Date :
Page No :

unit - V.

Relativistic Wave equation.

The Klevin - Garden equation - charge and Current densities in four vectors - K.G equation in electromagnetic field - The Dirac relativistic equation, The Dirac ~~magnetic~~ matrices - free particle solution - Meaning of negative energy states - Electromagnetic potential : magnetic moment of the electron - Existance of electron spin - spin orbit energy.

Klein - Gorden equation ::

The relativistic relation between total energy, rest mass energy and momentum of a particle is given by,

$$E^2 = p^2c^2 + m^2c^4 \rightarrow (1)$$

Where,

m is the rest mass of the particle.

Replacing E and P by the respective operators we get the operator equation.

$$E = i\hbar \frac{\partial}{\partial t} \text{ and}$$

$$P = -i\hbar \nabla$$

$$\left(i\hbar \frac{\partial}{\partial t}\right)^2 = (-i\hbar\nabla)^2 c^2 + m^2c^4$$

$$-\hbar^2 \frac{\partial^2}{\partial t^2} = -\hbar^2 \nabla^2 c^2 + m^2c^4.$$

$$-\hbar^2 \frac{\partial^2}{\partial t^2} = -\hbar^2 c^2 \nabla^2 + m^2c^4 \rightarrow (2)$$

Allowing this operator equation is operate on the wave function $\psi(r,t)$.

$$-\hbar^2 \frac{\partial^2 \psi(r,t)}{\partial t^2} = -\hbar^2 c^2 \nabla^2 \psi(r,t) + m^2c^4\psi(r,t) \rightarrow (3)$$

This equation is called Klevin - Gorden equation (or) Schrodinger's relativistic equation.

Rearranging eqn (3), we get.

$$\hbar^2c^2\nabla^2\psi - \hbar^2 \frac{\partial^2\psi}{\partial t^2} - m^2c^4\psi = 0$$

Divide by $\hbar^2 c^2$

$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi = 0 \rightarrow (4)$$

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi - \frac{m^2c^2}{\hbar^2}\psi = 0$$

$$\Box^2\psi - \frac{m^2c^2}{\hbar^2}\psi = 0 \rightarrow (5)$$

Where

$$\Box^2 = \left(\nabla^2 - \frac{1}{c^2}\cdot\frac{\partial^2}{\partial t^2}\right) \rightarrow (6)$$

$\Box^2$ is a D-Alembertian operator which is relativistically invariant

Eqn (5) can be written as,

$$\left(\Box^2 - \frac{m^2c^2}{\hbar^2}\right)\psi = 0 \rightarrow (7)$$

This is the Klein - Gorden equation for a free particle.

Interpretation of klein - Gorden equation (or) Charge and Current density :-

Klein - Gorden equation for a free particle is,

$$\left(\Box^2 - \frac{m^2c^2}{\hbar^2}\right)\psi = 0$$

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\psi = 0$$

$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi = 0 \rightarrow (1)$$

Taking Complex Conjugate of above equation we get.

$$\nabla^2\psi^* - \frac{1}{c^2}\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi^* = 0 \rightarrow (2)$$

multiple ψ^* on equation (1) becomes

$$\psi^*\nabla^2\psi - \frac{1}{c^2}\psi^*\frac{\partial^2\psi}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi^*\psi = 0 \rightarrow (3)$$

multiple ψ on eqn (2),

$$\psi\nabla^2\psi^* - \frac{1}{c^2}\psi\frac{\partial^2\psi^*}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\psi\psi^* = 0 \rightarrow (4)$$

(3) − (4),

$$\psi^* \nabla^2\psi - \frac{1}{c^2}\psi^*\frac{\partial^2\psi}{\partial t^2} - \cancel{\frac{m^2c^2}{\hbar^2}\psi^*\psi} - \psi\nabla^2\psi^* +$$

$$\frac{1}{c^2}\psi\frac{\partial^2\psi^*}{\partial t^2} + \cancel{\frac{m^2c^2}{\hbar^2}\psi\psi^*} = 0$$

$$\psi^*\nabla^2\psi - \frac{1}{c^2}\psi^*\frac{\partial^2\psi}{\partial t^2} - \psi\nabla^2\psi^* + \frac{1}{c^2}\psi\frac{\partial^2\psi^*}{\partial t^2} = 0.$$

$$\psi^*\nabla(\nabla\psi) - \frac{1}{c^2}\psi^*\frac{\partial}{\partial t}\left(\frac{\partial\psi}{\partial t}\right) - \psi\nabla(\nabla\psi^*) + \frac{1}{c^2}\psi\frac{\partial}{\partial t}\frac{\partial\psi^*}{\partial t} = 0$$

$$\nabla(\psi^*\nabla\psi - \psi\nabla\psi^*) - \frac{1}{c^2}\frac{\partial}{\partial t}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right) = 0$$

multiply by $\frac{\hbar}{2im}$

$$\nabla\left[\frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*)\right] - \frac{\hbar}{2imc^2}\frac{\partial}{\partial t}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right) = 0 \rightarrow (5)$$

Sub,

$$S(r,t) = \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) \rightarrow (6)$$

$$P(r,t) = \frac{\hbar}{2imc^2}\left(\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right) \rightarrow (7)$$

From eqn (6) and (7) sub in eqn (5),

$$\nabla S(r,t) - \frac{\partial}{\partial t}(-P(r,t)) = 0$$

(or)

$$\nabla \cdot S(r,t) + \frac{\partial}{\partial t}P(r,t) = 0 \rightarrow (8)$$

This equation is known as equation for Continuity

The Current density expression $S(r,t)$ as same form as a non-relativistic case, But the expression $P(r,t)$ indicates that cannot be interperated its position probability density due to the following ~~[illegible]~~ reason

Expression $P(r,t)$ may be expressed as

$$P(r,t) = \frac{\hbar}{2imc^2}\left[\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right]$$

$i\hbar\frac{\partial\psi}{\partial t} = E\psi$

$$= \frac{1}{2mc^2}\left[(-i\hbar)\psi\frac{\partial\psi^*}{\partial t} - (-i\hbar)\psi^*\frac{\partial\psi}{\partial t}\right]$$

$-i\hbar\frac{\partial\psi^*}{\partial t} = E\psi^*$

$\frac{-1}{2mc^2}\left[-i\hbar\psi\frac{\partial\psi^*}{\partial t} + i\hbar\psi^*\frac{\partial\psi}{\partial t}\right]$

$$= \frac{1}{2mc^2}\left[E\psi^*\psi + \psi^* E\psi\right]$$

$\frac{1}{2mc^2}\left[i\hbar\frac{\partial\psi^*}{\partial t}\psi + i\hbar\frac{\partial\psi}{\partial t}\psi^*\right]$

$$= \frac{1}{2mc^2}\left[2E\psi^*\psi\right]$$

$$P(r,t) = \frac{E}{mc^2}\psi^*\psi \rightarrow (9)$$

Here,

$$E = \pm(p^2c^2 + m^2c^4)^{1/2}$$

From this expression we note that the energy of the particle can be either positive (or) negative that it follows the expression for $P(r,t)$ is not definitely positive and hence it cannot be regarded as conventional position probability density.

Klein-Gordon equation in an electromagnetic field (or) Non-relativistic schrodinger equation for a particle of energy E in electromagnetic field:

An electromagnetic field can be represented by a vector potential A and a scalar potential ϕ. These potential form a four vector A_μ, whose components are $A_1, A_2, A_3, A_4 = i\phi$ and momentum energy four vector ϕ_μ having components

$$P_1, P_2, P_3, P_4 = \frac{iE}{c}$$

Therefore the potentials A and E should be included in Klevin-Gorden equation with momentum and energy.

