$\beta = \frac{v}{c}$ relativistic effects become important as $\beta \to 1$.

$$0 \le \beta \le 1$$

$$\boxed{c = 137.036 \text{ in atomic units}}$$

Hydrogen like atoms.

$$E = -\frac{Z^2}{2} = -\underbrace{\langle T \rangle}_{\text{average Kinetic Energy}}$$

$$\langle T \rangle = \frac{1}{2} \langle v^2 \rangle \qquad \langle v^2 \rangle = Z^2$$

$$\therefore \beta = \frac{\langle v \rangle}{c} \approx \frac{Z}{c}$$

So the effects of Relativity will increase with β.

$$E = \gamma mc^2 = \frac{mc^2}{\sqrt{1-\beta^2}}$$

$$E = mc^2 \left[1 + \frac{\beta^2}{2} + \frac{3}{8}\beta^4 + \cdots \right]$$

$$= mc^2 + \frac{1}{2}mv^2 + \frac{3}{8}mv^2 \beta^2$$

$$= mc^2 + \frac{1}{2}mv^2 \left[1 + \frac{3}{4}\beta^2 \right]$$

rest mass

non-relativistic $\Downarrow$ first correction

Energy $\sim \beta^2$. for $Z = 40$ $\frac{3}{4}\left(\frac{Z}{138}\right)^2 = 6.3\%$

Relativistic contraction :-

$$a_0 \propto \frac{1}{m_e}$$

$m = \gamma m_e$. $\longrightarrow \gamma = \frac{1}{\sqrt{1-\beta^2}} > 1$.

$$\boxed{a_0 \propto \frac{1}{\gamma}} < 1.$$

Some obitals contract, but to maintai

Dirac Hamiltonian:-

$$H = c\,\underline{\alpha}\,p + \beta m c^2.$$

t-dependent Eqn :

$$i\frac{\partial \psi}{\partial t} = (c\alpha p + \beta m c^2)\psi.$$

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \qquad \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}.$$

$\alpha_x, \sigma_y, \sigma_z$.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Let's write dirac Eqn in the long form.

$$P_x = -i\frac{\partial}{\partial x}. \qquad P_y = -i\frac{\partial}{\partial y} \qquad P_z = -i\frac{\partial}{\partial z}.$$

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

$$\begin{bmatrix} [mc^2 - E]I & c\,\sigma\cdot p \\ c\,\sigma\cdot p & [-mc^2 - E]I \end{bmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = 0.$$

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

$(-i)(-i)$

$$\begin{pmatrix} mc^2 - E & 0 & -ic\frac{\partial}{\partial z} & c\left(-i\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right) \\ 0 & mc^2 - E & c\left(-i\frac{\partial}{\partial x} + \frac{\partial}{\partial y}\right) & ci\frac{\partial}{\partial z} \\ c\left(-i\frac{\partial}{\partial z}\right) & c\left(-\frac{i\partial}{\partial x} - \frac{\partial}{\partial y}\right) & -mc^2 - E & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = 0.$$

$$\begin{pmatrix} \cdots \\ c\left(-\frac{i\partial}{\partial x}+\frac{\partial}{\partial y}\right) & c\left(+\frac{i\partial}{\partial z}\right) & 0 & -mc^2-E \end{pmatrix}\begin{pmatrix} \vdots \\ \psi_4 \end{pmatrix}$$

Dirac Equation for free particle

with potential.

$$(c\,\alpha\cdot p + \beta mc^2 + V)\,\psi(t) = E\,\psi(t).$$

with magnetic field.

$$(c\,\alpha\cdot\pi + \beta mc^2 + V)\,\psi(t) = E\,\psi(t).$$

$$\pi = p - qA.$$

For free particles:

$$\psi = e^{(k\cdot x - Et)}\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = e^{i(k_x\cdot x + k_y\cdot y + k_z\cdot z - Et)}\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix}$$

$$(mc^2 - E)a_1 \quad + ck_z\, a_3 + c(k_x - ik_y)\, a_4 = 0.$$

$$(mc^2 - E)a_2 + c(k_x + ik_y)a_3 \quad - ck_z\, a_4 = 0.$$

$$+ck_z a_1 \quad + c(k_x - ik_y)a_2 \quad (-mc^2 - E)a_3 = 0.$$

$$+c(k_x + ik_y)\, a_1 \quad - ck_z\, a_2 \quad (-mc^2 - E)a_4 = 0$$

a_1, a_2, a_3, a_4 only if determinant is zero.

