Quantum Chemistry (1)

INTRODUCTION TOWARDS QUANTUM MECHANICS

The end of the 19th century, Maxwell's electromagnetic theory unified existing knowledge in the areas of electricity, magnetism, and waves. This theory, combined with the well-established field of Newtonian mechanics, ushered in a new era of maturity for the physical sciences. Many scientists of that era believed that there was little left in the natural sciences to learn. However, the growing ability of scientists to probe natural phenomena at an atomic level soon showed that this presumption was incorrect. The field of quantum mechanics arose in the early 1900s as scientists became able to investigate natural phenomena at the newly accessible atomic level. A number of key experiments showed that the predictions of classical physics were inconsistent with experimental outcomes.

The failure of classical physics to explain several microscopic phenomena had cleared **a new way of modelling nature, describe the behaviour of matter at atomic level by a better theory called quantum mechanics.**

Quantum mechanics is the study of describing, explaining and predicting behaviour of matter at atomic and molecular level. It is the theory that describes the dynamics of matter at microscopic scale. **Theory is based on several statement called postulates.** These postulates are assumed not proven. It may seems difficult to understand the entire model of electron atom and molecule is based on assumptions but the reason is simple because the statements based on these assumptions lead to prediction about atoms and molecules that agree with observation. With agreement between theory and experiment is so abundant, the unproven postulates were accepted and no longer questioned. The statement and equations based on these postulates agree with experiment and so constitute an appropriate model for the description of subatomic matter, especially electrons.

Quantum mechanics is sometimes difficult at first glance, partly because some new ideas and some new ways of thinking about matter are involved. Remember that **the ultimate goal is to have a theory that proposes how matter behaves, and that predicts events that agree with observation;** that is, to have theory and experiment agree. Otherwise, a different theory is necessary to understand the experiment.

The main ideas are:

The behaviour of electrons, by now known to have wavelike properties can be described by a mathematical expression called a **wavefunction**.

The wavefunctions contains within it all possible information that can be known about a system.

Wavefunctions are not arbitrary mathematical functions, but must satisfy certain simple conditions. For example, they must be continuous.

The most important condition is that the wavefunction must satisfy the time-dependent Schrodinger equation. With certain assumptions, time can be separated from the wavefunction, and what remains is a time-independent Schrodinger equation. We focus mainly on the time-independent Schrodinger equation.

In the application of these conditions to real systems, wavefunctions are found that do indeed yield information that agrees with experimental observations of these systems: **quantum mechanics predicts values that agree with experimentally determined measurements.** To the extent that quantum mechanics not only reproduces their success but also extends it, quantum mechanics is superior to their theories trying to describe the behaviour of subatomic particles. A proper understanding of quantum mechanics requires an understanding of the principles that it uses.

On the basis of above discussion we may conclude that quantum mechanics properly, describes the behaviour of matter, as determined by observation.

In short, quantum mechanics is the founding basics of all modern physics. Quantum mechanics forms the foundation upon which all of the chemistry is build No understanding of chemical systems is possible without knowing the basics of current theory of matter.

1. Evaluate the commutator [x, d/dx] operating on an arbitrary function $\psi(x)$

2. Find A^2 if A = x + (d/dx) operating on an arbitrary function $\psi(x)$

3. The operation of commutator [x, d/dx] on a function f(x) is equal to

   (a) 0 (b) f(x) (c) –f(x) (d) 0

4. The value of $[x, p_y]$, $[p_x, p_y]$ respectively are (arbitrary function state function)

   (a) 0, 0 (b) 0, not zero (c) not zero, 0 (d) not zero, not zero

5. Consider the statement

   (i) If A is linear operator then the value of $[A\ f(x)]^2 = A^2\ f(x)$

   (ii) The value of commutator $[x, (x, p_x^2)]$ is equal to 0.

   (iii) The multiplication of two linear operator is linear.

   The correct statements above are

   (a) i and iii (b) ii and iv (c) i, ii, iii (d) iii only

6. The value of the commutator $[x, [x, p_x]]$ is

   (a) $i\hbar x$ (b) $-i\hbar$ (c) $i\hbar$ (d) 0

7. Which of the following pairs of operator commute

   (a) x and (d/dx) (b) (d/dx) and $(d^2/dx^2) + 2$

   (c) $x^2(d/dx)$ and (d^2/dx^2) (d) x^3 and (d/dx)

8. The value of $[p_x, y]$ is equal to

   (a) $ih/2\pi$ (b) $-ih/2\pi$ (c) zero (d) can not determine

9. The angular momentum operator L_y is

   (a) $-\frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$ (b) $\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$ (c) $\frac{i\hbar}{2m}\frac{\partial}{\partial x}$ (d) $\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - y\frac{\partial}{\partial y}\right)$

10. Given the operator $a_+ = (1/\sqrt{2})(x + ip_x)$ and $a_- = (1/\sqrt{2})(x - ip_x)$ where x and p_x are the position and linear momentum operator, respectively the value of commutator $[a_+, a_-]$ is equal to

    (a) $ih/2\pi$ (b) $-ih/2\pi$ (c) $h/2\pi$ (d) $-h/2\pi$

11. The value of A^2 [if A = x – (d/dx)] is

    (a) $x^2 + (d^2/dx^2) - 2x(d/dx)$ (b) $(d^2/dx^2) - 2x(d/dx) + x^2 - 1$

    (c) $-(d^2/dx^2) - 2x(d/dx) + x^2 - 1$ (d) $x^2 + (d^2/dx^2) - 2x(d/dx) + 1$

12. The value of commutator (x^3, p_x) is equal to

(a) $-\frac{3h}{2\pi i}x^2$ (b) $-\frac{3ih}{2\pi}x^2$ (c) $\frac{hx}{2\pi i}$ (d) $\frac{h}{2\pi i}x^2$

13. The value of commutator $[x, p_x^2]$ is given by

(a) $2ih/\pi$ (b) $(h^2/2\pi^2)(d/dx)$ (c) $(h^2/4\pi^2)(d/dx)$ (d) $-(h^2/2\pi^2)(d/dx)$

14. The value of $[x, p_x]$ is equal to

(a) 0 (b) $\hbar/i$ (b) $-i\hbar$ (d) $-\hbar/i$

15. The commutator of kinetic energy operator T_x and the momentum operator p_x for the one dimensional case is

(a) $(ih/2\pi)$ (b) $(ih/2\pi)(d/dx)$ (c) 0 (d) $(ih/2\pi)x$

16. If [A, B] = 0 and [A, C] = 0 then which of the following necessary holds {A, B and C are operator}

(a) [B, C] = 0 (b) [A, BC] = 0 (c) [B, AC] = 0 (d) [C, AB] = 0

17. The commutator of x with Hamiltonian H, [x, H] is

(a) 0 (b) $i\hbar$ (c) $-(\hbar^2/2m)p_x$ (d) $(i\hbar/m)p_x$

18. Denote the commutator of two matrices A and B by [A, B] = AB – BA

The anti commutator {A, B} = AB + BA

If {A, B} = 0, we can write [A,BC] =

(a) –B[A, C] (b) B[A, C] (c) –B{A, C} (d) {A, C}B

19. The value of commutator $(1/x, p_x)$

(a) $-(h/2\pi i)x^{-2}$ (b) $(h/2\pi i)x^{-2}$ (c) $(h/2\pi i)x^2$ (d) $-(h/2\pi i)x^2$

20. THe value of commutator $[L_y, p_z]$

(a) $(ih/2\pi)p_y$ (b) $(ih/2\pi)p_z$ (c) 0 (d) $(ih/2\pi)p_x$