If e is the charge on the particle, then the non-relativistic expression p and E are replaced by,

$$\left.\begin{aligned} P &= P - \frac{eA}{c} \\ E &= E - e\phi \end{aligned}\right\} \rightarrow (1)$$

So the relativistic expression of a particle of charge 'e' in electromagnetic field becomes.

$$E^2 = p^2c^2 + m^2c^4$$

$$(E - e\phi)^2 = \left(P - \frac{eA}{c}\right)^2 c^2 + m^2c^4$$

$$(E - e\phi)^2 = \left(\frac{cP - eA}{c}\right)^2 c^2 + m^2c^4$$

$$(E - e\phi)^2 \psi = [(cp - eA)^2 + m^2c^4]\psi \rightarrow (2)$$

Replacing the operators E and p i,e)

$$E = i\hbar\frac{\partial}{\partial t}$$

$$P = -i\hbar\nabla$$

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2\psi = \left[[(-i\hbar\nabla)c - eA]^2 + m^2c^4\right]\psi \rightarrow (3)$$

Now we take, L.H.S of equation (3),

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2\psi = \left[-\hbar^2\frac{\partial^2}{\partial t^2} - i\hbar e\frac{\partial\phi}{\partial t} - 2i\hbar e\phi\frac{\partial}{\partial t} + e^2\phi^2\right]\psi$$

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi\right)^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial t^2} - i\hbar\frac{\partial\phi}{\partial t}\psi - 2i\hbar e\phi\frac{\partial\psi}{\partial t} + e^2\phi^2\psi \rightarrow (4)$$

Then we take, R.H.S of equation (3)

$$(-i\hbar\nabla c - eA)^2\psi = [-\hbar^2\nabla^2c^2 + e^2A^2 - i\hbar ce\nabla\cdot A - i\hbar ceA\cdot\nabla]\psi$$

$$[(-i\hbar\nabla\cdot c - eA)^2 + m^2c^4]\psi = \left[[-\hbar^2\nabla^2c^2\psi + e^2A^2\psi - i\hbar ce\nabla(A\psi) - i\hbar ceA\cdot\nabla\psi] + m^2c^4\psi\right] \rightarrow (5)$$

Sub eqn (4) and (5) in eqn (3), we get,

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} - i\hbar e \frac{\partial \phi}{\partial t}\psi - 2i\hbar e\phi \frac{\partial \psi}{\partial t} + e^2\phi^2\psi =$$

$$-\hbar^2\nabla^2 c^2\psi + e^2A^2\psi - i\hbar c e \nabla\cdot(A\psi) - i\hbar c e A\cdot\nabla\psi + m^2c^4\psi \rightarrow (6)$$

To find the connection between eqn (6) and non-relativistic equation. Let us used the following wave function

$$\psi(r,t) = \psi'(r,t)\, e^{-imc^2t/\hbar} \rightarrow (7).$$

$$\frac{\partial \psi}{\partial t} = \frac{\partial \psi'}{\partial t} e^{-imc^2t/\hbar} + \left(-\frac{imc^2}{\hbar}\right) e^{-imc^2t/\hbar}\psi'$$

$$\frac{\partial \psi}{\partial t} = \left[\frac{\partial \psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right] e^{-imc^2t/\hbar} \rightarrow (8)$$

$$\frac{\partial^2 \psi}{\partial t^2} = \frac{\partial^2 \psi'}{\partial t^2} e^{-imc^2t/\hbar} + \frac{\partial \psi'}{\partial t} e^{-imc^2t/\hbar}\left(-\frac{imc^2}{\hbar}\right) + \left(-\frac{imc^2}{\hbar}\right)\frac{\partial \psi'}{\partial t} e^{-imc^2t/\hbar} + \left(-\frac{imc^2}{\hbar}\right)\psi' e^{-imc^2t/\hbar}\left(-\frac{imc^2}{\hbar}\right)$$

$$\frac{\partial^2 \psi}{\partial t^2} = \left[\frac{\partial^2 \psi'}{\partial t^2} - \frac{2imc^2}{\hbar}\frac{\partial \psi'}{\partial t} - \frac{m^2c^4}{\hbar^2}\psi'\right] e^{-imc^2t/\hbar} \rightarrow (9)$$

Sub eqn (7), (8) and (9) in (6), we get.

$$-\hbar^2\left(\frac{\partial^2 \psi'}{\partial t^2} - \frac{2imc^2}{\hbar}\frac{\partial \psi'}{\partial t} - \frac{m^2c^4}{\hbar^2}\psi'\right) e^{-imc^2t/\hbar} - i\hbar e \frac{\partial \phi}{\partial t}\psi' e^{-imc^2t/\hbar} - 2i\hbar e\phi\left(\frac{\partial \psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right) e^{-imc^2t/\hbar} + e^2\phi^2\psi' e^{-imc^2t/\hbar}$$

$$= \left[-\hbar^2\nabla^2c^2\psi' + e^2A^2\psi' - i\hbar c e \nabla A\cdot\psi' - i\hbar c e A\cdot\nabla\psi' + m^2c^4\psi'\right] e^{-imc^2t/\hbar}.$$

$$\left[-\hbar^2\left(\frac{\partial^2 \psi'}{\partial t^2} - \frac{2imc^2}{\hbar}\frac{\partial \psi'}{\partial t} - \frac{m^2c^4\psi'}{\hbar^2}\right) - i\hbar e\frac{\partial \phi}{\partial t}\psi' - 2i\hbar e\phi\left(\frac{\partial \psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right)\right] e^{-imc^2t/\hbar} = \left[\hbar^2\nabla^2c^2\psi' + e^2A^2\psi' - i\hbar c e\nabla A\psi' - i\hbar c e A\cdot\nabla\psi' + m^2c^4\psi'\right] e^{-imc^2t/\hbar}$$

(or)

$$\left[-\frac{\partial^2\psi'}{\partial t^2}\hbar^2 + \frac{2imc^2\hbar^2}{\hbar}\frac{\partial\psi'}{\partial t} + \cancel{\frac{m^2c^4\hbar^2}{\hbar^2}\psi'} - i\hbar e\frac{\partial\phi}{\partial t}\psi' - 2i\hbar e\phi\frac{\partial\psi'}{\partial t} + \frac{2i\hbar e\phi imc^2}{\hbar}\psi'\right]$$

$$e^{-imc^2t/\hbar} = \left[-\hbar^2\nabla^2c^2\psi' + e^2A^2\psi' - i\hbar ce\nabla A\psi' - i\hbar ceA\cdot\nabla\psi' + m^2c^4\psi'\right]e^{-imc^2t/\hbar}$$

Canceling out common factor $e^{-imc^2t/\hbar}$ and $m^2c^4\psi'$ on both sides and also dividing through out $2mc^2$, we get

$$\left[-\frac{\partial^2\psi'}{\partial t^2}\frac{\hbar^2}{2mc^2} + \frac{2imc^2\hbar}{2mc^2}\frac{\partial\psi'}{\partial t} - \frac{i\hbar e}{2mc^2}\frac{\partial\phi}{\partial t}\psi' - \frac{2i\hbar e\phi}{2mc^2}\frac{\partial\psi'}{\partial t} + \frac{2i^2e\phi mc^2}{2mc^2}\psi'\right]$$

$$= \left[-\frac{\hbar^2\nabla^2c^2\psi'}{2mc^2} + \frac{e^2A^2\psi'}{2mc^2} - \frac{i\hbar ce\nabla A\psi'}{2mc^2} - \frac{i\hbar ceA\nabla\psi'}{2mc^2}\right]$$

$$-\frac{\partial^2\psi'}{\partial t^2}\frac{\hbar^2}{2mc^2} + i\hbar\frac{\partial\psi'}{\partial t} - \frac{i\hbar e}{2mc^2}\frac{\partial\phi}{\partial t}\psi' - \frac{i\hbar e\phi}{mc^2}\frac{\partial\psi'}{\partial t} - e\phi\psi' =$$

$$\left[-\frac{\hbar^2\nabla^2\psi'}{2m} + \frac{e^2A^2\psi'}{2mc^2} - \frac{i\hbar e\nabla A\psi'}{2m} - \frac{i\hbar eA\nabla\psi'}{2mc}\right]$$

We know that the rest energy $mc^2 >$ non-relativistic energy 'E' and $mc^2 >> e\phi$ we may neglet the terms of order $\frac{1}{2mc^2}$ and $\frac{1}{2mc^2}$

$$i\hbar\frac{\partial\psi'}{\partial t} - e\phi\psi' = -\frac{\hbar^2\nabla^2\psi'}{2m} + \frac{e^2A^2\psi'}{2mc^2} - \frac{i\hbar e\nabla A\psi'}{2m} - \frac{i\hbar eA\nabla\psi'}{2mc}$$

$$i\hbar\frac{\partial\psi'}{\partial t} = \left[-\frac{\hbar^2\nabla^2}{2m} + \frac{e^2A^2}{2mc^2} - \frac{i\hbar e\nabla A}{2m} - \frac{i\hbar eA\nabla}{2mc} + e\phi\right]\psi'$$

This equation is a non-relativistic schrodinger equation for a particle of charge E in electromagnetic field..

