2.12.1 Solution of T.D.S.E

Since the T.D.S.E. expressed by equation (2-8) is a partial differential equation of second order, hence, the method of separating of variables can be used to solve such equation. Suppose, a solution of the form,

$$\psi(r,t)=\psi(r)\ \psi(t)$$

From which we have;

$$\frac{\partial\psi(r,t)}{\partial t}=\psi(r)\frac{\partial\psi(t)}{\partial t} \qquad \text{.................. (a)}$$

$$\nabla^2\psi(r,t)=\psi(t)\nabla^2\psi(r) \qquad \text{................ (b)}$$

Substitute of equations (a and b) in equation (2-8) we get;

$$\frac{-\hbar^2}{2m}\psi(t)\nabla^2\psi(r)+V(r)\psi(r)\ \psi(t)=i\hbar\psi(r)\frac{\partial\psi(t)}{\partial t}$$

Dividing by $\psi(r,t)$ we find;

$$i\hbar\frac{1}{\psi(t)}\cdot\frac{d\psi(t)}{dt}=\frac{-\hbar^2}{2m}\frac{\nabla^2\psi(r)}{\psi(r)}+V(r)$$

It is seen that; the left hand side is time depend while the right hand side is space depend. Thus, the equation become valid if and only if when each side being equal to the same constant. Assume this constant is E we can write that;

$$i\hbar\frac{1}{\psi(t)}\frac{d\psi(t)}{dt}=E \qquad \text{............. (2-26)}$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi(r)+V\psi(r)=E\psi(r) \qquad \text{............. (2-27)}$$

It seen that equation (2-26) is the T.D.S.E while equation (2-27) is the T.I.S.E. However, integration of equation (2-26) yield to;

$$\int_0^t\frac{d\psi(t)}{\psi(t)}=\frac{-i}{\hbar}E\int_0^t dt$$

$$\ln\psi(t)\Big|_0^t=-\frac{i}{\hbar}Et$$

$$\ln\frac{\psi(t)}{\psi(\circ)}=-\frac{i}{\hbar}Et$$

$$\psi(t)=\psi(\circ)\ e^{\frac{-i}{\hbar}Et}$$

So;

$$\psi(r,t)=\psi(r)\{\psi(\circ)\ e^{-\frac{i}{\hbar}Et}\}$$

Considering that; $\psi(\circ)=1$, we get;

$$\psi(r,t)=\psi(r)e^{\frac{-i}{\hbar}Et} \qquad \text{……..........(2-28)}$$

$$\int\psi^*(r,t)\psi(r,t)d\tau=\int\psi^*(r)\ e^{\frac{i}{\hbar}Et}\ \psi(r)\ e^{-\frac{i}{\hbar}Et}\ d\tau=1$$

Therfore;

$$\int\psi^*(r)\ \psi(r)\,d\tau=1$$

It is seen that, the probability is time independent for this case and due to that any system has a wave function given equation (2-28) is said to be in a stationary state.

2-13 Conservation of probability and probability current density

Since the total probability must be equal to unity. i.e.

$$P_t=\int\psi^*\psi\ d\tau=1$$

We can immediately decide that the probability is conserved. i.e. it is time independent and mathematically;

$$\frac{dp_t}{dt}=0$$

We can prve that in another way as follow;

$$\frac{dp_t}{dt}=\frac{d}{}\int\psi^*\psi\ d\tau$$
$$=\int(\frac{\partial\psi^*}{\partial t}\psi+\psi^*\frac{\partial\psi}{\partial t})\ d\tau$$

Using the equations;

$$i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi \longrightarrow \frac{\partial\psi}{\partial t}=\frac{-i}{\hbar}\hat{H}\psi$$

$$-i\hbar\frac{\partial\psi^*}{\partial t}=(\hat{H}\psi)^* \longrightarrow \frac{\partial\psi^*}{\partial t}=\frac{i}{\hbar}(\hat{H}\psi)^*$$

So;

$$\frac{dp_t}{dt} = \frac{i}{\hbar}\int [(\hat{H}\psi)^* \psi - \psi^* (\hat{H}\psi)] \; d\tau$$

Since $\hat{H}$ is Hermitian operator. i.e.

$$\int (\hat{H}\psi)^* \psi d\tau = \int \psi^* (\hat{H}\psi) \; d\tau$$

$$\frac{dp_t}{dt} = \frac{i}{\hbar}\int (\psi^* \hat{H}\psi - \psi^* \hat{H}\psi) \; d\tau$$

Therfore;

$$\frac{dp_t}{dt} = 0$$

Let us now consider the probability density;

$$p_d = \psi^* \psi$$

Derive this formula implicitly with respect to time we get;

$$\frac{\partial p_d}{\partial t} = \frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t}$$

$$\because \quad i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \quad , \; -i\hbar \frac{\partial \psi^*}{\partial t} = (\hat{H}\psi)^*$$

