3 Relativistic wave equations

3.1 Klein-Gordon

The Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{3.1}$$

$$H = \frac{p^2}{2m} + V \tag{3.2}$$

contains first derivatives with respect to time, t, and second derivatives with respect to (xyz). We now wish to handle all four coordinates $(x_1x_2x_3x_4)$ on equal footing.

The **Klein-Gordon** equation was introduced by **Fock** (1926ab), Gordon (1926), Klein (1926-1927), **Kudar** (1926) and Schrödinger (1926). We wish to satisfy

$$E^2 = c^2p^2 + m^2c^4 \tag{3.3}$$

(Compare with (1.40), $m = m_0$).

Taking the square root, we would get

$$H = \sqrt{c^2p^2 + m^2c^4} + V \tag{3.4}$$

but the problem would be to actually take the square root.

Reorganizing, we get

$$(E - V)\psi = \sqrt{c^2p^2 + m^2c^4}\psi \tag{3.5}$$

Squaring (operating twice)

$$\underline{\underline{(E-V)^2\psi}} = (E^2 - 2EV + V^2)\psi = \underline{\underline{(c^2p^2 + m^2c^4)\psi}} \;\Big|\; : 2mc^2 \tag{3.6}$$

$$\Big[\frac{p^2}{2m} + \frac{1}{2}mc^2 - \frac{1}{2mc^2}(E^2 - 2EV + V^2)\Big]\psi = 0 \;\Big|\; E = mc^2 + \epsilon$$

$$\Big[\frac{p^2}{2m} + \underline{\frac{1}{2}mc^2} - \frac{1}{2mc^2}(\underline{m^2c^4} + \underline{\underline{\underline{2\epsilon mc^2}}} + \epsilon^2 - \underline{\underline{\underline{2mc^2V}}} - 2\epsilon V + V^2)\Big]\psi = 0$$

$$\Big[\frac{p^2}{2m} + \underline{\underline{\underline{V - \epsilon}}} - \underbrace{\frac{1}{2mc^2}(\epsilon - V)^2}_{h_m \text{ (mass-velocity) of Pauli}}\Big]\Psi = 0 \tag{3.7}$$

h_m is often expressed as

$$h_m = -\frac{p^4}{8m^3c^2}$$

The external electromagnetic field $\underline{A}, V$ can be included through the *minimal substitution* $\underline{p} \rightarrow \underline{p} - \frac{q}{c}\underline{A}$, q being the charge of the particle. For $e \equiv |e|$, (3.6) becomes, for electrons,

$$\underline{\underline{(E - V)^2\psi = \big[c^2(\underline{p} + \frac{e}{c}\underline{A})^2 + m^2c^4\big]\psi}} \tag{3.8}$$

[This is valid in the Gauss-cgs system of units or in atomic units. In SI, use $\underline{p} \to \underline{p} - q\underline{A}$]

For a free particle, replacing

$$E \to \mathrm{i}\hbar\frac{\partial}{\partial t} \tag{3.9}$$

and introducing the **d'Alembert** operator

$$\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}, \tag{3.10}$$

$$\big[-\hbar^2\frac{\partial^2}{\partial t^2} - m^2c^4 + \hbar^2c^2\nabla^2\big]\psi = 0 \quad | : \hbar^2c^2$$

$$\big[\Box - \frac{m^2c^2}{\hbar^2}\big]\psi = 0 \tag{3.11}$$

The equation (3.7) is good for a *pionic* atom, se e.g. **K-C Wang** *et al.* PRA*22*(1980), 1072. It gives a wrong answer for the fine structure of *electronic* atoms[3].

