STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

Subject: Chemistry

Topic: Schrödinger's Time Independent Wave Equation

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Basic (time-dependent) Schrödinger Equation(BSE or TDSE)

The last postulate of wave mechanics is the new master equation of motion for a dynamical system. The evolution of the system is completely described by the Basic Schrödinger Equation. It is not a derivable equation, but constructed following the postulates of wave mechanics, by replacing the variables in the classical (Hamilton's) expression for total energy (kinetic + potential energy) by the relevant quantum mechanical operators. For a single particle (mass *m*) moving in one dimension,

$$\text{Hamilton's expression for total energy} \quad H = \frac{P_x^2}{2m} + v(x)$$

Quantum mechanical operator for P_x is $\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$

Quantum mechanical operator for position coordinate x is simply multiplication by x, $\hat{x} = x$. Replacing P_x with $-i\hbar\frac{\partial}{\partial x}$ and x with $\hat{x}$ in the expression of *H*, we get the Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + v(x)$

Another basic quantum mechanical operator is $\hat{E}$, the total energy operator, which is $i\hbar\frac{\partial}{\partial t}$. $\hat{E}$ and $\hat{H}$ are different operators. Schrödinger's postulate was that for an acceptable wavefunction $\psi(x,t)$,

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + v(x)\right]\psi = \hat{E}\psi = i\hbar\frac{\partial}{\partial t}\psi$$ **which is TDSE.**

Time-independent Schrödinger Equation

Now we'll discuss the time-independent Schrödinger Equation (TISE).

TDSE is a second order partial differential equation, for which we can have special solutions having separable space and the time parts as $\psi(x,t) = \phi(x)g(t)$

For these special solutions we can write:

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

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

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

$$\Rightarrow \hat{H}\,\phi(x)/\phi(x) = \frac{i\hbar}{g(t)}\frac{\partial}{\partial t}g(t) = E \quad \textbf{(a constant)}$$

Now we have two independent equations:

*** One equation involving only space coordinate:**

$$\hat{H}\frac{\phi(x)}{\phi(x)} = E$$

or,

$$\hat{H}\,\phi(x) = E\phi(x) \ldots\ldots\ldots(1)$$

This is nothing but the eigenvalue equation corresponding to the total energy of a system. This is called the Time-independent Schrödinger Equation (TISE). E **is the energy eigenvalue.**

Time-independent Average values for separable solutions

We have got the Time-independent Schrödinger Equation (TISE) from the space-dependent equation (equation 1). Another equation, depends only on time:

$$\frac{i\hbar}{g(t)}\frac{\partial}{\partial t}g(t) = E \ldots\ldots\ldots..(2)$$

Integrating this equation we get

$$\Rightarrow \int_0^{g(t)} \frac{dg(t)}{g(t)} = \frac{E}{i\hbar}\int_0^t dt$$

$$\Rightarrow \ln g(t) = \frac{Et}{i\hbar}$$

$$\Rightarrow g(t) = exp\frac{Et}{i\hbar}$$

$$g(t) = exp\frac{-iEt}{\hbar}$$

This complex exponential form of the time-dependent part of the special solution has an important implication. Expectation value of any operator (which does not involve time explicitly) will be independent of time.

$$\langle A\rangle = \frac{\int \psi^*\hat{A}\psi\,dx}{\int \psi^*\psi\,dx} = \frac{\int \phi^* e^{\frac{iEt}{\hbar}}\hat{A}\phi e^{-\frac{iEt}{\hbar}}\,dx}{\int \phi^* e^{\frac{iEt}{\hbar}}\phi e^{-\frac{iEt}{\hbar}}\,dx} = \frac{\int \phi^*\hat{A}\phi\,dx}{\int \phi^*\phi\,dx}$$

$$\langle A\rangle = \int \phi^*\hat{A}\phi\,dx \quad \text{(Independent of time)}$$