$e^{-imc^2t/\hbar}$

$\psi(r,t) = \psi'(r,t)$ e

$-imc^2t/\hbar$

$imc^2t/\hbar$

Dirac - Relativistic equation:

In 1962, Dirac's formulated an equation to avoid some difficulty arising in Klein-Gordan equation on the basis of Lorentz invariant.

Dirac's approach the problem finding a relativistic wave equation of the form

$$H\psi = E\psi$$

$$H\psi(r,t) = +i\hbar \frac{\partial \psi}{\partial t}(r,t) \rightarrow (1).$$

The Hamiltonian for a free particle

$$H = c\alpha \cdot p + \beta mc^2 \rightarrow (2)$$

Sub H value in equation (1), we get.

$$[c\alpha \cdot p + \beta mc^2]\psi(r,t) = i\hbar \frac{\partial \psi}{\partial t}(r,t)$$

Sub operator for P, i.e

$$p = -i\hbar\nabla$$

$$[c\alpha \cdot (-i\hbar\nabla) + \beta mc^2]\psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t}$$

Rearrange the equation

$$\left[i\hbar \frac{\partial}{\partial t} + c\alpha i\hbar\nabla - \beta mc^2\right]\psi(r,t) = 0 \rightarrow (4)$$

Eqn (4) represents a Dirac-relativistic equation for a free particle

From the above equation it is clear that no term in the Hamiltonian that depends upon the space and time co-ordinate

Consequently α and β are independent of r, t, P and E and hence commutate with all of them

For simplicity writing again $i\hbar\frac{\partial}{\partial t} = E$ and $-i\hbar\nabla = p$ in eqn (4), we get

$$[E - c\alpha \cdot p - \beta mc^2]\psi(r,t) = 0$$

(or)

$$[E - (c\alpha p + \beta mc^2)]\psi(r,t) = 0 \rightarrow (5)$$

multiply by $[E + (c\alpha \cdot P + \beta mc^2)]$,

$$[E - (c\alpha \cdot P + \beta mc^2)][E + (c\alpha \cdot P + \beta mc^2)]\psi = 0$$

$(a+b)^2 = a^2 + b^2 + 2ab$

$$[E^2 - (c\alpha \cdot P + \beta mc^2)^2]\psi = 0$$

$$[E^2 - c^2(\alpha \cdot p)^2 - \beta^2 m^2 c^4 - c(\alpha \cdot P)\beta mc^2 - c(\alpha \cdot p)\beta mc^2]\psi = 0 \rightarrow (6)$$

We put,

$$\alpha = i\alpha_x + j\alpha_y + k\alpha_z.$$

$$P = iP_x + jP_y + kP_z$$

$$(\alpha \cdot P) = \alpha_x P_x + \alpha_y P_y + \alpha_z P_z$$

Therefore, eqn (6) becomes

$$[E^2 - c^2(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z)^2 - \beta mc^3(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z) - \beta mc^3(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z) - \beta^2 m^2 c^4]\psi = 0 \rightarrow$$

$(a+b+c)^2 = a^2 + b^2 + c^2 + 2ab + 2bc + 2ca$

$$[E^2 - c^2(\alpha_x^2 P_x^2 + \alpha_y^2 P_y^2 + \alpha_z^2 P_z^2 + 2\alpha_x P_x \alpha_y P_y + 2\alpha_y P_y \alpha_z P_z + 2\alpha_z P_z \alpha_x P_x) - mc^3(\alpha_x P_x \beta + \alpha_y P_y \beta + \alpha_z P_z \beta) - mc^3(\alpha_x P_x \beta + \alpha_y P_y \beta + \alpha_z P_z \beta) - m^2\beta^2 c^4]\psi = 0$$

$$[E^2 - c^2[\alpha_x^2 P_x^2 + \alpha_y^2 P_y^2 + \alpha_z^2 P_z^2 + (\alpha_x\alpha_y + \alpha_y\alpha_x)P_x P_y + (\alpha_y\alpha_z + \alpha_z\alpha_y)P_y P_z + (\alpha_z\alpha_x + \alpha_x\alpha_z)P_z P_x] - mc^3[(\alpha_x\beta + \beta\alpha_x)P_x + (\alpha_y\beta + \beta\alpha_y)P_y + (\alpha_z\beta + \beta\alpha_z)P_z] - \beta^2 m^2 c^4]\psi = 0 \rightarrow (7)$$

Applying the four quantities

$$\alpha_x^2 = 1$$

$$\alpha_y^2 = 1$$

$$\alpha_z^2 = 1$$

$$\beta^2 = 1$$

$$(\alpha_x\alpha_y + \alpha_y\alpha_x) = (\alpha_y\alpha_z + \alpha_z\alpha_y) = (\alpha_z\alpha_x + \alpha_x\alpha_z) = 0$$

$$(\alpha_x\beta + \beta\alpha_x) = (\alpha_y\beta + \beta\alpha_y) = (\alpha_z\beta + \beta\alpha_z) = 0$$

Therefore eqn (7) becomes,

$$[E^2 - c^2(P_x^2 + P_y^2 + P_z^2) - m^2c^4]\psi = 0 \rightarrow (8)$$

The four quantities $\alpha_x, \alpha_y, \alpha_z$ and β are anti-commutate with one another in pairs and their squares are unity.

It can be concluded that α and β anticommute rather than commutate with each other, therefore these quantities can be expressed in terms of matrices.

Matrices for α and β: (DIRAC MATRICES):

- The squares of all the four matrices are unity. So that their eigen values are +1 and -1

Let us consider the matrix β can be expressed as

$$\beta = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{vmatrix}$$

Then,

$$\alpha_x = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} ; \alpha_y = \begin{vmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & +i & 0 \\ 0 & -i & 0 & 0 \\ +i & 0 & 0 & 0 \end{vmatrix} ; \alpha_z = \begin{vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{vmatrix}$$

As Dirac operator α and β are 4×4 matrices. Then Dirac operands must have four components. The Dirac wave function $\psi(r,t)$ must be four column vector

$$\psi(r,t) = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \rightarrow (10)$$

ψ^* (or) $\bar{\psi}$ corresponding to above equation are denoted by row symbol

$$\psi^* \text{ (or) } \bar{\psi} = [\bar{\psi_1}, \bar{\psi_2}, \bar{\psi_3}, \bar{\psi_4}] \rightarrow (11)$$

Then $\psi\bar{\psi}$ is

$$\psi\bar{\psi} = [\psi_1\bar{\psi_1}, \psi_2\bar{\psi_2}, \psi_3\bar{\psi_3}, \psi_4\bar{\psi_4}] \rightarrow (12)$$

The time dependance of a Dirac pertaining to a system whose Hamiltonian H is determined through the equation $H\psi = i\hbar\, \partial\psi/\partial t \rightarrow (13)$

Where $\dfrac{\partial\psi}{\partial t} = \dfrac{\partial}{\partial t}\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} \therefore \dfrac{\partial\psi}{\partial t} = \begin{bmatrix} \partial\psi_1/\partial t \\ \partial\psi_2/\partial t \\ \partial\psi_3/\partial t \\ \partial\psi_4/\partial t \end{bmatrix} \rightarrow (14)$

The Dirac equation :

We know the Hamiltonian of a system,

$$H = c(\alpha \cdot p) + \beta mc^2 \rightarrow (1)$$

We know, $H\psi = E\psi$

$$[c(\alpha \cdot p) + \beta(mc^2)]\psi = E\psi \rightarrow (2)$$

$$[c(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z) + \beta mc^2]\psi = E\psi$$

$$[c\alpha_x P_x + c\alpha_y P_y + c\alpha_z P_z + \beta mc^2]\psi = E\psi \rightarrow (3)$$