Multiply now (3.11) from left by ψ^*:

$$\begin{aligned} \psi^*\big[\Box - \frac{m^2c^2}{\hbar^2}\big]\psi \quad &= 0, \quad \text{and} \quad | \quad + \\ \big[\Box - \frac{m^2c^2}{\hbar^2}\big]\psi^*\psi \quad &= 0 \qquad\qquad | \quad - \end{aligned}$$

$$\psi^*(\Box\psi) - (\Box\psi^*)\psi = 0 \tag{3.12}$$

Using the definition of $\Box$

$$\psi^*(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2})\psi - \big[(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi^*\big]\psi = 0 \tag{3.13}$$

As

$$\psi^*(\psi'') - (\psi^*)''\psi = \big[\psi^*\psi' - (\psi^*)'\psi\big]' \tag{3.14}$$

and

$$\psi^*(\nabla^2\psi) - \psi(\nabla^2\psi^*) = \nabla\cdot\big[\psi^*\nabla\psi - \psi(\nabla\psi^*)\big] \tag{3.15}$$

we get the continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\underline{j} = 0 \tag{3.16}$$

where

$$\rho(\underline{r},t) = \frac{\mathrm{i}\hbar}{2mc^2}\big(\psi^*\frac{\partial\psi}{\partial t} - \frac{\partial(\psi^*)}{\partial t}\psi\big) \tag{3.17}$$

$$\underline{j}(\underline{r},t) = -\frac{\mathrm{i}\hbar}{2m}\big(\psi^*\nabla\psi - (\nabla\psi^*)\psi\big) \tag{3.18}$$

[3]The proof is left as an exercise for the reader

reduce to the right non-relativistic limit (see e.g. Kvantkemi I, p. 20-21). Now the ρ is still real, but not necessarily positive definite. Replace in (3.17) $\mathrm{i}\hbar\frac{\partial}{\partial t} \to E \Rightarrow$

$$\rho = \frac{E}{mc^2}|\psi|^2. \text{ Now, if } E < 0,\ \rho < 0 \tag{3.19}$$

3.2 Dirac

We are searching for an equation of the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = \mathrm{H}\psi \tag{3.20}$$

Because of the first derivative $\frac{\partial}{\partial t}$, we would like to have first derivatives $\frac{\partial}{\partial x}$ etc. as well. Note that the series expansion of the square root in

$$(E - V)\psi = mc^2\sqrt{1 + p^2/c^2}$$

would contain *all* powers of (p^2/c^2).

Suppose now that the Hamiltonian is linear in all $\frac{\partial}{\partial x_\mu}$ and that the wave function Ψ has N components,

$$\Psi = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} \tag{3.21}$$

Then the most general free-particle wave equation is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi_n = \sum_{l=1}^{N}[c\underline{\alpha}_{nl} \cdot \underline{p} + \beta_{nl}mc^2]\Psi_l \tag{3.22}$$

where n runs from $1 \ldots N$, and

$$\underline{\alpha}_{nl} \cdot \underline{p} = -\mathrm{i}\hbar[(\alpha_{nl})_x\frac{\partial}{\partial x} + (\alpha_{nl})_y\frac{\partial}{\partial y} + (\alpha_{nl})_z\frac{\partial}{\partial z} \tag{3.23}$$

In terms of the $N \times N$ matrices $\underline{\alpha}$ and $\underline{\beta}$,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = [-\mathrm{i}\hbar c\underline{\alpha} \cdot \nabla + \beta mc^2]\Psi \equiv h_D\Psi \tag{3.24}$$

with the Dirac Hamiltonian

$$h_D = c\underline{\alpha} \cdot \underline{p} + \beta mc^2 \tag{3.25}$$

The D in h_D stands for Dirac.

The components of α are the $N \times N$ matrices ($N \geq 4$, see below) α_x, α_y and α_z. In order for h_D to be Hermitian, $\underline{\alpha}$ and β must be Hermitian:

$$\underline{\alpha}^\dagger = \underline{\alpha}, \quad \beta^\dagger = \beta \tag{3.26}$$

For all points in space-time to be equivalent, $\underline{\alpha}$ and β must be constant and dimensionless. Consequently they commute with $\underline{r}$ and $\underline{p}$.

