Chemistry 3P51 – Fall 2013
Quantum Chemistry

Lecture No. 12
Sep 30th, 2013

1

Objectives

- To remind the student the meaning of spread in measurements.
- To introduce the Heisenberg's uncertainty principle.
- To introduce the Dirac (braket) notation of quantum mechanics.
- To present the postulates of quantum mechanics.

2

The spread in measurements

The spread in measurements is characterized by:

variance:	$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2$
standard deviation ("uncertainty"):	$\sigma_a = \sqrt{\sigma_a^2}$

If a wave function ψ of a particle is an eigenfunction of $\hat{A}$, then

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^* (\hat{A}\psi)\, dx = \int_{-\infty}^{\infty} \psi^* (a\psi)\, dx = a\int_{-\infty}^{\infty} \psi^* \psi\, dx = a$$

$$\langle a^2 \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A}^2 \psi\, dx = \int_{-\infty}^{\infty} \psi^* \hat{A}(\hat{A}\psi)\, dx = a\left(\int_{-\infty}^{\infty} \psi^* \hat{A}\psi\, dx\right) = a^2$$

so the variance is zero: $\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = a^2 - a^2 = 0$

If ψ is *not* an eigenfunction of $\hat{A}$, then $\sigma_a^2 > 0$

3

Heisenberg's uncertainty principle

- Statement: The position and linear momentum of a particle cannot simultaneously have definite values. For any state of a particle, the product of uncertainties in the position and linear momentum is

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$$

- In the above expression

σ_x is the standard deviation of position meassurements

σ_p is the standard deviation of position meassurements

- In practice, the uncertainty principle is a non-negligible effect only on a macroscopic scale because Planck's constant is very small.

4

The braket notation in quantum mechanics

- A very common notation used in quantum mechanics is the **Dirac notation**, also known as the **braket notation**.
- The idea is to represent the integrals that arise in quantum mechanics by a **braket**

$$\boxed{\langle f | g \rangle = \int_{-\infty}^{\infty} f^*(x)\, g(x)\, dx} \qquad \boxed{\langle f | \hat{A} | g \rangle = \int_{-\infty}^{\infty} f^*(x)\, \hat{A} g(x)\, dx}$$

- This also motivates the idea of associating function with **kets** and complex conjugates of functions with **bras**

$$\text{ket } |g\rangle \to g(x)$$

$$\Rightarrow \quad \langle f | g \rangle = \int_{-\infty}^{\infty} f^*(x)\, g(x)\, dx$$

$$\text{bra } \langle f| \to f^*(x)$$

5

Summary of postulates of quantum mechanics

For simplicity, we will present the postulates in the form suitable only for single particles in 1D. These can be readily generalized to 3D and to systems of many particles (many-electron atoms, molecules, etc.)

Postulate 1

The state of a particle is completely specified by a position- and time-dependent function $\Psi(x,t)$, called the wave function. All information about the particle is contained in Ψ.

The wave function $\Psi(x,t)$ has the following interpretation:

$$|\Psi(x,t)|^2\, dx \equiv \Psi^*(x,t)\Psi(x,t)\, dx$$

is the probability that the particle is found between x and $x + dx$ at the time t.

6

Summary of postulates of quantum mechanics

Postulate 2

The wave function of a particle evolves in time according to the time-dependent Schrödinger equation:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

where $\hat{H}$ is the Hamiltonian operator given by

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

Whenever the potential energy operator V does not depend on t, the solution of the time-dependent Schrödinger has the form

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

The time-independent wave function $\psi(x)$ is obtained as the solution of the time-independent Schrödinger equation:

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

7

Summary of postulates of quantum mechanics

Postulate 3

To every observable property in classical mechanics there corresponds a Hermitian operator in quantum mechanics.

Postulate 4

In any measurement of the physical property represented by the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues of that operator:

$$\hat{A}\psi_n = a_n\psi_n$$

When the particle is in an eigenstate ψ_n of $\hat{A}$, every measurement of property $\hat{A}$ yields the same (definite) value: the eigenvalue a_n

8

Summary of postulates of quantum mechanics

Postulate 5

If the particle can be in any of the eigenstates ψ_1, ψ_2, ψ_3, ..., then it can also be in a linear superposition of these states:

$$\varphi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \ldots = \sum_n c_n\psi_n$$

Postulate 6

If the particle is in a state described by a normalized wave function ψ, then the average value of the property represented by the operator $\hat{A}$ is given by:

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, dx$$

9

Appendix: The commutator of two operators is crucial in the uncertainty principle

- ***Theorem***. If a system is described by the wave-function ψ and the operators $\hat{A}$ and $\hat{B}$ represent two observable quantities, then

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4} \left\{ \int_{-\infty}^{+\infty} \psi^*(x) \left[\hat{A}, \hat{B} \right] \psi(x) \, dx \right\}^2$$

- ***Corollary***. If the operators $\hat{A}$ and $\hat{B}$ do not commute, then their corresponding observable quantities do not have simultaneously definite values. This is the most general formulation of the **uncertainty principle** for a pair of physical quantities represented by operators $\hat{A}$ and $\hat{B}$

10