Quantum Chemistry

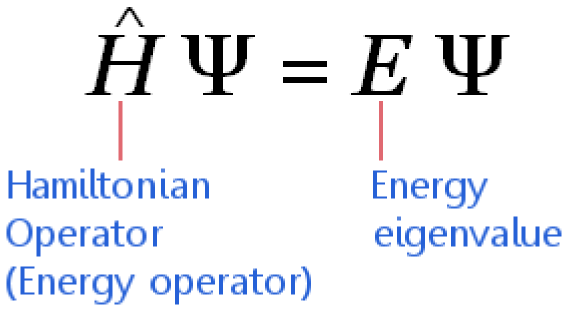
❖Postulates of Quantum Mechanics:

1. The properties of a quantum mechanical system are determined by a wave function Ψ(x,t) that depends upon the spatial coordinates of the system and time, x and t.
2. The wave function is interpreted as probability amplitude with the square of the wave function $\Psi^*(x,t)\Psi(x,t)$ interpreted at the probability density at time t. Because of the probabilistic interpretation, the wave function must be normalized.

$$\int \Psi^*(x,t)\Psi(x,t)\, d\tau = 1$$

$$where\ d\tau = dx.dy.dz = small\ volume\ element$$

3. The time - independent wavefunctions of a time – independent Hamiltonian are found by solving the time – independent Schrodinger equation.



4. If a system is described by the eigen function ψ of an operator A then the value measured for the observable property corresponding to A will always be the eigen value a, which can be calculated from the eigenvalue equation.

A ψ = a ψ

5. The average value of the observable corresponding to operator $\hat{A}$ is given by

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau}.$$

❖Wave – Particle Duality:

Wave-particle duality refers to the fundamental property of matter where, at one moment it appears like a wave, and yet at another moment it acts like a particle. $de - Broglie$ proposed that just as light shows both wave & particle aspects matter also has a dual nature, wave as well as showing particle like behavior.

From photoelectric effect, energy of photon, $E = h\gamma$

According to Einstein's theory, $E = mc^2$

Comparing two equations,

$$h\gamma = mc^2$$

$$Or, \frac{hc}{\lambda} = (mc).c$$

$$Or, \lambda = \frac{h}{mc} = \frac{h}{P}$$

$$where, P = mc = momentum$$

So, for a moving particle with mass (m) & velocity(v), we can write,

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$

➢ From the de-Broglie equation prove that $\lambda = h/\sqrt{2meV}$ where V is potential difference.

Let us consider an electron of charge e is accelerated by a potential difference V. Then its K.E. will be eV. Now if velocity of electron is v & $mass\ is\ m, then -$

$$E = \frac{1}{2}mv^2 = eV, Or, v = (\frac{2eV}{m})^{\frac{1}{2}}$$

According to de-Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{h}{m}(\frac{m}{2eV})^{\frac{1}{2}} = \frac{h}{\sqrt{2meV}}\ (proved)$$

❖ Normalization & probability of Wave Function:

Normalization and Probability

- The probability $P(x)\,dx$ of a particle being between x and $X + dx$ was given in the equation

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

- The probability of the particle being between x_1 and x_2 is given by

$$P = \int_{x_1}^{x_2} \Psi^*\Psi\,dx$$

- The wave function must also be normalized so that the probability of the particle being somewhere on the x axis is 1.

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

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<u>Necessity of Normalization</u>**:** The normalization of a wave function necessary otherwise a wave function can't be considered as an acceptable wave function.

<u>Significance:</u> From the normalization of wave function, we can find the probability of finding the particle within the given range.

- Normalize the function $Sinx$ in the intervals $(0, \pi)$

$$\int_0^{\pi} N^2\, Sin^2 x dx = 1$$

$$Or, \frac{N^2}{2}\int_0^{\pi} 2Sin^2 x dx = 1$$

$$Or, \frac{N^2}{2}\int_0^{\pi} (1 - Cos2x)dx = 1$$

$$Or, \frac{N^2}{2}\left[\left|x|_0^{\pi} - \frac{1}{2}\right| Sin2x|_0^{\pi}\right] = 1$$

$$Or, \frac{N^2}{2}\left(\pi - \frac{1}{2}\, Sin2\pi\right) = 1$$

$$Or, \frac{N^2}{2}(\pi - 0) = 1\ (since\ Sin2\pi = 0)$$

$$Or, N = \pm\sqrt{\frac{2}{\pi}}(Ans.)$$

- Normalize the function $Cos\frac{n\pi x}{a}$ in the intervals $(-a \le x \le +a)$