We still want to satisfy

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

for all components $\psi_1 \dots \psi_N$:

$$-\hbar^2 \frac{\partial^2}{\partial t^2}\Psi = [-\hbar^2 c^2 \nabla^2 + m^2c^4]\Psi \tag{3.27}$$

Then the Dirac equation

$$h_D \Psi = \mathrm{i}\hbar \frac{\partial}{\partial t}\Psi$$

will connect the different components while every individual component, ψ_i, will satisfy the Klein-Gordon (K-G) equation (3.27).

3.2.1 Why must $N \geq 4$?

Starting from

$$\begin{aligned} \beta\alpha_i &= -\alpha_i\beta \quad |\beta \times \\ \alpha_i &= \underbrace{-\beta}_{A}\,\underbrace{\alpha_i\beta}_{B} \quad (\text{as } \beta^2 = \mathbf{I}) \end{aligned}$$

we see that

$$\begin{aligned} \mathrm{Tr}\ AB &= \mathrm{Tr}\ BA \\ \mathrm{Tr}\ \alpha_i &= -\mathrm{Tr}\ (\alpha_i\beta)\beta \quad |\beta^2 = \mathbf{I} \\ &= -\mathrm{Tr}\ \alpha_i \\ &= 0 \end{aligned}$$

The α_i were ± 1. We have the same number of both $\Rightarrow N$ must be even. On page 17 it was shown that 2 was too small $\Rightarrow N \geq 4$. $\square$

3.2.2 Properties of Dirac matrices

Multiply now

$$(\mathrm{i}\hbar \frac{\partial}{\partial t} - h_D)\Psi = 0$$

from the left by the operator $\mathrm{i}\hbar\frac{\partial}{\partial t} + h_D \Rightarrow$

$$(-\hbar^2 \frac{\partial^2}{\partial t^2} - h_D^2)\Psi = 0$$

in other words

$$-\hbar^2\frac{\partial^2}{\partial t^2}\Psi = \big[-\hbar^2c^2\textstyle\sum_{i,j=1}^3\frac{1}{2}(\alpha_i\alpha_j+\alpha_j\alpha_i)\frac{\partial^2}{\partial x_i\partial x_j}$$
$$-\mathrm{i}\hbar c\textstyle\sum_{i=1}^3(\beta\alpha_i+\alpha_i\beta)\frac{\partial}{\partial x_i}+m^2c^4\beta^2\big]\Psi \tag{3.28}$$

where we have used the fact that $[\frac{\partial}{\partial x_i},\frac{\partial}{\partial x_j}=0$.

From (3.27),

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

$$\begin{cases}\alpha_i\alpha_j+\alpha_j\alpha_i=2\delta_{ij}\mathbf{I}\\ \beta\alpha_i+\alpha_i\beta=0\\ \beta^2=\mathbf{I}\end{cases} \tag{3.29}$$

$\mathbf{I}$ being the $N\times N$ unit matrix. Because $\underline{\alpha}$ and β were Hermitian, their eigenvalues are real. According to (3.29), the squares of these eigenvalues equal 1. Hence the eigenvalues are ±1. Dirac noticed that (3.29) is satisfied by

$$\beta = \begin{pmatrix}\mathbf{I} & \\ & -\mathbf{I}\end{pmatrix} \tag{3.30}$$

$$\underline{\alpha} = \begin{pmatrix}0 & \underline{\sigma}\\ \underline{\sigma} & 0\end{pmatrix} \tag{3.31}$$

where

$$\mathbf{I}=\begin{pmatrix}1&0\\0&1\end{pmatrix},\quad \sigma_1=\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad \sigma_2=\begin{pmatrix}0&-\mathrm{i}\\ \mathrm{i}&0\end{pmatrix},\quad \sigma_3=\begin{pmatrix}1&0\\0&-1\end{pmatrix} \tag{3.32}$$