$$\begin{vmatrix} mc^2-E & 0 & ck_z & ck_- \\ 0 & mc^2-E & ck_+ & -ck_z \\ ck_z & ck_- & -mc^2-E & 0 \\ ck_+ & -ck_z & 0 & -mc^2-E \end{vmatrix} = 0$$

$$\left[E^2 - m^2c^4 - c^2(k_x^2+k_y^2+k_z^2)\right]^2 = 0$$

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

(α)

$$E_1 = \sqrt{m^2c^4+c^2k^2} \qquad \psi_1 = a e^{i(k\cdot r - Et/\hbar)} \begin{bmatrix} 1 \\ 0 \\ ck_z/(E_+ + mc^2) \\ ck_+/(E_+ + mc^2) \end{bmatrix}$$

(β)

$$\psi_2 = a e^{i(k\cdot r - Et/\hbar)} \begin{pmatrix} 0 \\ 1 \\ ck_-/(E_+ + mc^2) \\ -ck_z/(E_+ + mc^2) \end{pmatrix}$$

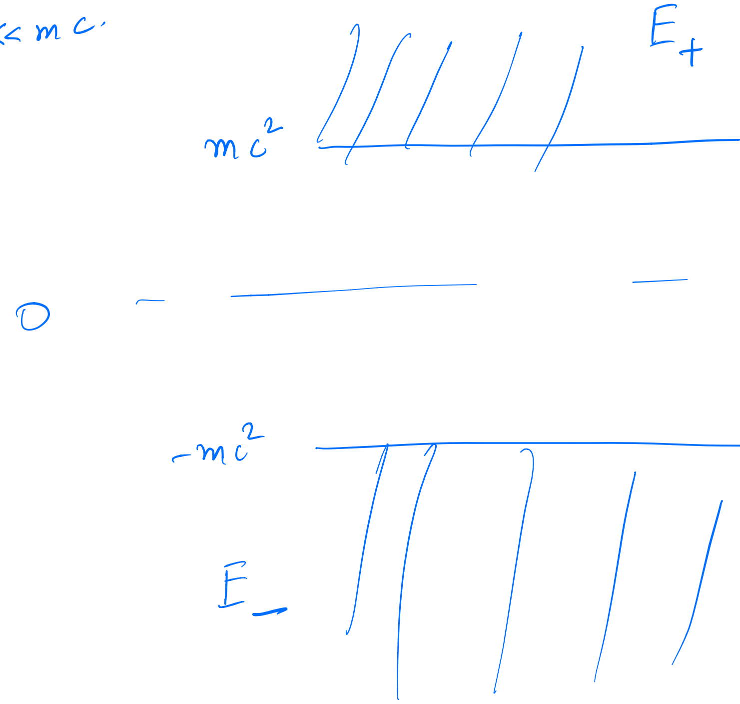
$$E_3 = -\sqrt{m^2c^4+k^2} \qquad \psi_3 = a e^{i(k\cdot r - Et/\hbar)} \begin{pmatrix} ck_z/(E_- - mc^2) \\ ck_+/(E_- - mc^2) \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 \end{pmatrix}$$

$$\begin{pmatrix} ck_- / (E_- - mc^2) \\ -ck_z / (E_- - mc^2) \\ 0 \\ 1 \end{pmatrix}$$

$$\frac{K}{E + mc^2} = \frac{cp}{\sqrt{m^2c^4 + p^2c^2} + mc^2} < \frac{p}{2mc}$$

$p \ll mc.$



$$\begin{bmatrix} \psi_L \\ \boxed{\psi_S} \end{bmatrix}$$

$$\boxed{\psi_S \sim \frac{p}{2mc}}$$

and small.

