". Therefore the probability of finding the particle in those regions is zero

$$\psi_1(x) = \psi_3(x) = 0$$

Solving the Schrödinger equation for a particle in a box

- For region II the Schrödinger equation looks like

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2}(x) + 0 \cdot \psi_2(x) = E\psi_2(x)$$

which can be re-written as

$$\frac{d^2\psi_2}{dx^2}(x) + k^2\psi_2(x) = 0 \quad ; \quad k^2 = \frac{2mE}{\hbar^2}$$

- The general solution to this second order differential equation is

$$\psi_2(x) = A\sin(kx) + B\cos(kx)$$

- In order to determine the constants *A* and *B* we need to enforce conditions on the wave-function to make it well-behaved

Solving the Schrödinger equation for a particle in a box

- In order to make the wave-function continuous, the following conditions should be satisfied

$$\psi_2(0) = \psi_1(0) = 0 \quad \Rightarrow \quad B = 0$$

$$\psi_2(L) = \psi_3(L) = 0 \quad \Rightarrow \quad A\sin(kL) = 0$$

- The second condition implies that either *A = 0* or sin(*kL*) = 0. The former cannot be, otherwise would imply there is no wave-function in region II; **which would imply having probability zero of finding the particle in region II!**

- Therefore sin(*kL*) = *0,* which implies

$$k = \frac{n\pi}{L}$$

- The only part left to be determined is *A*; which is computed by normalizing the wave-function.

Normalizing the wave-function for a particle in a box

- So far we have that the wave-function has the form

$$\psi(x) = \begin{cases} 0 \; ; & x < 0 \\ A\sin\left(\dfrac{n\pi x}{L}\right) \; ; & 0 \le x \le L \\ 0 \; ; & x > L \end{cases}$$

- In order to determine the unknown *A* we normalize the wave-function. That is,

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = 1$$

Normalizing the wave-function for a particle in a box

- The previous integral leads to the following development

$$\int_{-\infty}^{+\infty}\left|\psi(x)\right|^2 dx = \underbrace{\int_{-\infty}^{0}\left|\psi_1(x)\right|^2 dx}_{\text{Region I}} + \underbrace{\int_{0}^{L}\left|\psi_2(x)\right|^2 dx}_{\text{Region II}} + \underbrace{\int_{L}^{+\infty}\left|\psi_3(x)\right|^2 dx}_{\text{Region III}}$$

$$= \underbrace{0}_{\text{Region I}} + \underbrace{A^2\int_{0}^{L}\sin^2\left(\frac{n\pi x}{L}\right)dx}_{\text{Region II}} + \underbrace{0}_{\text{Region III}}$$

$$= A^2\left(\frac{L}{2}\right)$$

- Therefore, the normalization constant is

$$A = \sqrt{\frac{2}{L}}$$

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Normalized wave-function and eigenvalues for a particle in a box

- The normalized **wave-function** for a particle in a box is then

$$\psi_n(x) = \begin{cases} 0 \; ; & x < 0 \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \; ; & 0 \le x \le L \\ 0 \; ; & x > L \end{cases}$$
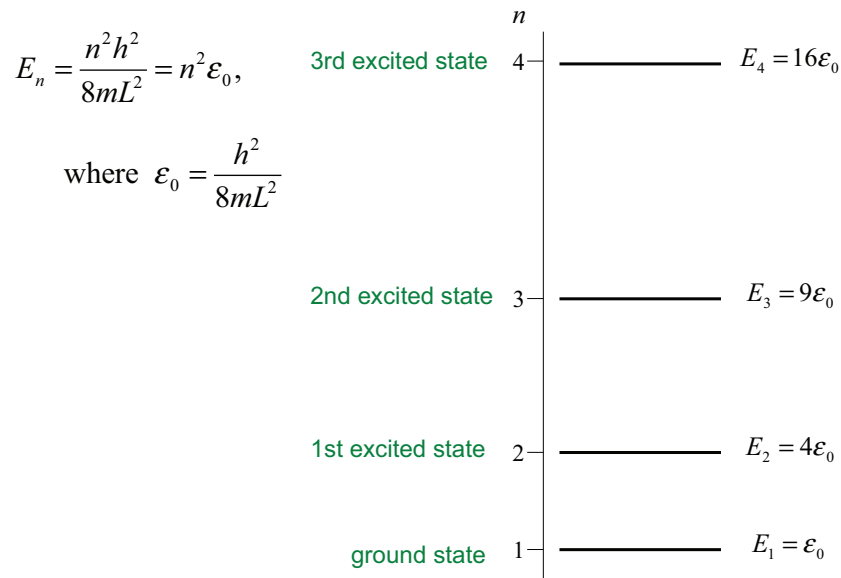
- From slides 11 and 12 of this lecture we conclude

$$k^2 = \frac{2mE}{\hbar^2} \; ; \; k = \frac{n\pi}{L} \implies E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2 = \frac{h^2}{8mL^2}n^2$$

- Notice that the energy levels are an integer multiple of a "basic energy" for the system. That is, **energy is quantized!**
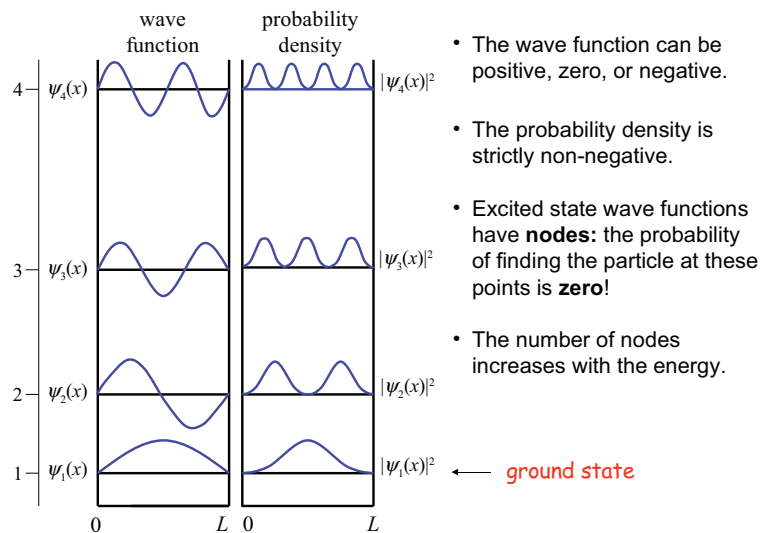
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Energy level diagram for a particle in a box

$$E_n = \frac{n^2 h^2}{8mL^2} = n^2 \varepsilon_0,$$

where $\varepsilon_0 = \dfrac{h^2}{8mL^2}$

n

3rd excited state	4	———	$E_4 = 16\varepsilon_0$
2nd excited state	3	———	$E_3 = 9\varepsilon_0$
1st excited state	2	———	$E_2 = 4\varepsilon_0$
ground state	1	———	$E_1 = \varepsilon_0$

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Wave-functions and probability densities for a particle in a box

wave function   probability density

4 — $\psi_4(x)$ $|\psi_4(x)|^2$

3 — $\psi_3(x)$ $|\psi_3(x)|^2$

2 — $\psi_2(x)$ $|\psi_2(x)|^2$

1 — $\psi_1(x)$ $|\psi_1(x)|^2$ ← ground state

0   L 0 L

- The wave function can be positive, zero, or negative.

- The probability density is strictly non-negative.

- Excited state wave functions have **nodes:** the probability of finding the particle at these points is **zero**!

- The number of nodes increases with the energy.

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