Now,

$$P_x = \begin{vmatrix} P_x & 0 & 0 & 0 \\ 0 & P_x & 0 & 0 \\ 0 & 0 & P_x & 0 \\ 0 & 0 & 0 & P_x \end{vmatrix} \quad \& \quad \alpha_x = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix}$$

$$\alpha_x P_x = \begin{vmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} \begin{vmatrix} P_x & 0 & 0 & 0 \\ 0 & P_x & 0 & 0 \\ 0 & 0 & P_x & 0 \\ 0 & 0 & 0 & P_x \end{vmatrix}$$

$$\alpha_x P_x = \begin{vmatrix} 0 & 0 & 0 & P_x \\ 0 & 0 & P_x & 0 \\ 0 & P_x & 0 & 0 \\ P_x & 0 & 0 & 0 \end{vmatrix}$$

$$\alpha_y P_y = \begin{vmatrix} 0 & 0 & 0 & -iP_y \\ 0 & 0 & iP_y & 0 \\ 0 & -iP_y & 0 & 0 \\ +iP_y & 0 & 0 & 0 \end{vmatrix}$$

$$\alpha_z P_z = \begin{vmatrix} 0 & 0 & P_z & 0 \\ 0 & 0 & 0 & -P_z \\ P_z & 0 & 0 & 0 \\ 0 & -P_z & 0 & 0 \end{vmatrix}$$

Sub these values in eqn (3), we get

$$\left\{ c \begin{bmatrix} 0 & 0 & 0 & P_x \\ 0 & 0 & P_x & 0 \\ 0 & P_x & 0 & 0 \\ P_x & 0 & 0 & 0 \end{bmatrix} + c \begin{bmatrix} 0 & 0 & 0 & -iP_y \\ 0 & 0 & iP_y & 0 \\ 0 & -iP_y & 0 & 0 \\ +iP_y & 0 & 0 & 0 \end{bmatrix} + c \begin{bmatrix} 0 & 0 & P_z & 0 \\ 0 & 0 & 0 & -P_z \\ P_z & 0 & 0 & 0 \\ 0 & -P_z & 0 & 0 \end{bmatrix} \right.$$

$$+\left[\begin{matrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{matrix}\right] mc^2 \Bigg\} \begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} = E\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} \rightarrow (4)$$

$$\left.\begin{aligned}
mc^2\psi_1 + 0\psi_2 + cP_z\psi_3 + c(P_x - iP_y)\psi_4 &= E\psi_1\\
0\psi_1 + mc^2\psi_2 + c(P_x + iP_y)\psi_3 - cP_z\psi_4 &= E\psi_2\\
cP_z\psi_1 + c(P_x - iP_y)\psi_2 - mc^2\psi_3 + 0\psi_4 &= E\psi_3\\
c(P_x + iP_y)\psi_1 - cP_z\psi_2 + 0\psi_3 - mc^2\psi_4 &= E\psi_4
\end{aligned}\right\} \rightarrow (5)$$

$$\begin{bmatrix}mc^2 & 0 & cP_z & c(P_x - iP_y)\\ 0 & mc^2 & c(P_x+iP_y) & -cP_z\\ cP_z & c(P_x - iP_y) & -mc^2 & 0\\ c(P_x+iP_y) & -cP_z & 0 & -mc^2\end{bmatrix}\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix} = E\begin{bmatrix}\psi_1\\\psi_2\\\psi_3\\\psi_4\end{bmatrix}$$

So that this equation reduces to four simultaneous equation.

$$\left.\begin{aligned}
mc^2\psi_1 + cP_z\psi_3 + c(P_x - iP_y)\psi_4 &= E\psi_1\\
mc^2\psi_2 + c(P_x + iP_y)\psi_3 - cP_z\psi_4 &= E\psi_2\\
cP_z\psi_1 + c(P_x - iP_y)\psi_2 - mc^2\psi_3 &= E\psi_3\\
c(P_x + iP_y)\psi_1 - cP_z\psi_2 - mc^2\psi_4 &= E\psi_4
\end{aligned}\right\} \rightarrow (7)$$

$$\left.\begin{aligned}
(E - mc^2)\psi_1 - cP_z\psi_3 - c(P_x - iP_y)\psi_4 &= 0\\
(E - mc^2)\psi_2 - c(P_x + iP_y)\psi_3 + cP_z\psi_4 &= 0\\
(E + mc^2)\psi_3 - cP_z\psi_1 - c(P_x - iP_y)\psi_2 &= 0\\
(E + mc^2)\psi_4 - c(P_x + iP_y)\psi_1 + cP_z\psi_2 &= 0
\end{aligned}\right\} \rightarrow (8)$$

finally replace,

$$P_x = -i\hbar\frac{\partial}{\partial x}$$

$$P_y = -i\hbar\frac{\partial}{\partial y}$$

$$P_z = -i\hbar\frac{\partial}{\partial z}$$

$$\left.\begin{aligned}
&[E-mc^2]\psi_1 + i\hbar c\frac{\partial\psi_3}{\partial z} + i\hbar c\left[\frac{\partial\psi_4}{\partial x} - i\frac{\partial\psi_4}{\partial y}\right] = 0\\
&[E-mc^2]\psi_2 + i\hbar c\left(\frac{\partial\psi_3}{\partial x} + i\frac{\partial\psi_3}{\partial y}\right) - i\hbar c\frac{\partial\psi_4}{\partial z} = 0\\
&[E+mc^2]\psi_3 + i\hbar c\left(\frac{\partial\psi_1}{\partial z}\right) + i\hbar c\left(\frac{\partial\psi_2}{\partial x} - i\frac{\partial\psi_2}{\partial y}\right) = 0\\
&[E+mc^2]\psi_4 + i\hbar c\left(\frac{\partial\psi_1}{\partial x} + i\frac{\partial\psi_1}{\partial y}\right) - i\hbar c\left(\frac{\partial\psi_2}{\partial z}\right) = 0
\end{aligned}\right\} \rightarrow (9)$$

Dirac free particle solution (or) plane wave solution :-

The wave function ψ has four component and the dirac equation is exactly a set of four first order linear partial differential equation.

The plane wave solutions of these component wave function is

$$\psi_j(r,t) = u_j\, e^{i(kr-\omega t)} \rightarrow (1)$$

Where, $j = 1, 2, 3 \ldots$

u_j are numbers

$\psi_j(r,t)$ are eigen functions of the energy and momentum operators with eigen values.

$E = \hbar\omega$ and

$P = \hbar k$ respectively

The Dirac equation for a free particle is given by

$$\left.\begin{aligned}
&(E-mc^2)u_1 - cP_z u_3 - c(P_x - iP_y)u_4 = 0\\
&(E-mc^2)u_2 - c(P_x+iP_y)u_3 + cP_z u_4 = 0\\
&(E+mc^2)u_3 - cP_z u_1 - c(P_x-iP_y)u_2 = 0\\
&(E+mc^2)u_4 - c(P_x+iP_y)u_1 + cP_z u_2 = 0
\end{aligned}\right\} \rightarrow (2)$$

The above equation may be written as

$$\begin{vmatrix}
E-mc^2 & 0 & -cP_z & -c(P_x-iP_y)\\
0 & (E-mc^2) & -c(P_x+iP_y) & cP_z\\
-cP_z & -c(P_x-iP_y) & E+mc^2 & 0\\
-c(P_x+iP_y) & cP_z & 0 & E+mc^2
\end{vmatrix} = 0 \rightarrow (3)$$

Date :
Page No :

This equation is known as momentum energy relation for free particle

This determinant gives

$$(E^2 - p^2c^2 - m_0^2c^4)^2 = 0 \rightarrow (4)$$

(or)

$$E^2 = p^2c^2 + m_0^2c^4$$

$$E = \pm\sqrt{p^2c^2 + m_0^2c^4} \rightarrow (5)$$

$E_+ = +\sqrt{p^2c^2+m_0^2c^4}$

① → +

+ → −

②

4 terms divide

$E_+ + mc^2$

$E_- = -\sqrt{p^2c^2+m_0^2c^4}$

① → + ②

4 terms divide

$E_- - mc^2$

So that the relation between E and p is in agreement with schrodinger equation.