3.3 Some properties of the Dirac equation

3.3.1 Solutions with $\pm E$

For a free particle,

$$[h_D,\underline{p}]=0 \tag{3.33}$$

and hence the two operators have simultaneous eigenfunctions $\Psi(\underline{p},x)$:

$$\begin{aligned}\hat{\underline{p}}\Psi &= \underline{p}\Psi\\ h_D\Psi &= E(\underline{p})\Psi\end{aligned} \tag{3.34}$$

Operating again with h_D,

$$h_D^2\Psi = E(\underline{p})^2\Psi \tag{3.35}$$

with the solutions

$$h_D\Psi_\pm = \pm E(\underline{p})\Psi_\pm, \qquad (3.36)$$
$$E(\underline{p}) = \sqrt{c^2p^2+m^2c^4}$$

corresponding to "electron-like" and "positron-like" solutions, respectively. If only one of them existed, h_D would be a multiple of $\mathbf{I}$, and commute with all matrices.

As (3.29) $\Rightarrow$

$$\{\underline{\alpha},\beta\} = 0 \Rightarrow$$
$$\left[\underline{\alpha},\beta\right] = \underline{\alpha}\beta - \beta\underline{\alpha} = -2\beta\underline{\alpha} \Rightarrow$$
$$\left[h_D,\beta\right] = -2c\beta\underline{\alpha}\cdot\underline{p} \neq 0 \Rightarrow$$
$$\exists\beta \text{ so that } [h_d,\beta] \neq 0 \Rightarrow h_D \neq a\mathbf{I} \Rightarrow \exists +E \text{ and } -E$$

3.3.2 Inclusion of electromagnetic fields

Use again the minimal substitution $\Rightarrow$

$$h_D = c\underline{\alpha}\cdot\left(\underline{p}-\frac{e}{c}\underline{A}\right) + V + \beta mc^2 \qquad (3.37)$$

[In Gauss-cgs. In SI, use $\underline{p}-e\underline{A}$. Now $e<0$.] The non-relativistic "diamagnetic" term is recovered here in 2^{nd}-order perturbation theory with intermediate positron-like states. Using the closure,

$$\sum_n |\psi_n^-\rangle\langle\psi_n^-| = 1 \qquad (3.38)$$
$$\Delta E = 2mc^2$$

we get

$$E^{(2)} = \sum_n |\langle\psi^+|h_D|\psi_n^-\rangle|^2/(E^+-E_n^-)$$
$$\cong e^2\langle\psi^+|\underline{A}^2|\psi^+\rangle/2mc^2 \qquad (3.39)$$

the usual diamagnetic term. (Recall that $\frac{1}{2m}(\underline{p}-\frac{e}{c}\underline{A})^2 \rightarrow$ the term $\frac{1}{2m}\frac{e^2}{c^2}\underline{A}^2$.)

3.3.3 Free-particle solutions

In atomic units ($e=m_e=\hbar=4\pi\epsilon_0=1$, $c=137.036$),

$$h_D = c\underline{\alpha}\cdot\underline{p} + c^2\beta \qquad (3.40)$$

Using the Ansatz

$$\Psi = u(p)\mathrm{e}^{\mathrm{i}\underline{p}\cdot\underline{r}} \qquad (3.41)$$

the Dirac equation $h_D\Psi = E\Psi$ gives

$$\begin{bmatrix} -E+c^2 & 0 & cp_z & c(p_x - \mathrm{i}p_y) \\ 0 & -E+c^2 & c(p_x+\mathrm{i}p_y) & -cp_z \\ cp_z & c(p_x-\mathrm{i}p_y) & -E-c^2 & 0 \\ c(p_x+\mathrm{i}p_y) & -cp_z & 0 & -E-c^2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = 0 \tag{3.42}$$

This linear, homogenous equation has solutions if det $[] = 0 \Rightarrow$

$$(E^2 - c^4 - c^2p^2)^2 = 0 \tag{3.43}$$

$$E = \pm c\sqrt{(p^2 + c^2)} = \pm E_p \tag{3.44}$$

Denoting $E_p + c^2$ by A, the spinors become (σ_z= the spin):

