

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 5
Sep 13th, 2013

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Objectives

- To learn the definition of eigenvalues and eigenfunctions for a given operator.
- To understand the time-independent Schrödinger equation as an eigenvalue problem.
- To learn the probabilistic interpretation of the wave-function of a system.
- To learn the requirements of a wave-function to be valid.

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Eigenfunctions and eigenvalues

- Let \hat{A} and $f(x)$ be, respectively, an **operator** and a **function**. It is said that $f(x)$ is an **eigenfunction** of \hat{A} , with **eigenvalue** a if

$$\hat{A}f(x) = af(x)$$

in words, the **operator** returns the original **function** multiplied by a **constant**.

- Examples

$$\frac{d}{dx}(e^{-4x}) = -4e^{-4x}$$

$$\frac{d^2}{dx^2}[\cos(\alpha x)] = -\alpha^2 \cos(\alpha x)$$

$$-i\frac{\partial}{\partial x}[e^{i(kx-\omega t)}] = ke^{i(kx-\omega t)}$$

The **functions** are **eigenfunctions** of the **operators** with the indicated **eigenvalues**

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The time-independent Schrödinger equation can be formulated as an eigenvalue problem

- Let us recall that the time-independent Schrödinger equation is given by

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

- If we introduce the following **Hamiltonian operator**

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

the time-independent Schrödinger equation reads as

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

- Thus, the time-independent Schrödinger equation can be treated as an **eigenvalue problem** involving the **Hamiltonian** with eigenvalue E

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Physical interpretation of the wave-function

- In general, the wave-function is complex-valued and does not represent any observable property by itself.
- However, the **module of the wave-function** (the product of its complex conjugate with itself) is always real-valued and has a physical meaning: it gives the **probability density** of finding the particle in the vicinity of x
- The **probability density** for a particle in one dimension is:

$$p(x) = |\psi(x)|^2 = \psi^*(x)\psi(x)$$

- The **probability** finding the particle between a and b is, therefore,

$$P(a \leq x \leq b) = \int_a^b |\psi(x)|^2 dx$$

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Probabilistic interpretation of the wave-function



- The probabilistic interpretation of the wave-function was proposed by Max Born. It is sometimes referred as the Born interpretation.
 - Moreover, the wave-function contains **all the information about the system**. It can be used to determine position, momentum, energy and other observables.
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- Given the probabilistic interpretation of the wave-function, it will be crucial to have **normalized wave-functions**.

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Normalization of the wave-function

- When utilized in practical application, the wave-function has to be **normalized**. That is

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

- The normalization condition means that the particle is somewhere between $-\infty$ and $+\infty$ with probability equal to 1.
- A **square-integrable** wave-function $\psi(x)$ that satisfies

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

is not normalized, but is normalized after is multiplied by $1/\sqrt{C}$

- The factor $1/\sqrt{C}$ is called **normalization factor**

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Normalizing a wave-function

- Step 1.** Evaluate

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

- Step 2.** Multiply the wave-function by $N_c = 1/\sqrt{C}$

$$\psi(x) \rightarrow \frac{1}{\sqrt{C}} \psi(x)$$

- Important note.** In order to normalize a wave-function, **C** must be finite. That is, the wave-function should be **square-integrable** (see the previous slide). In this case it is said that the wave-function is **normalizable**.

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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

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

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**