Explicit solution can be found for any momentum p by chosing a sign for energy

$$E_+ = +\sqrt{p^2c^2 + m_0^2c^4} \rightarrow (6)$$

There are two linearly independent solutions which are written as;

$$u_1 = 1,\ u_2 = 0,\ u_3 = \frac{cP_z}{E_+ + mc^2};\ u_4 = \frac{c(P_x + iP_y)}{E_+ + mc^2}$$

$$u_1 = 0;\ u_2 = 1;\ u_3 = \frac{c(P_x - iP_y)}{E_+ + mc^2};\ u_4 = \frac{-cP_z}{E_+ + mc^2}$$

Similarly if we choose the negative square root.

$$E_- = -\sqrt{p^2c^2 + m_0^2c^4} \rightarrow (7)$$

We obtain new two solutions

$$u_1 = \frac{cP_z}{E_- - mc^2};\ u_2 = \frac{c(P_x + iP_y)}{E_- - mc^2};\ u_3 = 1,\ u_4 = 0$$

$$u_1 = \frac{c(P_x - iP_y)}{E_- - mc^2};\ u_2 = \frac{-cP_2}{E_- - mc^2};\ u_3 = 0;\ u_4 = 1.$$

Each of these solutions can be normalised it by multiplying it N.

i,e) $\psi\psi^* = 1$

i,e) $u_1u_1^* + u_2u_2^* + u_3u_3^* + u_4u_4^* = 1.$

Here we taken 1st soln

$$\left[N^2\left(1^2 + 0^2 + \frac{c^2P_z^2}{(E_+ + mc^2)^2} + \frac{c^2(P_x^2 + P_y^2)}{(E_+ + mc^2)^2}\right)\right] = 1$$

$$N^2\left(1+\frac{c^2\,(P_x^2+P_y^2+P_z^2)}{(E_+ + mc^2)^2}\right)=1$$

$$N^2\left(1+\frac{c^2p^2}{(E_+ + mc^2)^2}\right)=1$$

$$N^2=\frac{1}{1+\dfrac{c^2p^2}{(E_+ + mc^2)^2}}$$

$$N=\left[\frac{1}{1+\dfrac{c^2p^2}{(E_+ + mc^2)^2}}\right]^{1/2}$$

(or)

$$N=\left[1+\frac{c^2p^2}{(E_+ + mc^2)^2}\right]^{-1/2}$$

Probability density and Current density :-

The Dirac equation for a free Particle is

$$[E - c\alpha\cdot p - \beta mc^2]\,\psi = 0 \rightarrow (1)$$

Where E and p are operators and it is given by,

$$E = i\hbar\frac{\partial}{\partial t}$$

$$P = -i\hbar\nabla$$

Sub these values in eqn (1), we get

$$i\hbar\frac{\partial\psi}{\partial t} - c\alpha\cdot(-i\hbar\nabla)\psi - \beta mc^2\psi = 0$$

(or)

$$i\hbar\frac{\partial\psi}{\partial t} + i\hbar c\alpha\nabla\psi - \beta mc^2\psi = 0 \rightarrow (2)$$

$\psi \rightarrow \psi^*;\ i \rightarrow -i$

A Hermitian conjugate equation gives

$$-i\hbar\frac{\partial\psi^+}{\partial t} - i\hbar c\alpha\nabla\psi^+ - mc^2\beta\psi^+ = 0 \rightarrow (3)$$

multiplied eqn (2) on left by ψ^+

$$i\hbar\frac{\partial\psi}{\partial t}\psi^+ + i\hbar c\alpha\psi^+\nabla\psi - mc^2\psi^+\beta\psi = 0 \rightarrow (4)$$

multiplied eqn (3) on the right by ψ.

$$-i\hbar \frac{\partial \psi^{+}}{\partial t}\psi - i\hbar c\alpha \nabla \psi^{+} \psi - mc^2 \psi^{+} \beta \psi = 0 \rightarrow (5)$$

(4) − (5) ⟹

$$i\hbar \psi^{+} \frac{\partial \psi}{\partial t} + i\hbar c\alpha \psi^{+} \nabla \psi - \cancel{mc^2 \psi^{+} \beta \psi} + i\hbar \frac{\partial \psi^{+}}{\partial t}\psi +$$

$$i\hbar c\alpha \nabla \psi^{+} \psi + \cancel{mc^2 \psi^{+} \beta \psi} = 0.$$

$$i\hbar \psi^{+} \frac{\partial \psi}{\partial t} + i\hbar c\alpha \psi^{+} \nabla \psi + i\hbar \frac{\partial \psi^{+}}{\partial t}\psi + i\hbar c\alpha \nabla \psi^{+} \psi = 0$$

$$i\hbar \frac{\partial}{\partial t}(\psi^{+}\psi) + i\hbar \nabla (\psi^{+} c\alpha \psi) = 0.$$

(or)

$$\frac{\partial}{\partial t}(\psi^{+}\psi) + \nabla (\psi^{+} c\alpha \psi) = 0 \rightarrow (6)$$

Comparing this equation with equation of Continuity.

$$\frac{\partial P}{\partial t} + \nabla \cdot S = 0$$

The propability density and Current density is

$$\left.\begin{aligned} P(r,t) &= \psi^{+}\psi \\ S(r,t) &= \psi^{+} c\alpha \psi \end{aligned}\right\} \rightarrow (7)$$

The Current density expression looks more plausible if we note that $c\alpha$ is the Velocity of the particle

We know,

$$i\hbar \frac{\partial x}{\partial t} = [x, H]$$

$$i\hbar \frac{\partial x}{\partial t} = [x, [c\alpha \cdot p + \beta mc^2]]$$

$$i\hbar \frac{\partial x}{\partial t} = [x, p\, c\alpha]$$

$$i\hbar \frac{\partial x}{\partial t} = c\alpha [x, p]$$

$$i\hbar \frac{\partial x}{\partial t} = c\alpha i\hbar$$

$$\frac{\partial x}{\partial t} = c\alpha \rightarrow (8)$$

This result is now used to the interpretation of uncertainity Principle.

Negative energy states :

We know that the momentum and energy relation of a free particle

$$E = \pm\sqrt{p^2c^2+m^2c^4}$$

The above equation shows that the energy occur in two states i,e) E_+ and E_-.

When $p=0$; $E_+ = +\sqrt{m^2c^4}$ (or)

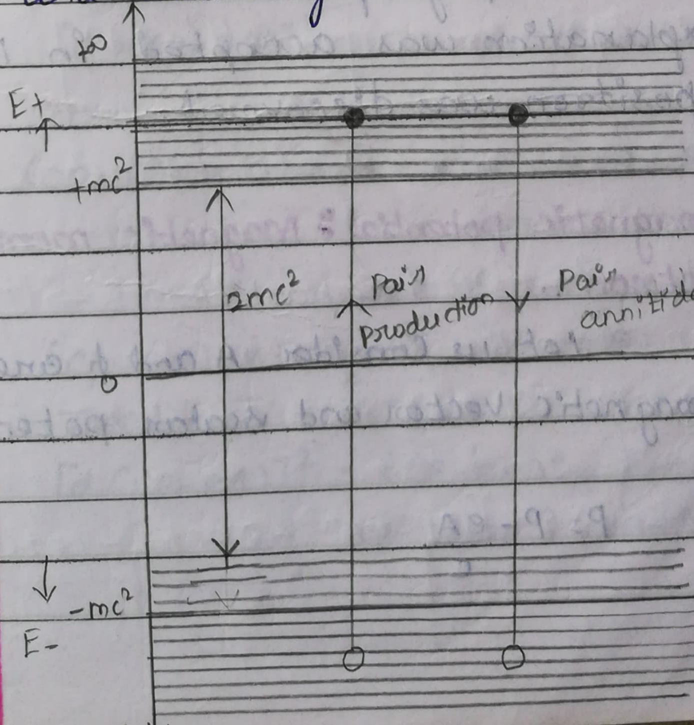
$$E_+ = mc^2$$

and $E_- = -\sqrt{m^2c^4}$ (or)

$$E_- = -mc^2$$

The energy spectrum of a free particle has two branches corresponding to E_+ and E_-.

One energy state starting at mc^2 and extending to $+\infty$ and others starting at $-mc^2$ and extending to $-\infty$ as shown in figure.



The two branches are separated by a forbidden gap of width $2mc^2$. no energy level exists in the forbidden gap.

It is very difficult to imagin such a negative energy state because even a small perturbation could cause a transition in an electron in a positive energy state to a state of negative energy.

To solve this difficulty, Dirac assumed that all negative energy states are occupied by a electrons and this sea of negative energy electron have no physically observable effects.

It is further assumed that when a electron placing a negative energy states picks up energy and goes to the positive energy states, It takes place as an ordinary observable electron.

The empty space in the midst of the negative energy state behaves as if its a particle of positive charge. It response to electric and magnetic field.

The empty spaces called a hole. This explanation was accepted in 1932. When positron was discovered.