Thus;

$$\frac{\partial p_d}{\partial t} = \frac{i}{\hbar}\hat{H}^* \psi^* \psi + \psi^* (\frac{-i}{\hbar})\hat{H}\psi$$

$$= \frac{i}{\hbar}(\hat{H}^* \psi^* \psi - \psi^* \hat{H}\psi)$$

The form of , so; $\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(r)$ is given by; $\hat{H}$

$$= \frac{i}{\hbar}[\psi (\frac{-\hbar^2}{2m}\nabla^2 + V(r))\psi^* - \psi^* (\frac{-\hbar^2}{2m}\nabla^2 + V(r))\psi]$$

$$= \frac{-i\hbar}{2m}\psi \; \nabla^2 \psi^* + \frac{i}{\hbar}\psi \; V(r)\psi^* + \frac{i\hbar}{2m}\psi^* \nabla^2 \psi - \frac{i}{\hbar}\psi^* V(r)\psi$$

$$= \frac{-i\hbar}{2m}\psi \; \nabla^2 \psi^* + \frac{i\hbar}{2m}\psi^* \nabla^2 \psi$$

$$= \frac{\hbar}{2mi}\psi \; \nabla^2 \psi^* - \frac{\hbar}{2mi}\psi^* \nabla^2 \psi$$

$$= \frac{-\hbar}{2mi}(\psi^{*}\nabla^{2}\psi - \psi\ \nabla^{2}\psi^{*})$$

Since; $\psi^{*}\nabla^{2}\psi - \psi\ \nabla^{2}\psi^{*} = \vec{\nabla}\cdot(\psi^{*}\vec{\nabla}\psi - \psi\ \vec{\nabla}\psi^{*})$, thus;

$$\frac{dp_d}{dt} = -\vec{\nabla}.\frac{\hbar}{2mi}(\psi^{*}\vec{\nabla}\psi - \psi\ \vec{\nabla}\psi^{*})$$

$$\frac{dp_d}{dt} + \vec{\nabla}.\frac{\hbar}{2mi}(\psi^{*}\vec{\nabla}\psi - \psi\ \vec{\nabla}\psi^{*}) = 0$$

Define the **probability current density** to be;

$$\vec{S} = \frac{-i\hbar}{2m}(\psi^{*}\vec{\nabla}\psi - \psi\vec{\nabla}\psi^{*}) \qquad)$$

We get;

$$\frac{dP_t}{dt} + \vec{\nabla}.\vec{S} = 0 \qquad \text{………… (2-29)}$$

Equation (2-29) called the **continuity equation**, which is similar to that found in electromagnetism and thermodynamic. The physical meaning of equation (2-29) is that the time variation of the probability density is due to the flow of the probability current density.

2-14 Degeneracy

Degeneracy define as the case when there are more than one wave function corresponds to the same eigen value. In other word, the energy level is call degenerate when there are several wave functions corresponds to the value E_n. The degree of degeneracy for such a level is the number of these wave functions, which in general linearly independent functions.

Accordingly, when we have a degenerate energy level E_n of degree N, the corresponding wave functions are; ψ_n^1 , ψ_n^2 , ψ_n^3 , ... , ψ_n^N. The linear composition of these functions is also a wave function for this level. i.e.

$$\phi_n^p = \sum_{i=1}^{N} c_{pi}\,\psi_n^i \qquad 1 \le p \le N \qquad \text{…………… (2-30)}$$

The orthonormal condition for these functions are;

$$\int \{\psi_n^p\}^* \{\psi_m^q\} d\tau = \delta_{nm}\delta_{pq} \qquad \text{............... (2-31)}$$

2-13 Parity

Some functions have an important property, which they have an even or odd symmetry with respect to reflection in coordinates around the origin. This symmetrical property called **Parity**, and mathematically defined by;

$$\psi(x) = \begin{cases} \psi(-x) & \text{even parity} \\ \\ -\psi(-x) & \text{odd parity} \end{cases}$$

Example 1

$$y(x) = \sin x$$

$$y(-x) = \sin(-x)$$

$$y(-x) = -\sin x = -y(x)$$

Example 2

$$y(x) = \cos x$$

$$y(-x) = \cos(-x)$$

$$y(-x) = \cos x = y(x)$$

We can prove that, the solution of T.I.S.E for the case when degeneracy is absence and symmetrical potential ($V(-x) = V(x)$) has one of the following forms; either $\psi(-x) = \psi(x)$ or $\psi(-x) = -\psi(x)$, as follows;

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

Replace x by –x we get;

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

So $\psi(x)$ is also a solution for S.E. Assume that, there is only one solution for S.E., so;

$$\psi(-x) = r_n \psi(x) \qquad \text{............... (2-31)}$$

$$\psi(x) = r_n \psi(-x)$$

$$\psi(x) = r_n r_n \psi(x)$$

$$\psi(x) = r_n^2 \psi(x) \Longrightarrow r_n = \pm 1$$

Therefore;

$$\psi(-x) = \pm\psi(x)$$

For the case when r_n=+1 the function ψ is said to be even while for r_n =-1 the function ψ is said to be odd. Now we can consider that, $r_n = \pm 1$ is an eigen values corresponds to the operator $\hat{R}$ which we called **Reflection Operator**, and define as that operator when acts of a function reflects it around the origin, such that;

$$\hat{R}\psi_n(x) = r_n\psi_n(-x)$$
$$= \mp\psi_n(-x)$$
$$= \psi_n(x)$$

H.W: Using the last formula, prove that; $r_n = \mp 1$

<u>**Example**</u>

Let $\psi(x) = x^2$, $\hat{R}\psi(x) = (-x)^2 = x^2 \rightarrow r_n = 1$