$(\sigma \cdot \mathbf{A})(\sigma \cdot \mathbf{B}).$

$$= (\sigma_x A_x + \sigma_y A_y + \sigma_z A_z)(\sigma_x B_x + \sigma_y B_y + \sigma_z B_z).$$

$$\sigma_x \sigma_x = I = \sigma_y \sigma_y = \sigma_z \sigma_z.$$

$$A_x B_x + A_y B_y + A_z B_z.$$

$$+ \sigma_x \sigma_y A_x B_y + \sigma_y \sigma_x A_y B_x. \quad = \quad A \cdot B + \underbrace{i\,\sigma \cdot (A \times B)}_{\text{How?}}$$

$$+ \sigma_x \sigma_z A_x B_z + \sigma_z \sigma_x A_z B_x.$$

$$+ \sigma_y \sigma_z A_y B_z + \sigma_z \sigma_y A_z B_y.$$

Atomic Dirac Eqn :

$$\left(\beta m c^2 + c \alpha p + \frac{1}{r}\right) \psi(r) = E\, \psi(r).$$

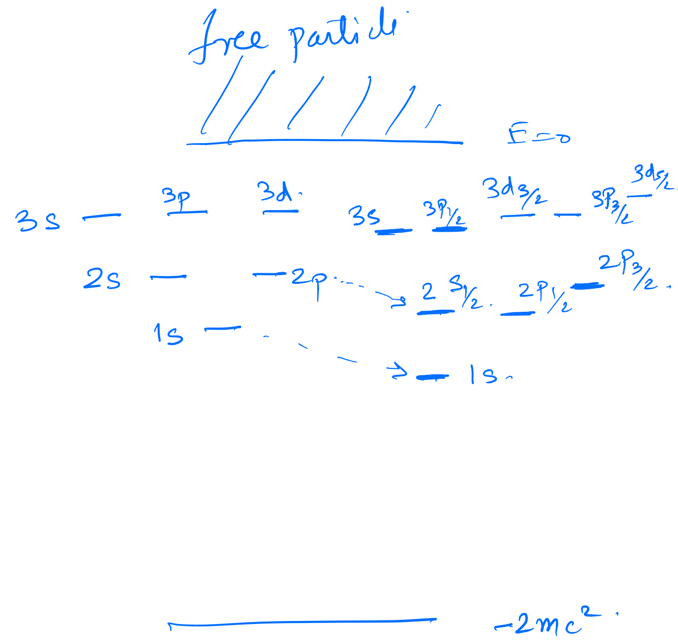
$$E = m c^2 \left\{ 1 + \left[\frac{Z/c}{n - j - \frac{1}{2} + \sqrt{\left(j + \frac{1}{2}\right)^2 - \frac{Z^2}{c^2}}} \right]^2 \right\}^{1/2}.$$

$$E = mc^2 - \frac{Z^2}{2n^2} + \frac{Z^4}{2n^4 c^2}\left(\frac{3}{4} - \frac{n}{j + \frac{1}{2}}\right)$$

n - principle quantum numbe.

$j = l \pm s$

l: angular momentum; $s \rightarrow 1/2$



Many-Electron System :-

Dirac-Coulomb

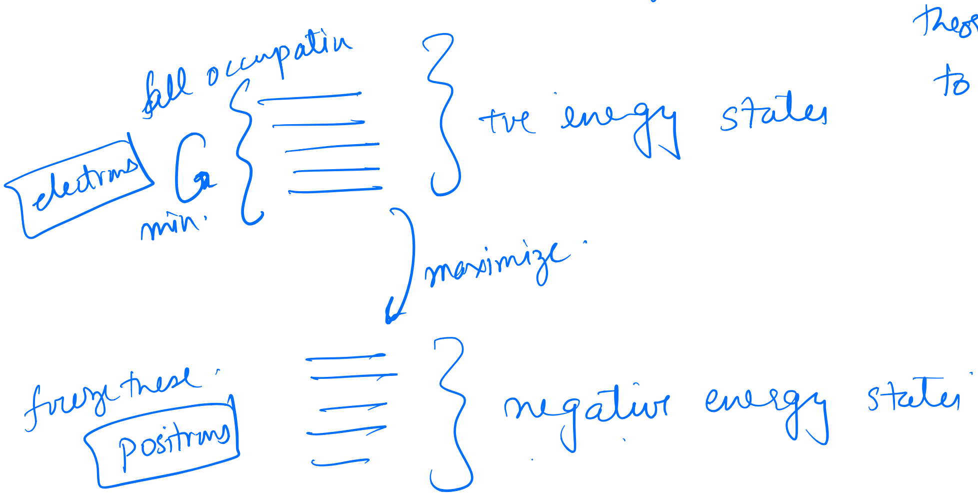
$$H = \sum_i h_i^{D} + \underbrace{\sum_{i>j} \frac{1}{r_{ij}}}_{\text{instantaneous interaction}}$$