Electromagnetic potential: Magnetic moment of an electron :. (or) free particle

Let us consider A and ϕ are electromagnetic vector and scalar potential Then,

$$P = P - \frac{eA}{c}$$

$$P = \frac{cP - eA}{c}$$

$$cP = cP - eA \quad , \quad E = E - e\phi$$

Where, e is the charge on the particle

The Dirac equation for a free particle is

$$[E - c\alpha \cdot p - \beta mc^2]\psi = 0 \rightarrow (1)$$

In electromagnetic field the above equation takes the form

$$[(E - e\phi) - \alpha(cP - eA) - \beta mc^2]\psi = 0 \rightarrow (2)$$

Eqn (2) is operated by,

$$[(E - e\phi) + \alpha(cP - eA) + \beta mc^2]$$

Eqn(2) becomes.

$$[(E - e\phi) + \alpha(cP - eA) + \beta mc^2][(E - e\phi) - \alpha(cP - eA) - \beta mc^2]\psi = 0$$

$$[(E - e\phi)^2 - (E - e\phi)\alpha(cP - eA) - \cancel{(E - e\phi)}\beta mc^2 + \alpha(cP - eA)(E - e\phi) - [\alpha(cP - eA)]^2 - \alpha(cp - eA)\beta mc^2 + \beta mc^2\cancel{(E - e\phi)} - \beta mc^2\alpha(cP - eA) - \beta^2 m^2 c^4]\psi = 0$$

Because α & β are anticommutation and $\beta^2 = 1$.

$$[(E - e\phi)^2 - (E - e\phi)\alpha(cp - eA) + \alpha(cP - eA)(E - e\phi) - [\alpha(cP - eA)]^2 - m^2c^4]\psi = 0 \rightarrow (3)$$

Now, we use the vector identity.

$$[\alpha(cP - eA)]^2 = (cp - eA)(cP - eA) + i\sigma(cP - eA) \times (cP - eA)$$

Here,

$$(cp - eA) \times (cP - eA) = -ce(A \times P + P \times A)$$

$$= -ce \times -i\hbar\nabla \times A$$

$$= iec\hbar\nabla \times A$$

$$(cp - eA) \times (cP - eA) = iec\hbar B.$$

Then,

$$[\alpha(cP - eA)]^2 = (cP - eA)^2 + i\sigma(iec\hbar B)$$

$$= (cP - eA)^2 - ec\hbar\sigma B \rightarrow (4)$$

Then from eqn(5), we take

$$-(E-e\phi)\,\alpha\,(cP-eA)+\alpha(cP-eA)\,(E-e\phi)=-ie\hbar c\alpha E \rightarrow (5)$$

Sub eqn (4) & (5) in eqn (3), we get

$$[(E-e\phi)^2-m^2c^4-(cP-eA)^2+\sigma ec\hbar B-ie\hbar c\alpha E]\psi=0 \rightarrow (6)$$

In the case above equation the first three terms are precisouly the same as in relativistic wave equation in electromagnetic field.

The physical significance of last two terms may be understood by taking non-relativistic Limit of the entire equation

In the non-relativistic limit

$$E=E'+mc^2$$

i,e)

$$(E-e\phi)^2=(E'+mc^2-e\phi)^2$$

(or)

$$(E-e\phi)^2=m^2c^4\left(1+\frac{E'-e\phi}{mc^2}\right)^2$$

$$\boxed{\begin{array}{l}(E'-e\phi+mc^2)^2=(E-e\phi)^2+m^2c^4+2(E-e\phi)mc^2\\ \text{Neglecting higher order}\\ (E-e\phi)^2+m^2c^4\\ m^2c^4\left[1+\frac{E-e\phi}{mc^2}\right]^2\end{array}}$$

$$(E-e\phi)^2=m^2c^4\left[1+\frac{2(E'-e\phi)}{mc^2}\right]$$ By Binomial $(1+x)^n=1+nx+\frac{n(n-1)}{2!}\ldots$

$$(E-e\phi)^2=m^2c^4+2(E'-e\phi)mc^2$$

(or)

$$(E-e\phi)^2-m^2c^4=2(E'-e\phi)mc^2 \rightarrow (7)$$

Sub eqn (7) in (6), we get

$$[2mc^2(E'-e\phi)-(cP-eA)^2+\sigma ec\hbar B-ie\hbar c\alpha\cdot E]\psi=0$$

(or)

$$2mc^2(E'-e\phi)\psi=[(cP-eA)^2-\sigma ec\hbar B+ie\hbar c\alpha\cdot E]\psi$$

$$(E' - e\phi)\psi = \frac{1}{2mc^2}\left[(cp - eA)^2 - ec\hbar\sigma B + ie\hbar c\alpha E\right]\psi$$

$$(E' - e\phi)\psi = \left[\frac{(cP - eA)^2}{2mc^2} - \frac{ec\hbar\sigma B}{2mc^2} + \frac{ie\hbar c\alpha E}{2mc^2}\right]\psi$$

$$E'\psi = \left[\frac{(cp - eA)^2}{2mc^2} + e\phi - \frac{e\hbar\sigma B}{2mc} + \frac{ie\hbar\alpha E}{2mc}\right]\psi \rightarrow (8)$$

The last two terms in the above equation represents the magnetic and electric energy.

Therefore the magnetic moment of the electron is given by

$$\mu = \frac{e\hbar\sigma}{2mc}$$

$$\mu = \frac{es}{mc}$$

Where

$$S = \frac{1}{2}\hbar\sigma$$

Existence of electron spin:-

The Dirac's Hamiltonian in a stationary central field potential $V(r)$ represented by,

$$H = c\alpha \cdot p + \beta mc^2 + V(r) \rightarrow (1)$$

Classically the orbital angular momentum $L = r \times p$ is a constant of motion in a central field.

In quantum mechanics any operator that commutes with Hamiltonian H is a constant of motion

Let us examine this for x - component of momentum

$$i\hbar\frac{dL_x}{dt} = [L_x, H]$$

$$i\hbar\frac{dL_x}{dt} = [L_x, c\alpha \cdot p + \beta mc^2 + V(r)] \rightarrow (2)$$

(or)

$$i\hbar \frac{dL_x}{dt} = [L_x, c(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z) + \beta mc^2 + V(r)]$$

$$i\hbar \frac{dL_x}{dt} = [L_x, c\alpha_x P_x] + [L_x, c\alpha_y P_y] + [L_x, c\alpha_z P_z] + [L_x, \beta mc^2], [L_x, V(r)] \rightarrow (3)$$

But L_x commutes with every quantity in H except for P_y, P_z, Therefore eqn (3) becomes

$$i\hbar \frac{dL_x}{dt} = [L_x, c\alpha_y P_y] + [L_x, c\alpha_z P_z] \rightarrow (4)$$

Now we take

$$[L_x, c\alpha_y P_y] = c\alpha_y [L_x, P_y]$$
$$= c\alpha_y (i\hbar P_z) \rightarrow (5)$$
$$[L_x, c\alpha_z P_z] = c\alpha_z [L_x, P_z]$$
$$= c\alpha_z (-i\hbar P_y) \rightarrow (6)$$

Sub eqn (5) & (6) in (4), we get

$$i\hbar \frac{dL_x}{dt} = c\alpha_y (i\hbar P_z) + c\alpha_z (-i\hbar P_y)$$

$$i\hbar \frac{dL_x}{dt} = -i\hbar c (\alpha_z P_y - \alpha_y P_z) \rightarrow (7)$$

i,e) $i\hbar \frac{dL_x}{dt} \neq 0$

$\therefore L_x \neq$ constant

Hence in Dirac's Theory the 'x' component of orbital angular momentum of an electron moving in a central electrostatic field is not a constant of motion.

