$$\vec{\mu_s} = -\frac{e}{m_0}\mathbf{S}$$

where $-e$ is charge and m_0 the mass of electron, $\mathbf{S}$ the spin angular momentum of electron.

9.10 (PAULI) SPIN MATRICES FOR ELECTRON

Like orbital angular momentum operators L_x, L_y, L_z, the spin operators, S_x, S_y and S_z to be associated with the components of spin angular momentum satisfy the commutation relations

$$\left.\begin{aligned}[S_x, S_y] &= S_xS_y - S_yS_x = i\hbar\, S_z\\ [S_y, S_z] &= S_yS_z - S_zS_y = i\hbar\, S_x\\ [S_z, S_x] &= S_zS_x - S_xS_z = i\hbar\, S_y\end{aligned}\right] \quad ...(1)$$

If we consider the case with spin $= \frac{1}{2}$ *i.e.* electron, then according the Unlenbeck and Goudsmit hypothesis each of operators S_x, S_y and S_z must have just two eigen values $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Now we introduce new auxiliary operators σ_x, σ_y and σ_z such that

$$\left.\begin{aligned}S_x &= \tfrac{1}{2}\hbar\,\sigma_x\\ S_y &= \tfrac{1}{2}\hbar\,\sigma_y\\ S_z &= \tfrac{1}{2}\hbar\,\sigma_z\end{aligned}\right] \quad ...(2)$$

The following properties of σ's may be noted :

Since the eigen values of each S are to be just $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, the eigen values of each σ must be $+1$ and -1. Each of the operators σ_x^2, σ_y^2 and σ_z^2 must therefore have only the eigen value 1 and such operator is only unit operator, therefore

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1. \quad ...(3)$$

According to (2) and (3), the commutation rules satisfied by σ's must be :

$$\left.\begin{aligned}[\sigma_x, \sigma_y] &= \sigma_x\sigma_y - \sigma_y\sigma_x = 2i\,\sigma_z\\ [\sigma_y, \sigma_z] &= \sigma_y\sigma_z - \sigma_z\sigma_y = 2i\,\sigma_x\\ [\sigma_z, \sigma_x] &= \sigma_z\sigma_x - \sigma_x\sigma_z = 2i\,\sigma_y\end{aligned}\right\} \quad ...(4)$$

Now
$$\begin{aligned}2i\,(\sigma_x\sigma_y + \sigma_y\sigma_x) &= (2i\,\sigma_x)\,\sigma_y + \sigma_y\,(2i\,\sigma_x)\\ &= (\sigma_y\sigma_z - \sigma_z\sigma_y)\,\sigma_y + \sigma_y\,(\sigma_y\sigma_z - \sigma_z\sigma_y)\\ &= -\sigma_z + \sigma_z = 0.\end{aligned}$$

Hence $\sigma_x\sigma_y = -\sigma_y\sigma_x$, so that σ_x and σ_y anticommute.

Similarly any two of the σ's anticommute in pairs

$$\left.\begin{aligned}\sigma_x\sigma_y + \sigma_y\sigma_x &= 0\\ \sigma_y\sigma_z + \sigma_z\sigma_y &= 0\\ \sigma_z\sigma_x + \sigma_x\sigma_z &= 0\end{aligned}\right\} \quad ...(5)$$

Finally from (4) and (5) we have

$$\left.\begin{aligned}\sigma_x\sigma_y &= i\,\sigma_z, \quad ...(6a)\\ \sigma_y\sigma_z &= i\,\sigma_x, \quad ...(6b)\\ \sigma_z\sigma_x &= i\,\sigma_y, \quad ...(6c)\end{aligned}\right\}$$

Since each σ has two eigen values, so (2×2) matrix may be expected to fulfil the purpose and we begin by associating with σ_z, the simplest (2×2) matrix having the eigen values 1 and -1.