	(E, σ_z)			
u_i	$(E_p, \frac{1}{2})$	$(E_p, -\frac{1}{2})$	$(-E_p, \frac{1}{2})$	$(-E_p, -\frac{1}{2})$
u_1	1	0	$-cp_z/A$	$-c(p_x - \mathrm{i}p_y)/A$
u_2	0	1	$-c(p_x + \mathrm{i}p_y)/A$	cp_z/A
u_3	cp_z/A	$c(p_x - \mathrm{i}p_y)/A$	1	0
u_4	$c(p_x + \mathrm{i}p_y)/A$	$-cp_z/A$	0	1

(3.45)

The normalised spinors become

$$u(\underline{p}, E_p) = \sqrt{\frac{E_p+c^2}{2E_p}} \begin{pmatrix} 1 \cdot \binom{\alpha}{\beta} \\ \frac{c(\underline{\sigma}\cdot\underline{p})}{E_p+c^2}\binom{\alpha}{\beta} \end{pmatrix} = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{3.46}$$

$$u(\underline{p}, -E_p) = \sqrt{\frac{E_p+c^2}{2E_p}} \begin{pmatrix} \frac{-c(\underline{\sigma}\cdot\underline{p})}{E_p+c^2}\binom{\alpha}{\beta} \\ 1 \cdot \binom{\alpha}{\beta} \end{pmatrix} = \sqrt{\frac{E_p + c^2}{2E_p}} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \tag{3.47}$$

where $\binom{\alpha}{\beta}$ is either $\binom{1}{0}$ or $\binom{0}{1}$.

The ratio of the norms for $E_p > 0$,

$$\frac{\psi_2^2}{\psi_1^2} = \frac{c^2p^2}{(E+c^2)^2} \cong \frac{c^2p^2}{(2c^2)^2} = \frac{1}{4}(\frac{p}{mc})^2 \approx \frac{1}{4}(\frac{v}{c})^2 \tag{3.48}$$

for small v/c. Therefore ψ_1 and ψ_2 are called the **large** and **small components**, respectively.

For electrons in light atoms, $v \approx 1$ a.u. and this plane-wave estimate gives

$$\frac{1}{4}(\frac{v}{c})^2 \approx \frac{1}{4}(\frac{1}{137})^2 \approx 10^{-5}$$

3.3.4 Probability density

For Ψ, satisfying

$$\mathrm{i}\hbar\frac{\partial}{\partial t} = -\mathrm{i}\hbar c\underline{\alpha}\cdot\nabla\Psi + \beta mc^2\Psi \quad |\Psi^\dagger\times \tag{3.49}$$

where the Hermitian conjugate

$$\Psi^\dagger = (\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*) \tag{3.50}$$

satisfies

$$-\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi^\dagger = \mathrm{i}\hbar c(\nabla\Psi^\dagger)\cdot\underline{\alpha} + mc^2\Psi^\dagger\beta \quad | \times \Psi \tag{3.51}$$

Performing the two multiplications and subtracting, we get

$$\mathrm{i}\hbar\frac{\partial}{\partial t}(\Psi^\dagger\Psi) = -\mathrm{i}\hbar c(\Psi^\dagger\underline{\alpha}\cdot\nabla\Psi + \nabla\Psi^\dagger\cdot\underline{\alpha}\Psi) \tag{3.52}$$

$$\frac{1}{c}\frac{\partial}{\partial t}(\Psi^\dagger\Psi) + \nabla\cdot(\Psi^\dagger\underline{\alpha}\Psi) = 0 \tag{3.53}$$