Then we must find another operator such that the commutator of its x component with H is equal and opposite of the RHS of eqn (7)

Now let us take x component of $\vec{\sigma}'$ ie

$$i\hbar \frac{d\sigma'_x}{dt} = [\sigma'_x, H]$$

$$i\hbar \frac{d\sigma'}{dt} = [\sigma_x', c\alpha\cdot p + \beta mc^2 + V(r)] \rightarrow (8)$$

$$= [\sigma_x', c(\alpha_x P_x + \alpha_y P_y + \alpha_z P_z) + \beta mc^2 + V(r)]$$

$$= [\sigma_x', c\alpha_x P_x] + [\sigma_x', c\alpha_y P_y] + [\sigma_x', c\alpha_z P_z] + [\sigma_x', \beta mc^2] + [\sigma_x', V(r)] \rightarrow (9)$$

But σ_x' commutates with every quantity in above equation except α_y and α_z.

$$i\hbar \frac{d\sigma_x'}{dt} = [\sigma_x', c\alpha_y P_y] + [\sigma_x', c\alpha_z P_z] \rightarrow (10)$$

Consider,

$$[\sigma_x', c\alpha_y P_y] = cP_y[\sigma_x', \alpha_y]$$
$$= cP_y(2i\alpha_z) \rightarrow (11)$$

$$[\sigma_x', c\alpha_z P_z] = cP_z[\sigma_x', \alpha_z]$$
$$= cP_z(-2i\alpha_y) \rightarrow (12)$$

Sub eqn (11) and (12) in (10), we get

$$i\hbar \frac{d\sigma_x'}{dt} = cP_y(2i\alpha_z) + cP_z(-2i\alpha_y)$$

$$i\hbar \frac{d\sigma_x'}{dt} = 2ic[P_y\alpha_z - P_z\alpha_y]$$

multiply $\frac{1}{2}\hbar$ on both sides,

$$i\hbar \frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = \frac{1}{2}\hbar \times 2ic(P_y\alpha_z - P_z\alpha_y)$$

$$i\hbar \frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = \hbar ic(P_y\alpha_z - P_z\alpha_y) \rightarrow (13)$$

Adding eqn (7) and (13), we get

$$i\hbar \frac{dL_x}{dt} + i\hbar\frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = \hbar ic(P_y\alpha_z - P_z\alpha_y) - \hbar ic(\alpha_z P_y - \alpha_y P_z)$$

$$i\hbar \frac{dL_x}{dt} + i\hbar\frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = 0$$

$$\frac{dL_x}{dt} + \frac{d}{dt}\left(\frac{1}{2}\hbar\sigma_x'\right) = 0$$

$$\frac{d}{dt}\left(L_x + \frac{1}{2}\hbar\sigma_x'\right) = 0$$

$$L_x + \frac{1}{2}\hbar\sigma_x' = \text{Constant} \rightarrow (4)$$

Hence the quantity $J \cdot (L + \frac{1}{2}\hbar\sigma)$ commutes with H and therefore can be taken as a total angular momentum

Here $S = \frac{1}{2}\hbar\sigma$ as the spin angular momentum of the electron.

Spin orbit interaction :-

The Dirac's equation for the central field is

$$[c(\alpha \cdot p) + \beta mc^2 + V(r)]\psi = E\psi \rightarrow (1)$$

substitute

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} ; \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ; \psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$$\left[c\begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} p + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} mc^2 + V(r)\right]\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$$\begin{pmatrix} 0 & c\sigma p \\ c\sigma p & 0 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} + \begin{pmatrix} mc^2 & 0 \\ 0 & -mc^2 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \rightarrow (2)$$

This equation can be separated into the following two coupled equations

$$0\psi_1 + c\sigma p\psi_2 + mc^2\psi_1 + 0\psi_2 + V\psi_1 = E\psi_1$$

(or) $(E - mc^2 - V)\psi_1 - c\sigma p\psi_2 = 0 \rightarrow (3)$

Similarly

$$c\sigma p\psi_1 + 0\psi_2 + 0\psi_1 - mc^2\psi_2 + V\psi_2 = E\psi_2$$

$$(E + mc^2 - V)\psi_2 - c\sigma p\psi_1 = 0 \rightarrow (4)$$

Assuming that both ψ_1 and ψ_2 constitute non-relativistic energy eigen function which means that $E = E' + mc^2$

~~Sp~~ Therefore, eqn (3) and (4) becomes.

From eqn (3)

$$(E' + mc^2 - mc^2 - V)\psi_1 - c\sigma P\psi_2 = 0$$

$$(E' - V)\psi_1 = c\sigma P\psi_2$$

$$\psi_2 = \frac{(E' - V)\psi_1}{c\sigma P} \rightarrow (5)$$

From eqn (4)

$$(E' + mc^2 + mc^2 - V)\psi_2 - c\sigma P\psi_1 = 0$$

$$(E' + 2mc^2 - V)\psi_2 - c\sigma P\psi_1 = 0$$

$$(E' + 2mc^2 - V)\psi_2 = c\sigma P\psi_1$$

$$\psi_2 = \frac{c\sigma P\psi_1}{(E' + 2mc^2 - V)}$$

$$\psi_2 = \frac{c\sigma P\psi_1}{2mc^2\left(1 + \frac{E' - V}{2mc^2}\right)}$$

$$\psi_2 = \frac{c\sigma P\psi_1}{2mc^2}\left(1 + \frac{E' - V}{2mc^2}\right)^{-1}$$

(or)

$$\psi_2 = \frac{c\sigma P\psi_1}{2mc^2}\left(1 - \frac{E' - V}{2mc^2}\right)$$

Sub ψ_2 value from eqn (2)

$$\frac{(E' - V)\psi}{c\sigma P} = \frac{c\sigma P\psi_1}{2mc^2}\left(1 - \frac{E' - V}{2mc^2}\right)$$

$$\frac{(E' - V)\psi}{c\sigma P} = \frac{c\sigma P\psi_1}{2mc^2} - \frac{(E' - V)c\sigma P\psi_1}{4m^2c^4}$$

$$(E' - V)\psi = \frac{c(\sigma.P)c(\sigma.P)\psi_1}{2mc^2} - \frac{(E' - V)c(\sigma.P)c(\sigma.P)\psi_1}{4m^2c^4}$$

$$(E' - V)\psi = \frac{(\sigma.P)(\sigma.P)}{2m}\psi_1 - \frac{(E' - V)(\sigma.P)(\sigma.P)\psi_1}{4m^2c^2}$$

$$(E' - V)\psi = \frac{(\sigma.P)(\sigma.P)}{2m}\psi_1 - \frac{(\sigma.P)E'(\sigma.P)\psi_1}{4m^2c^2} + \frac{(\sigma.P)V'(\sigma.P)\psi_1}{4m^2c^2} \rightarrow (6)$$

We know,

$$(\sigma.P)(\sigma.P) = p^2 \rightarrow (7)$$

and $(\sigma.P)V(\sigma.P) = Vp^2 - \sigma i\hbar \nabla V(\sigma.P) \rightarrow (8)$

sub eqn (7) & (8) in eqn (6), we get

$$(E'-V)\psi_1 = \frac{p^2}{2m}\psi_1 - \frac{E'p^2}{4m^2c^2}\psi_1 + \frac{(Vp^2 - \sigma i\hbar \nabla V(\sigma.P))}{4m^2c^2}\psi_1$$

$$(E'-V)\psi_1 = \frac{p^2}{2m}\psi_1 - \frac{E'p^2}{4m^2c^2}\psi_1 + \frac{Vp^2}{4m^2c^2}\psi_1 - \frac{\sigma i\hbar \nabla V(\sigma.P)}{4m^2c^2}\psi_1$$

$$(E'-V)\psi_1 = \frac{p^2}{2m} - \frac{(E'-V)p^2}{4m^2c^2}\psi_1 - \frac{\sigma}{4m^2c^2}[i\hbar \nabla V(\sigma.P)]\psi_1$$

$$(E'-V)\psi_1 = \frac{p^2}{2m} - \frac{p^2.p^2}{2m \times 4m^2c^2}\psi_1 - \frac{i\hbar}{4m^2c^2}(\nabla V.P + i\sigma \nabla V \times P)\psi_1$$

Here in R.H.S $E-V = \frac{p^2}{2m}$

$$(E'-V)\psi_1 = \frac{p^2}{2m}\psi_1 - \frac{p^4}{8m^3c^2}\psi_1 - \frac{i\hbar}{4m^2c^2}(\nabla V.P)\psi_1 + \frac{\hbar}{4m^2c^2}\sigma(\nabla V \times P)\psi_1$$

$$(E'-V)\psi_1 = \left[\frac{p^2}{2m} - \frac{p^4}{8m^3c^2}(\nabla V . P) + \frac{\hbar}{4m^2c^2}\sigma(\nabla V \times P)\right]\psi_1 \rightarrow (9)$$