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ...(7)$$

Now we have

$$\sigma_x \sigma_z \equiv \begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} a & -b \\ c & -d \end{bmatrix} \quad ...(8)$$

and

$$\sigma_z \sigma_x \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} a & b \\ -c & -d \end{bmatrix} \quad ...(9)$$

But σ_x and σ_z anticommute, we must have

$$\sigma_x \sigma_z + \sigma_z \sigma_x = \begin{bmatrix} a & -b \\ c & -d \end{bmatrix} + \begin{bmatrix} a & b \\ -c & -d \end{bmatrix} = 0$$

i.e.

$$\begin{bmatrix} 2a & 0 \\ 0 & -2d \end{bmatrix} = 0.$$

This yields $a = d = 0$

so that every matrix that anticommutes with (7) as σ_x and σ_y do, accordingly σ_x must have the form

$$\sigma_x = \begin{bmatrix} 0 & b \\ c & 0 \end{bmatrix} \quad ...(10)$$

The eigen values of (10) are $\pm \sqrt{(bc)}$ so that if they are to be 1 and -1, we must set $bc = 1$. And simple possibility is to take $b = c = 1$, so $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$.

It then follows from (6c) that the matrix to be associated with σ_y is $\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$, and hence complete list of σ's becomes

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ...(11)$$

These matrices σ_x, σ_y and σ_z are called *Pauli spin matrices* associated with the components of spin angular momentum

$$S_x = \tfrac{1}{2}\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \; S_y = \tfrac{1}{2}\hbar \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \; S_z = \tfrac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad ...(12)$$

These are same as J_x, J_y and J_z in total angular momenta (Angular Momentum chapter) when $j = \frac{1}{2}$

Thus we have

$$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3$$

and

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

$$= \frac{\hbar^2}{4} (\sigma_x^2 + \sigma_y^2 + \sigma_z^2) = \tfrac{3}{4}\hbar^2.$$

9.11 COMMUTATION RELATIONS

Commutation relations satisfied by three components σ_x, σ_y and σ_z.

Let us take the commutation relation $[\sigma_x, \sigma_y]$.

We have

$$[\sigma_x, \sigma_y] = \sigma_x \sigma_y - \sigma_y \sigma_x,$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\therefore \quad [\sigma_x, \sigma_y] = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} - \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} - \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix} = \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} + \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$$

$$= 2\begin{bmatrix} i & 0 \\ 0 & -1 \end{bmatrix} = 2i\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = 2i\,\sigma_z$$

Similarly $[\sigma_y, \sigma_z] = \sigma_y\sigma_z - \sigma_z\sigma_y$

$$= \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} - \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix} - \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix} + \begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}$$

$$= 2\begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix} = 2i\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = 2i\,\sigma_x$$

and $[\sigma_z, \sigma_x] = \sigma_z\sigma_x - \sigma_x\sigma_z$

$$= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} - \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} - \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

$$= -2\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

$$= 2i^2\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$$

$$= 2i\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = 2i\,\sigma_y$$

Commutation relation satisfied by σ^2 and its components σ_x, σ_y and σ_z. We know that

$$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2.$$

Let us take $[\sigma^2, \sigma_x] = [\sigma_x^2 + \sigma_y^2 + \sigma_z^2, \sigma_x]$

$$= [\sigma_x^2, \sigma_x] + [\sigma_y^2, \sigma_x] + [\sigma_z^2, \sigma_x]$$

But $[\sigma_x^2, \sigma_x] = \sigma_x^3 - \sigma_x^3 = 0$

so $[\sigma^2, \sigma_x] = [\sigma_y^2, \sigma_x] + [\sigma_z^2, \sigma_x]$

$$= [\sigma_y\sigma_y, \sigma_x] + [\sigma_z\sigma_z, \sigma_x]$$

We know that

$$[ab, c] = a\,[b, c] + [a, c]\,b.$$

So
$$\begin{aligned}[\sigma^2, \sigma_x] &= \sigma_y\,[\sigma_y, \sigma_y] + [\sigma_y, \sigma_x]\,\sigma_y + \sigma_z\,[\sigma_z, \sigma_x] + [\sigma_z, \sigma_x]\,\sigma_z \\ &= \sigma_y\,(-2i\,\sigma_z) + (-2i\,\sigma_z)\,\sigma_y + \sigma_z\,(2i\,\sigma_y) + (2i\,\sigma_y)\,\sigma_z \\ &= -2i\,\sigma_y\,\sigma_z - 2i\,\sigma_z\sigma_y + 2i\,\sigma_z\,\sigma_y + 2i\,\sigma_y\,\sigma_z \\ &= 0.\end{aligned}$$

∴
$$[\sigma^2, \sigma_x] = 0.$$

Similarly,
$$[\sigma^2, \sigma_y] = 0$$
$$[\sigma^2\,\sigma_z] = 0.$$

so that σ^2 commutes with each component σ_x, σ_y and σ_z.