$$\text{Breit} = -\frac{(\alpha_1 \cdot \alpha_2)}{2 r_{12}} - \frac{1}{2} \frac{(\alpha_1 \cdot r_{12})(\alpha_2 \cdot r_{12})}{r_{12}^3}$$

$$H^{DCB} = \sum_i h_i^{D} + \sum_{i<j} g_{ij}^{CB}$$

C → coulomb; B → Breit term

What about the wavefunction. (FCI in non-relativistic theory is invariant to choice of orbitals)



minmax procedure. { No pair approximation }.

<u>2-component theory</u> :-

<u>Breit-Pauli Hamiltonian</u> :-

$$\begin{pmatrix} V+mc^2 & \sigma\cdot p \\ \sigma\cdot p & -mc^2+V \end{pmatrix}\begin{pmatrix}\psi^L \\ \psi^S\end{pmatrix} = E\begin{pmatrix}\psi^L \\ \psi^S\end{pmatrix}$$

$$\begin{pmatrix} V & c(\sigma\cdot p) \\ c\sigma\cdot p & -2mc^2+V \end{pmatrix}\begin{pmatrix}\psi^L \\ \psi^S\end{pmatrix} = E\begin{pmatrix}\psi^L \\ \psi^S\end{pmatrix}$$

$$V\psi^L + c(\sigma\cdot p)\psi^S = E\psi^L .$$

$$c(\sigma\cdot p)\,\psi_L + (-2mc^2+V)\,\psi^S = E\,\psi^S$$

$$\psi^S = \frac{1}{(E+2mc^2-V)}\,c(\sigma\cdot p)\,\psi^L$$

$$= \left(1+\frac{E-V}{2mc^2}\right)^{-1}\frac{\sigma\cdot p}{2mc}\,\psi^L$$

$$\left[\frac{1}{2m}(\sigma\cdot p)\left(1+\frac{E-V}{2mc^2}\right)^{-1}(\sigma\cdot p) + V\right]\psi^L = E\,\psi^L$$

Expand:- $x = \frac{E-V}{2mc^2}$ and expand in orders of x.

$$(1+x)^{-1}$$

$$-\frac{\hbar^2}{2m}\nabla^2 + \left\{\frac{e^2A^2}{2m} + \frac{\hbar}{i}\frac{e}{m}A\cdot\nabla \underbrace{-\,e\,\phi(r)}_{\text{potential}} \underbrace{-\,\frac{e\hbar}{2m}\,\sigma\cdot B}_{\text{Zeeman}}\right)$$

$$+\underbrace{\frac{e\hbar^2}{8m^2c^2}\nabla\cdot E}_{\text{Darwin}} \underbrace{-\,\frac{\hbar^2 p^4}{8m^3c^3}}_{\text{Mass-velocity}} \underbrace{\underbrace{-\,\frac{e\hbar^2}{8m^2c^2}\,\sigma\cdot(p\times E - E\times p)}_{\text{Spin-orbit coupling}}}_{\text{Singular near nuclei}}$$

$$\frac{E-V}{2mc^2} \to \infty \text{ near nucleus}$$

$$\left(1+\frac{E-V}{2mc^2}\right)^{-1} = \left(1-\frac{V}{2mc^2}\right)^{-1}\left(1+\frac{E}{2mc^2-V}\right)^{-1}$$

$$\frac{2mc^2}{2mc^2+E-V} = \left(\frac{2mc^2}{2mc^2-V}\right)\times\left(\frac{2mc^2-V}{2mc^2-V+E}\right)$$