But,

$$\nabla V . P = -i\hbar \nabla V . \nabla$$

$$\nabla V . P = -i\hbar \frac{dV}{dr} . \frac{\partial}{\partial r} \rightarrow (10)$$

and

$$\frac{\hbar}{4m^2c^2}\sigma(\nabla V \times P) = \frac{1}{2mc^2}\frac{\hbar}{2}\sigma \frac{1}{r}\frac{dV}{dr}(r \times P)$$

$$= \frac{1}{2mc^2} S . \frac{1}{r}\frac{dV}{dr} L$$

$$= \frac{1}{2mc^2}\frac{1}{r}\frac{dV}{dr} S.L \rightarrow (11)$$

Here,

$$S = \frac{1}{2}\hbar\sigma \text{ and } L = r \times P$$

Sub eqn (10) & (11) in (9), we get

$$(E'-V)\psi_1 = \left[\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{i\hbar}{4m^2c^2}\left(-i\hbar \frac{dV}{dr}\frac{\partial}{\partial r}\right) + \frac{1}{2mc^2}\frac{1}{r}\frac{dV}{dr} S.L\right]\psi_1$$

$$(E' - V)\psi = \left[\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr} S.L\right]\psi_1$$

(or)

$$E'\psi = \left[V + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr} S.L\right]\psi_1$$

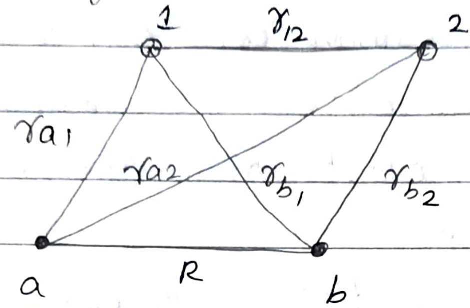
From the above eqn first and second terms gives the non-relativistic schoredinger equation

The third term is similar relativistic mass correction

The last term is the spin orbit coupling energy.

Hydrogen Molecule :-

Let us Consider 'a' and 'b' are the fixed nuclei of hydrogen molecule at a distance 'R' apart and two electrons 1 and 2 as shown in figure



The schrodinger equation is

$$H_0 \psi (R, 1, 2) = E(R) \psi (R, 1, 2) \rightarrow (1)$$

Where,

$$H = \left[\left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{r_{a1}}\right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_{b2}}\right)\right] - e^2\left(\frac{1}{r_{a2}} + \frac{1}{r_{b1}} - \frac{1}{r_{12}} - \frac{1}{R}\right)\Bigg] = (H_1^0 + H_2^0) + H_{12} \rightarrow (2)$$

Here, Heitler and London regarded H_{12} as a perturbation term.

For electron 1 attached to nucleus 'a' and electron 2 to nucleus 'b' the ground state wavefunction is

$$\psi_1 = \psi_a(1) \psi_b(2)$$

Where,

$$\left.\begin{aligned} \psi_a(1) &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r_{a1}}{a_0}\right) \\ \psi_b(2) &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r_{b2}}{a_0}\right) \end{aligned}\right\} \rightarrow (3)$$

The two electrons being identical an equally wave function belonging to the same energy is

$$\psi_2 = \psi_a(2) \psi_b(1)$$

Where,

Date :
Page No :

$$\left.\begin{aligned} \psi_a(2) &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r_{a2}}{a_0}\right) \\ \psi_b(1) &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r_{b1}}{a_0}\right) \end{aligned}\right\} \rightarrow (4)$$

There are two possible spin states of the electron i,e) the singlet (s) and the triplet (t) Then the total wavefunction is antisymmetric for the following linear Combinations of ψ_1 and ψ_2

$$\psi_s = A_+ (\psi_1 + \psi_2) \rightarrow (5)$$

$$\psi_t = A_- (\psi_1 - \psi_2) \rightarrow (6)$$

Where,

A_+, A_- represents normalization

The basic functions ψ_1 and ψ_2 are separately normalized, but not mutually orthogonal.

$$\int \psi_1^2 \, d^3r_1 \, d^3r_2 = 1$$

$$\int \psi_2^2 \, d^3r_1 \, d^3r_2 = 1$$

Then,

$$\int \psi_1^2 \psi_2^2 \, d^3r_1 \, d^3r_2 = \int [\psi_a(1)\, \psi_b(2)] [\psi_a(2)\, \psi_b(1)] \, d^3r_1 \, d^3r_2 = S_{ab} \rightarrow (7)$$

Where,

S_{ab} is the overlap integral

Since ψ_s and ψ_t for the system must be ortho-normalized functions

$$\langle \psi_s | \psi_s \rangle = 1, \; \langle \psi_t | \psi_t \rangle = 1, \; \langle \psi_s | \psi_t \rangle = 0 \rightarrow (8)$$

It is necessary that,

$$2A_+^2 + 2A_+^2 S_{ab} = 1$$

$$2A_-^2 - 2A_-^2 S_{ab} = 1$$

$$A_+ A_- - A_- A_+ = 0$$

(or)

$$A_\pm = \frac{1}{2\sqrt{(1 \pm S_{ab})}} \rightarrow (9)$$

The first order Corrections to the energy in the two possible states are,

$$E_s^{(1)} = \langle \psi_s | H_{12} | \psi_s \rangle = \frac{J+K}{1+S_{ab}} \rightarrow (10)$$

$$E_t^{(1)} = \langle \psi_t | H_{12} | \psi_t \rangle = \frac{J-K}{1-S_{ab}} \rightarrow (11)$$

Where,

$$J = \iint \psi_a^2(1)\, \psi_b^2(2) \left(\frac{e^2}{r_{12}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} \right) d\tau_1\, d\tau_2 + \frac{e^2}{R}$$

(or)

$$J = -\int \psi_a^2(1) \frac{e^2}{r_{b1}} d\tau_1 - \int \psi_b^2(2) \frac{e^2}{r_{a2}} d\tau_2 + \iint \psi_a^2(1) \frac{e^2}{r_{12}} \psi_b^2(2)\, d\tau_1\, d\tau_2 \rightarrow (12)$$

and

$$K = \iint \psi_a(1)\, \psi_b(2) \left(\frac{e^2}{r_{12}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{R} \right) \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2$$

(or)

$$K = \iint \psi_a(1)\, \psi_b(2) \frac{e^2}{r_{12}} \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2 - \iint \psi_a(1)\, \psi_b(2) \frac{e^2}{r_{a2}} \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2 - \iint \psi_a(1)\, \psi_b(2) \frac{e^2}{r_{b1}} \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2 + \iint \psi_a(1)\, \psi_b(2) \frac{e^2}{R} \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2 \rightarrow (13)$$

If $S = \int \psi_a(1)\, \psi_b(1)\, d\tau_1$ and $S^2 = S_{ab} = \int \psi_a(1)\, \psi_b(2)\, \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2$

eqn (13) becomes,

$$K = \iint \psi_a(1)\, \psi_b(2) \frac{e^2}{r_{12}} \psi_a(2)\, \psi_b(1)\, d\tau_1\, d\tau_2 - S \int \psi_b(2) \frac{e^2}{r_{a2}} \psi_a(2)\, d\tau_2 - S \int \psi_a(1) \frac{e^2}{r_{b1}} \psi_b(1) + \frac{e^2}{R} S_{ab} \rightarrow (14)$$

⇒ In the Coulomb integral J in eqn (12),

(i) The first term gives the average value of the Coulomb interaction between electron 1 and nucleus 'b'.

(ii) The second term gives the interaction between electron 2 and nucleus 'a'.

(iii) The third integral gives the repulsion of the two electron clouds, neglecting correlation
(iv) the last term gives the repulsion between nuclei.

Thus J represents the Coulomb energy between two classically distinguishable, spherically symmetric overlapping atoms. Its value is small.

⇒ K is the exchange integral K is connected with the motion of electrons arising from antisymmetrization of the wave function.

The sign of energy $E^{(1)}$ is determined by signs and relative magnitudes of J and K.

Case (i)

R large :-

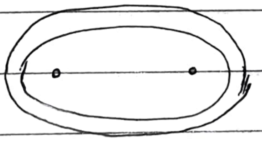
The exchange charge density ρ_{ex} is zero because ψ_a and ψ_b do not overlap. Both J and K tend to vanish for the R large.

$$E^{(1)} = 0.$$

Case (ii)

R Medium :-

In this case ρ_{ex} is large and also S_{ab} is large. Therefore the two charge clouds just overlap as shown in fig.



The sign of $E^{(1)}$ is determined by K, because K is negative i.e) $E_s^{(1)} < 0$ attraction

$E_t^{(1)} > 0$ repulsion

Case (iii)

R small :- In this case e^2/R dominates in both J and K and so $E_{s,t}^{(1)} > 0$