9.12 TWO COMPONENT WAVE FUNCTIONS

As Pauli operators σ_x, σ_y, σ_z are 2×2 matrices, therefore the Pauli operands must be two-component column matrix and since Pauli theory retains in essence the Schroedinger operators for dynamical variables having classical analogues, the components of these column symbols must be functions of (x, y, z) or (r, θ, ϕ) and so on as the case may be. Thus simplest Pauli operand ψ has the form

$$\psi = \begin{pmatrix} \psi_1\,(x, y, z) \\ \psi_2\,(x, y, z) \end{pmatrix} \qquad \text{...(1a)}$$

or in brief

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \qquad \text{...(1b)}$$

A Pauli wave-function ψ is said to be *well behaved* if at least one of its components is non-zero and if each of its non-zero components is well behaved in the sense of Schroedinger's theory. The complex conjugate of Pauli wave function corresponding to (1) is the row matrix

$$\psi^* = [\psi_1^*\ \ \psi_2^*] \qquad \text{...(2)}$$

so that

$$\psi^*\,\psi = [\psi_1^*\ \ \psi_2^*]\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \psi_1^*\,\psi_1 + \psi_2^*\,\psi_2 \qquad \text{...(3)}$$

The Pauli wave function is said to be normalised if

$$\int \psi^*\,\psi\,d\tau = 1 \qquad \text{...(4)}$$

or
$$\int (\psi_1^*\,\psi_1 + \psi_2^*\,\psi_2)\,d\tau = 1 \qquad \text{...(5)}$$

where the integration extends over the entire three-dimensional space.

Ex. 1. *If* σ_x, σ_y and σ_z *are Pauli spin matrices and* **A** *and* **B** *any constant vectors, show that*

$$(\vec{\sigma}\cdot A)\,(\vec{\sigma}\cdot B) = A \cdot B + i\,\vec{\sigma}\,(A \times B)$$

(Rohilkhand 1988; Meerut 1992, 81)

Solution. We have

$$\begin{aligned}(\vec{\sigma}\cdot A)\,(\vec{\sigma}\cdot B) &= (\sigma_x A_x + \sigma_y A_y + \sigma_z A_z)\,(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z) \\ &= \sigma_x^2 A_x B_x + \sigma_y^2 A_y B_y + \sigma_z^2 A_z B_z \\ &\quad + \sigma_x\sigma_y A_x B_y + \sigma_y\sigma_x A_y B_x + \sigma_y\sigma_z A_y B_z + \sigma_z\sigma_y A_z B_y + \sigma_x\sigma_z A_x B_z + \sigma_z\sigma_x A_z B_x\end{aligned}$$

Keeping in mind the following properties of Pauli spin matrices :

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \quad \text{(i.e., Squares of Pauli spin matrices are unity).}$$

$$\left.\begin{aligned} \text{and} \quad & \sigma_x\sigma_y = -\sigma_y\sigma_x = i\,\sigma_z \\ & \sigma_y\sigma_z = -\sigma_z\sigma_y = i\,\sigma_x \\ \text{and} \quad & \sigma_z\sigma_x = -\sigma_x\sigma_z = i\,\sigma_y \end{aligned}\right\} \text{ i.e. Pauli spin matrices anticommute in pairs}$$

we get

$$(\vec{\sigma}\cdot A)(\vec{\sigma}\cdot B) = A_xB_x + A_yB_y + A_zB_z + i\sigma_z(A_xB_y - A_yB_x) + i\sigma_x(A_yB_z - A_zB_y) + i\sigma_y(A_zB_x - A_xB_z)$$
$$= A \cdot B + i\,\vec{\sigma}\cdot(A \times B)$$

9 FURTHER PAULI OPERATORS

In order that any operator P may combine with the spin matrices or operators on two-component Pauli wave-function, it is first converted into a matrix form by multiplying with a 2×2 unit diagonal matrix, *i.e.*

$$\hat{P} = \hat{P}I = \hat{P}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \hat{P} & 0 \\ 0 & \hat{P} \end{pmatrix}$$