Comparing with the classical continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\underline{j} = 0 \tag{3.54}$$

we identify

$$\rho = \Psi^\dagger\Psi = (\psi_1^\dagger\psi_1 + \psi_2^\dagger\psi_2 + \ldots) \tag{3.55}$$

$$\underline{j} = c\Psi^\dagger\underline{\alpha}\Psi \tag{3.56}$$

From $\underline{j} = \rho\underline{v}$, the velocity operator (local velocity of the Dirac electron)

$$\underline{v} = c\underline{\alpha} \tag{3.57}$$

3.4 The Pauli limit

By substituting $E = mc^2 + \varepsilon$, the Dirac equation becomes

$$\left[c\underline{\alpha}\cdot\underline{p} + \underbrace{(\beta - 1)}_{=\begin{pmatrix}0 & 0\\ 0 & -2\mathbf{I}\end{pmatrix}} mc^2 + V\right]\Psi = \varepsilon\Psi \tag{3.58}$$

In terms of the two-spinors

$$\begin{cases} c\underline{\sigma}\cdot\underline{p}\psi_2 + V\psi_1 = \varepsilon\psi_1 \\ c\underline{\sigma}\cdot\underline{p}\psi_1 + (-2mc^2 + V)\psi_2 = \varepsilon\psi_2 \Rightarrow \end{cases} \tag{3.59}$$

$$\psi_2 = \frac{c\underline{\sigma}\cdot\underline{p}}{2mc^2+\varepsilon-V}\psi_1 \tag{3.60}$$

$$\approx \frac{\underline{\sigma}\cdot\underline{p}}{2mc}\psi_1 \tag{3.61}$$

(Note that (3.60) is still exact.) Using the above approximation with $\psi_1 = \psi_{\rm nr}, \langle\psi_1|\psi_1\rangle = 1 \Rightarrow$

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \langle\psi_1|\psi_1\rangle + \langle\psi_2|\psi_2\rangle \\ &= 1 + \langle\psi_2|\psi_2\rangle \qquad |\underline{p}\cdot\underline{\sigma}^\dagger\underline{\sigma}\cdot\underline{p} = \underline{p}^2\mathbf{I} \\ &= 1 + \frac{1}{4m^2c^2}\langle\psi_1|\underline{p}^2|\psi_1\rangle \end{aligned}\tag{3.62}$$

Then the expectation value of h_D becomes

$$\begin{aligned}\varepsilon =&\langle\Psi|h_D|\Psi\rangle/\langle\Psi|\Psi\rangle \\ =&\langle\Psi|c\underline{\alpha}\cdot\underline{p}+(\beta-1)mc^2+V|\Psi\rangle/\langle\Psi|\Psi\rangle \\ =&\Big[\langle\psi_1|c\underline{\sigma}\cdot\underline{p}|\psi_2\rangle + \langle\psi_2|c\underline{\sigma}\cdot\underline{p}|\psi_1\rangle - 2mc^2\langle\psi_2|\psi_2\rangle \\ &+\langle\psi_1|V|\psi_1\rangle + \langle\psi_2|V|\psi_2\rangle\Big]/\Big[1+\langle\psi_2|\psi_2\rangle\Big] \\ =&\Big[\frac{1}{2m}\langle\psi_1|p^2|\psi_1\rangle + \underline{\frac{1}{2m}\langle\psi_1|p^2|\psi_1\rangle} - \underline{\frac{2mc^2}{4m^2c^2}}\langle\psi_1|p^2|\psi_1\rangle \\ &+\langle\psi_1|V|\psi_1\rangle + \frac{1}{4m^2c^2}\langle\psi_1|\underline{\sigma}\cdot\underline{p}V\underline{\sigma}\cdot\underline{p}|\psi_1\rangle\Big]/\langle\Psi|\Psi\rangle \\ \varepsilon \cong&\Big[\langle\psi_1|\frac{p^2}{2m}|\psi_1\rangle + \langle\psi_1|V|\psi_1\rangle + \frac{1}{4m^2c^2}\langle\psi_1|\underline{\sigma}\cdot\underline{p}V\underline{\sigma}\cdot\underline{p}|\psi_1\rangle\Big] \\ &\times\Big[1-\frac{1}{4m^2c^2}\langle\psi_1|p^2|\psi_1\rangle\Big] + \mathcal{O}(c^{-4}) \quad \leftarrow 1/c^4 \text{ and higher order terms neglected} \\ =&\varepsilon_{\rm nr} - \frac{1}{8m^3c^2}\langle\psi_1|p^2|\psi_1\rangle\langle\psi_1|p^2|\psi_1\rangle \\ &-\frac{1}{4m^2c^2}\langle\psi_1|V|\psi_1\rangle\langle\psi_1|p^2|\psi_1\rangle \\ &+\frac{1}{4m^2c^2}\langle\psi_1\underline{\sigma}\cdot\underline{p}V\underline{\sigma}\cdot\underline{p}|\psi_1\rangle + \mathcal{O}(c^{-4})\end{aligned}\tag{3.63}$$