$$\int_{-a}^{+a} N^2\, Cos^2\frac{n\pi x}{a}dx = 1$$

$$Or, \frac{N^2}{2}\int_{-a}^{+a}(1 + Cos\frac{2n\pi x}{a})dx = 1$$

$$Or, \frac{N^2}{2}\left[\left|x|_{-a}^{+a} + \frac{a}{2n\pi}\right| Sin\frac{2n\pi x}{a}\,|\,_{-a}^{+a}\right] = 1$$

$$Or, \frac{N^2}{2}\left[\{a - (-a)\} + \frac{a}{2n\pi}(Sin\ 2n\pi + Sin\ 2n\pi)\right] = 1$$

$$Or, \frac{N^2}{2}\ \left[2a + \frac{a}{2n\pi}(0 + 0)\right] = 1$$

$$Or, N = \pm\sqrt{\frac{1}{a}}\ \ (Ans.)$$

- Normalize the function $\Psi(x) = NSin\frac{n\pi x}{a}$ in the intervals $(0 \le x \le a)$

$$\int_0^{a} N^2\, Sin^2\frac{n\pi x}{a}dx = 1$$

$$Or, \frac{N^2}{2}\int_0^{a}(1 - Cos\frac{2n\pi x}{a})dx = 1$$

$$Or, \frac{N^2}{2}\left[\left|x|_0^{a} - \frac{a}{2n\pi}\right| Sin\frac{2n\pi x}{a}\,|\,_0^{a}\right] = 1$$

$$Or, \frac{N^2}{2}\left[a - \frac{a}{2n\pi} Sin2n\pi\right] = 1$$

$$Or, \frac{N^2}{2}\ [a - 0] = 1\ \ (since\ Sin2n\pi = 0\ where\ n = 0, \pm1, \pm2\ etc)$$

$$Or, N = \pm\sqrt{\frac{2}{a}}\ \ (Ans.)$$

- Normalize the function $tanx$ in the intervals $\left(0 \le x \le \frac{\pi}{4}\right)$

$$\int_0^{\frac{\pi}{4}} N^2\ tan^2 x dx = 1$$

$$Or, N^2 \int_0^{\frac{\pi}{4}} (Sec^2 x - 1)dx = 1\quad (since\ Sec^2\theta = 1 + tan^2\theta)$$

$$Or, N^2 \left[\left| tanx|_0^{\frac{\pi}{4}} - \right| x|_0^{\frac{\pi}{4}}\right] = 1$$

$$Or, N^2 \left[(1 - 0) - \left(\frac{\pi}{4} - 0\right)\right] = 1$$

$$Or, N^2 \left(1 - \frac{\pi}{4}\right) = 1$$

$$Or, N = \pm\frac{2}{\sqrt{4 - \pi}} (Ans.)$$

- Normalize the function $e^{im\phi}(m\ is\ an\ integer)$ defined in the intervals $(0 \le \phi \le 2\pi)$

$$\int_0^{2\pi} (N\Psi).(N\Psi^*)\ dx = 1$$

$$\boldsymbol{Or}, N^2 \int_0^{2\pi} e^{im\phi}.e^{-im\phi} d\phi = 1$$

$$\boldsymbol{Or}, N^2 |\phi|_0^{2\pi} = 1$$

$$Or, N = \pm\sqrt{\frac{1}{2\pi}}$$

- Normalize the function $\sqrt{a^2 - x^2}$ in the interval $(0 \le x \le a)$

$$N^{\mathbf{2}} \int_{\mathbf{0}}^{a} (a^2 - x^2)dx = 1$$

$$Or, N^2\ [a^2 |x|_0^a - \left|\frac{x^3}{3}|_0^a\right| = 1$$

$$Or, N^2 \left(a^3 - \frac{a^3}{3}\right) = 1$$

$$Or, N^2.a^3.\frac{2}{3} = 1$$

$$Or, N = \pm\sqrt{\frac{3}{2a^3}}$$

❖ Operator:

An operator is a rule for transforming of given function into another function. For example:

$d/_{dx}$ is an operator which convert function $\sin x$ into $\cos x$,

$$\frac{d}{dx}(\sin x) = \cos x$$

Properties of operator:

i. The sum of two operators is given by,

$$(\hat{A} + \hat{B})f(x) = \hat{A}f(x) + \hat{B}f(x)$$

ii. The product of two operators is given by,

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

But $\hat{A}\,\hat{B}\,f(x)$ will be either equal to $\hat{B}\,\hat{A}\,f(x)$ or not. When $\hat{A}\,\hat{B}\,f(x) = \hat{B}\,\hat{A}\,f(x)$ then two operators are called commute to each other. When two operators are commute to each other then the corresponding commutator is given by as follows,

$$[\hat{A}, \hat{B}] = 0$$

iii. The square of an operator is given by,

$$\hat{A}^2\,f(x) = \hat{A}\,[\hat{A}\,f(x)]$$

iv. An operator $\hat{A}$ is called linear operator if

$$\hat{A}\,C\,f(x) = C\,\hat{A}\,f(x)$$

$$For\ example,\quad \frac{d}{dx}\,(2\sin x) = 2.\frac{d}{dx}(\sin x) = 2\cos x$$

$$So, \frac{d}{dx}\ is\ a\ linear\ operator.$$

➢ Classify the following operators as linear or non linear—

$$\frac{d^2}{dx^2}\,, (\,)^2\,, \int (\,)dx\,, exp.\,, (\,)^{\frac{1}{2}}, (\,)^*\,, \frac{d}{dx}$$

$(i)\,\frac{d^2}{dx^2}[cf(x)] = c\,\frac{d^2}{dx^2}[f(x)] = cf''(x), so\ it\ is\ linear\ operator.$

$(\boldsymbol{ii})[cf(x)]^2\ \neq c[f(x)]^2, so\ (\,)^2\ or\ SQR\ is\ non-linear\ operator.$

$(iii)\int [cf(x)]dx = c\int f(x)dx, so\ it\ is\ linear\ operator.$

$(iv)\,\exp[cf(x)] \neq c\,\exp[f(x)]\,, so\ it\ is\ non-linear\ operator.$

$(v)[cf(x)]^{\frac{1}{2}} \neq c[f(x)]^2, so\ SQRT\ is\ non-linear\ operator.$

$(vi)\ [cf(x)]^* \neq c[f(x)]^*, so\ it\ is\ non-linear\ operator.$

$(vii)\,\frac{d}{dx}[cf(x)] = c\,\frac{d}{dx}f(x), so\ it\ is\ linear\ operator.$

- Evaluate the result of the operator —

  $(i)\,\frac{d}{dx} + x$ &

  $(ii)\,\frac{d}{dx} - x$, *operating on the function* $(x^2 + 2x + 1)$

$(\boldsymbol{i})\left(\frac{d}{dx} + x\right)(x^2 + 2x + 1)$

$$= \frac{d}{dx}(x^2 + 2x + 1) + x(x^2 + 2x + 1)$$
$$= (2x + 2) + x^3 + 2x^2 + x = x^3 + 2x^{\mathbf{2}} + 3x + 2$$

$(\boldsymbol{ii})\ \left(\frac{d}{dx} - x\right)(x^2 + 2x + 1)$

$$= \frac{d}{dx}(x^2 + 2x + 1) - x(x^2 + 2x + 1)$$
$$= (2x + 2) - x^3 - 2x^2 - x = -(x^3 + 2x^{\mathbf{2}} - x - 2)$$

- Evaluate the result of the operator—

  $(i)\ x^2\frac{d^2}{dx^2}$ & $(ii)\,\frac{d^2}{dx^2}x^2$, *operating on the function* $(x^2 + 2x + 1)$

$(i)\ \left(x^2\frac{d^2}{dx^2}\right)(x^2 + 2x + 1)$

$$= x^2\frac{d}{dx}(2x + 2) = x^2\,.2 = 2x^2$$

$(ii)\left(\frac{d^2}{dx^2}x^2\right)(x^2 + 2x + 1)$

$$= \left(\frac{d^2}{dx^2}\right)(x^4 + 2x^3 + x^2\,)$$
$$= \frac{d}{dx}(4x^3 + 6x^2 + 2x)$$
$$= (12x^2 + 12x + 2) = 2(6x^2 + 6x + 1)$$

- *Given* $A = \frac{d}{dx}$ & $B = x^2$, *show* $(i)A^2f(x) \neq [Af(x)]^2$ & $(ii)\ AB\ f(x) \neq BAf(x)$

  This can be proved as follows –

$$(i)A^2f(x) = \frac{d}{dx}\,\frac{df}{dx} = \frac{d^2f}{dx^2}$$
$$[Af(x)]^2 = (\tfrac{df}{dx})^2 \neq \tfrac{d^2f}{dx^2}$$
$$(ii)AB\ f(x) = \frac{d}{dx}[x^2f(x)] = 2xf(x) + x^2\frac{df}{dx}$$
$$BAf(x) = x^2\frac{df}{dx} \neq AB\ f(x)$$