For example Pauli operators associated with x, p_x and L_z

$$x = \begin{bmatrix} \hat{x} & 0 \\ 0 & \hat{x} \end{bmatrix}, \; p_x = \begin{bmatrix} \hat{p}_x & 0 \\ 0 & \hat{p}_x \end{bmatrix}, \; L_z = \begin{bmatrix} \hat{L}_z & 0 \\ 0 & \hat{L}_z \end{bmatrix}$$

where the matrix elements are the appropriate Schroedinger operators. As the Schroedinger operators associated with $\hat{x}, \hat{p}_x, \hat{L}_z$ are $x, \frac{\hbar}{i}\frac{\partial}{\partial x}$ and $\frac{\hbar}{i}\frac{\partial}{\partial \phi}$ respectively, therefore the Pauli operators expressed by (2) take the following explicit forms :

$$x = \begin{bmatrix} \hat{x} & 0 \\ 0 & \hat{x} \end{bmatrix}; \; p_x = \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \end{bmatrix}, \; L_z = \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial \phi} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial \phi} \end{bmatrix} \quad ...(3)$$

Properties of Pauli Operators : As Pauli operators are 2×2 matrices, they obey standard laws of matrix algebra.

(1) *The Pauli operators are added together by the standard rule of matrix addition i.e.*

$$L_z + S_z = L_zI + \tfrac{1}{2}\hbar\,\sigma_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \tfrac{1}{2}\hbar\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
$$= \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial \phi} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial \phi} \end{bmatrix} + \begin{bmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{bmatrix}$$
$$= \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial \phi} + \frac{\hbar}{2} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial \phi} - \frac{\hbar}{2} \end{bmatrix} = \hbar\begin{bmatrix} -i\frac{\partial}{\partial \phi} + \frac{1}{2} & 0 \\ 0 & -i\frac{\partial}{\partial \phi} - \frac{1}{2} \end{bmatrix} \quad ...(4)$$

(2) *The Pauli operators are multiplied together by the standard rule of matrix multiplication e.g.*

$$p_xS_x = \begin{bmatrix} p_x & 0 \\ 0 & p_x \end{bmatrix}\tfrac{1}{2}\hbar\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \text{ since } S_x = \tfrac{1}{2}\hbar\,\sigma_x = \tfrac{1}{2}\hbar\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$= \frac{1}{2}\hbar\begin{bmatrix} 0 & p_x \\ p_x & 0 \end{bmatrix} = \frac{1}{2}\hbar\begin{bmatrix} 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \\ \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \end{bmatrix}$$

$$= \frac{1}{2}\frac{\hbar^2}{i}\begin{bmatrix} 0 & \frac{\partial}{\partial x} \\ \frac{\partial}{\partial x} & 0 \end{bmatrix} \qquad ...(5)$$

(3) *In the multiplication of Pauli matrices with non-commuting elements the order of the matrix factors and that of element factors must be preserved e.g.*

$$x\,p_x = \begin{bmatrix} x & 0 \\ 0 & x \end{bmatrix}\begin{bmatrix} p_x & 0 \\ 0 & p_x \end{bmatrix} = \begin{bmatrix} x & 0 \\ 0 & x \end{bmatrix}\begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \end{bmatrix}$$

$$= \frac{\hbar}{i}\begin{bmatrix} x\frac{\partial}{\partial x} & 0 \\ 0 & x\frac{\partial}{\partial x} \end{bmatrix}.$$

and

$$p_x x = \begin{bmatrix} p_x & 0 \\ 0 & p_x \end{bmatrix}\begin{bmatrix} x & 0 \\ 0 & x \end{bmatrix} = \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \end{bmatrix}\begin{bmatrix} x & 0 \\ 0 & x \end{bmatrix}$$

$$= \frac{\hbar}{i}\begin{bmatrix} \frac{\partial}{\partial x}x & 0 \\ 0 & \frac{\partial}{\partial x}x \end{bmatrix}. \qquad ...(7)$$

(4) *The Pauli operators, whatever they may be, operate on the two-component wave-function according to standard rule e.g.*

$$\sigma_x\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}\psi_2\\ \psi_1\end{pmatrix} \qquad ...(8)$$

$$\sigma_y\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}-i\psi_2\\ i\psi_1\end{pmatrix} \qquad ...(9)$$

$$\sigma_z\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}\psi_1\\ -\psi_2\end{pmatrix} \qquad ...(10)$$

