Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 4
Sep 11th, 2013

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Objectives

- To present the one-dimensional time-dependent Schrödinger equation.
- To introduce, by analogy with classical mechanics, the need and operators to represent observables in quantum mechanics.
- To present the definition of operators as well as operator algebra.

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The time-dependent Schrödinger equation

- The time-dependent Schrödinger equation reads as

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}(x,t)+V(x,t)\Psi(x,t)=i\hbar\frac{\partial\Psi}{\partial t}(x,t)}$$

- This one can be motivated following a similar procedure to the one performed for the time-independent equation.
- It is important to notice that if in the above equation the potential is time-independent and the wave-function is expressed as

$$\Psi(x,t)=\psi(x)e^{-iEt/\hbar}$$

then the time-independent equation is obtained

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

Introducing operators in quantum mechanics

- Let us take the expression for the **total mechanical energy** in classical mechanics, **kinetic energy** plus **potential energy**

$$E=T+V(x,t)$$

and let us multiply it by the **wave-function**

$$E\Psi(x,t)=T\Psi(x,t)+V(x,t)\Psi(x,t)$$

- Comparing this equation with the time-dependent Schrödinger (previous slide) equation we can motivate the following association

$E\rightarrow i\hbar\frac{\partial}{\partial t}$ **take partial derivative with respect time**

$T\rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ **take second partial derivative with respect position**

$V\rightarrow V(x,t)$ **multiply by the potential**

Observables in quantum mechanics are associated with operators

- The former slide introduces the fact that in quantum mechanics observables are represented by operators acting on functions.

Property	Classical-mechanical variable in 1D	Quantum-mechanical operator
position	x	$\hat{x}$ [multiply by x]
momentum	p_x	$\hat{p}_x = -i\hbar \dfrac{d}{dx}$
kinetic energy	$T = \dfrac{p_x^2}{2m}$	$\hat{T} = \dfrac{\hat{p}_x^2}{2m} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$
potential energy	$V(x)$	$\hat{V}$ [multiply by $V(x)$]
total energy	E	$\hat{H} = \hat{T} + \hat{V}$

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Observables and operators

- **Observable**. It is a measurable quantity in a physical/chemical system. For instance kinetic energy, momentum, position, etc.

- **Operator**. It is a function acting on the space of physical states (wave-functions).

- Due to the former discussion, it will be crucial to learn to perform operations with operators. In other words we will need to learn to make **algebraic manipulations with operators**.

- Most of the operations with operators are motivated by the traditional way we do algebra with real numbers.

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Operators algebra

- **Sum** or **difference** of two operators:

$$\left(\hat{A} \pm \hat{B}\right) f(x) = \hat{A}f(x) \pm \hat{B}f(x)$$

- **Product** of two operators:

$$\hat{A}\hat{B}f(x) = \hat{A}\left[\hat{B}f(x)\right]$$

- The **identity operator** multiplies by **one** the function is acting on

$$\hat{I}f(x) = 1 \cdot f(x) = f(x)$$

- The **inverse** of a **given operator** is defined as the one that satisfies the following

$$\hat{A}^{-1}\hat{A} = \hat{A}\hat{A}^{-1} = \hat{I}$$

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Operators algebra

- The **n^{nt} power of an operator** is given by

$$\hat{A}^n f(x) = \underbrace{\hat{A}\left[\hat{A}\left[\ldots\left[\hat{A}f(x)\right]\ldots\right]\right]}_{\text{apply the operator } n \text{ times}}$$

- General comments:
  a. The symbol $\hat{A}$ is usually read as *A* "hat". It is more "formal" to read it as *A* **circumflex**, which is the term we will use.
  b. The product of operators **is not commutative**.
  c. The "division" of operators is not "well defined" because the product of of operators is not commutative.
  d. In quantum mechanics the outcome of a measurement will be associated with the **eigenvalues** of an operator.
  e. Not every operator will be allowed to represent observables in quantum mechanics. The ones allowed are known as **Hermitian operators**.

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