Similarly

$$S_x\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\,\sigma_x\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}\psi_2\\ \psi_1\end{pmatrix}$$

$$S_y\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\,\sigma_y\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}-i\psi_2\\ i\psi_1\end{pmatrix} \qquad ...(11)$$

and

$$S_z\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\,\sigma_z\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}\psi_1\\ -\psi_2\end{pmatrix}$$

Also $$p_x \psi = \begin{pmatrix} p_x & 0 \\ 0 & p_x \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{\hbar}{i}\begin{pmatrix} \partial\psi_1/\partial x \\ \partial\psi_2/\partial x \end{pmatrix}$$

A Pauli operator can usually be written in various forms having different degree of explicitness. For example in the case of p_x, the alternative forms are

$$p_x, \begin{bmatrix} p_x & 0 \\ 0 & p_x \end{bmatrix}, \begin{bmatrix} \frac{\hbar}{i}\frac{\partial}{\partial x} & 0 \\ 0 & \frac{\hbar}{i}\frac{\partial}{\partial x} \end{bmatrix} \text{ or } \frac{\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial x} & 0 \\ 0 & \frac{\partial}{\partial x} \end{pmatrix} \quad ...(12)$$

Therefore any of the above forms may be substituted for another according to convenience.

9.14 PAULI EIGEN-VALUES AND EIGEN FUNCTIONS

In Pauli theory eigen-values and eigen functions are defined in the standard way. If $\hat{P}$ is an operator, ψ is a well-behaved operand and λ is a number and if they satisfy the equation

$$\hat{P}\psi = \lambda\psi \quad ...(1)$$

Then ψ is said to be an *eigen function* of operator P, λ is said to be *eigen value* of $\hat{P}$ in the state ψ. The eigen function ψ and the eigen value λ are said to belong to each other.

If $\hat{P}$ is a matrix involving numerical elements as σ_x, σ_y and σ_z, then eqn. (1) is an ordinary matrix eigen value equation and the eigen-values and eigen functions of $\hat{P}$ are computed by the usual matrix methods, except, that ψ_1 and ψ_2 are now allowed to be well behaved functions of (x, y, z).

If $\hat{P}$ is a differential operator such as p_x, p_y, p_z, then

$$\hat{P}\psi = \lambda\psi \text{ i.e. } \begin{pmatrix} \hat{P} & 0 \\ 0 & \hat{P} \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \lambda\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

i.e. $$\begin{pmatrix} \hat{P} & \psi_1 \\ \hat{P} & \psi_2 \end{pmatrix} = \begin{pmatrix} \lambda & \psi_1 \\ \lambda & \psi_2 \end{pmatrix} \quad ...(2)$$

This splits up into the following pair of simultaneous equations

$$\hat{P}\psi_1 = \lambda\psi_1$$
$$\hat{P}\psi_2 = \lambda\psi_2 \quad ...(3)$$

This set of equations does not possess dependent variables in common and each equation of the set just represents the Schroedinger equation for the operator $\hat{P}$. Thus it follows that *the Pauli theory and the Schroedinger theory agree for possible values of dynamical variables such as position, linear momenta and orbital angular momenta.*

If the Hamiltonian of a system depends on time t, then every Pauli wave-function satisfies the equation

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \quad ...(4)$$

where H is the pauli operator associated with the Hamiltonian *i.e.* $$H = \begin{pmatrix} H & 0 \\ 0 & H \end{pmatrix} \text{ and } \frac{\partial \psi}{\partial t} = \begin{pmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \end{pmatrix}.$$

∴ Equation (4) takes the form

$$\begin{pmatrix} H & 0 \\ 0 & H \end{pmatrix}\begin{pmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \end{pmatrix} = i\hbar\begin{pmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \end{pmatrix} \quad ...(5)$$

Equation (4) is identical with time dependent Schroedinger equation.

In Pauli's theory the expectation values of a dynamical variable p for a state ψ is taken to be

$$<p> = \frac{\int \psi^* \hat{p}\psi \, d\tau}{\int \psi^*\psi \, d\tau} \quad ...(6)$$

where $\hat{p}$ in the numerator is the Pauli operator associated with the dynamical variable p and the integral extends over all space. Obviously Pauli expectation formula is formally identical with Schroedinger expectation formula.

9.15 ELECTRON SPIN FUNCTIONS

In Pauli theory the eigen value equation of operator σ_x is

$$\sigma_x \psi = \alpha\psi \quad ...(1)$$

where α is the eigen value of σ_x in state ψ

As $$\psi = \begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} \text{ and } \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

Equation (1) takes the form

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \alpha\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

or $$\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \begin{bmatrix} \alpha\psi_1 \\ \alpha\psi_2 \end{bmatrix} \quad ...(2)$$

This equation is equivalent to two separate equations

$$\psi_1 = \alpha\psi_1 \quad ...(3a)$$

$$\psi_2 = \alpha\psi_2 \quad ...(3b)$$

From (3a) and (3b), we have

$$\alpha^2 = 1 \text{ or } \alpha = \pm 1.$$

A convenient set of orthonormal one-particle spin functions is provided by the normalized eigen functions of L^2 and L_z matrices. In this case the eigen functions are $(2S+1)$ row, one column matrices. For electron $S = \frac{1}{2}$.

So eigen function matrices for electron have

$(2 \times \frac{1}{2} + 1)$ row and one column.

or 2 rows and one column.

The respective normalised wave-functions are

$$\psi_x(\tfrac{1}{2}) = \frac{1}{\sqrt{2}}\begin{Bmatrix} 1 \\ 1 \end{Bmatrix} \text{ and } \psi_x(-\tfrac{1}{2}) = \frac{1}{\sqrt{2}}\begin{Bmatrix} 1 \\ -1 \end{Bmatrix}. \quad ...(4)$$

In a similar way,

$$\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix} = \beta\begin{bmatrix} \psi_1 \\ \psi_2 \end{bmatrix}$$

so that

$$-i\psi_2 = \beta\psi_1,$$

$$i\psi_1 = \beta\psi_2,$$

i.e.

$$\beta^2 = 1, \beta = \pm 1.$$

So the normalised wave functions are

$$\psi_y(\tfrac{1}{2}) = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} \text{ and } \psi_y(-\tfrac{1}{2}) = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix} \quad ...(5)$$

Similarly normalised wave-functions for z-component are

$$\psi_z(+\tfrac{1}{2}) = \begin{bmatrix} 1 \\ 0 \end{bmatrix};\ \psi_z(-\tfrac{1}{2}) = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad ...(6)$$

9.16 SPIN MATRICES AND EIGEN FUNCTIONS (GENERAL CASE)

Let the identical particles be represented by 1, 2, ... n. The spin co-ordinates differ from the space co-ordinates in that they take on only $(2s+1)$ values for a particle of spin s, instead of the infinite number of values that are taken by each space co-ordinate. The spin wave function of a particle is completely determined by the $(2s+1)$ numbers.

A set of orthonormal one particle spin functions is given by the normalized eigen functions of the total angular momentum J and its component J_z matrices. The eigen functions are $(2s+1)$ row, one column that have zero in all positions except one. For example if $s = \frac{3}{2}$, the four spin eigen functions are easily seen to be

$$\psi(\tfrac{3}{2}) = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \psi(\tfrac{1}{2}) = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \psi(-\tfrac{1}{2}) = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \psi(-\tfrac{3}{2}) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \quad ...(1)$$

and the corresponding eigen values of S_z are $\frac{1}{2}\hbar, \frac{3}{2}\hbar\ \ \frac{1}{2}\hbar$ and $-\frac{3}{2}\hbar$ respectively.

The orthonormality is demonstrated by multiplying the hermitian adjoint of one spin function into itself or another function, *i.e.*

$$[0\,1\,0\,0]\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = 1,\ [0\,1\,0\,0]\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = 0, \text{ etc.}$$

9.17 STATISTICAL WEIGHT OR A PRIORI PRABABILITY

In some cases there is only one eigen function corresponding to each eigen value. In such cases the eigen state or the energy level is said to be *non-degenerate.* However in some other cases there are a number of eigen functions corresponding to a single eigen value. In these cases the eigen state is said to be *degenerate.* In the degenerate cases ***the number of eigen states for the particular energy state or level is called the degeneracy of that state.*** Thus if g_i is the degeneracy for the eigen value ε_i, then g_i is the number of eigen states for the ith eigen state having energy ε_i. Obviously for a non degenerate case $g_i = 1$. An important postulate of quantum statistics concerning the probability of eigen-states is that ***every eigen state possesses an equal a priori probability.*** According to this postulate the eigen state in