Trick 1:

$$\begin{aligned}(\frac{p^2}{2m}+V)\psi_1 &= \varepsilon_{\rm nr}\psi_1, \\ V\psi_1 &= (\varepsilon_{\rm nr}-\frac{p^2}{2m})\psi_1\end{aligned}\tag{3.64}$$

$$\begin{aligned}\varepsilon = \varepsilon_{\rm nr} &- \frac{1}{4m^2c^2}\varepsilon_{\rm nr}\langle\psi_1|p^2|\psi_1\rangle \\ &+ \frac{1}{4m^2c^2}\langle\psi_1|\underline{\sigma}\cdot\underline{p}V\underline{\sigma}\cdot\underline{p}|\psi_1\rangle\end{aligned}\tag{3.65}$$

Trick 2:

$$\sigma_i\sigma_j = \mathrm{i}\delta_{ijk}\sigma_k + \delta_{ij}, \tag{3.66}$$

$$\begin{aligned}
\underline{\sigma}\cdot\underline{p}V\underline{\sigma}\cdot\underline{p} &= \sigma_i p_i V \sigma_j p_j \\
&= \mathrm{i}\delta_{ijk}\sigma_k p_i V p_j + p_k V p_k \\
&= \mathrm{i}\delta_{ijk}\sigma_k\big[(p_i V)p_j + V \underbrace{p_i p_j}_{=0}\big] + p_k V p_k \\
&= \hbar\underline{\sigma}\cdot(\nabla V \times \underline{p}) + p_k V p_k
\end{aligned} \tag{3.67}$$

[Note: $p_ip_j = 0$ as i and j run over all combinations (summation); $p_ip_j - p_jp_i = 0$.]

Here

$$\begin{aligned}
p_k V p_k &= \frac{1}{2}\big[p_k V p_k + p_k V p_k\big] \\
&= \frac{1}{2}\big[Vp^2 + p^2 V\big] + \frac{1}{2}\big[(p_k V)p_k - p_k(p_k V)\big]
\end{aligned} \tag{3.68}$$

where the first term becomes

$$\frac{1}{2}\langle\psi_1|Vp^2 + p^2V|\psi_1\rangle \overset{\mathbf{T1}}{=} \varepsilon_{\mathrm{nr}}\langle\psi_1|p^2|\psi_1\rangle - \frac{1}{2m}\langle\psi_1|p^4|\psi_1\rangle \tag{3.69}$$

and the second term becomes ($\partial_k \equiv \frac{\partial}{\partial k}$)

$$\begin{aligned}
&\frac{1}{2}\langle\psi_1|(p_kV)p_k - p_k(p_kV)|\psi_1\rangle \\
&= \frac{1}{2}\langle\psi_1|(p_kV)|p_k\psi_1\rangle - \frac{1}{2}\langle p_k\psi_1|(p_kV)|\psi_1\rangle \quad \Big| p_k = -\mathrm{i}\hbar\partial_k \\
&= -\frac{\hbar^2}{2}\Big[\int \psi_1^*(\partial_kV)(\partial_k\psi_1) + \int(\partial_k\psi_1)^*(\partial_kV)\psi_1\Big] \\
&= -\frac{\hbar^2}{2}\Big\{\big[\psi_1^*(\partial_kV)\psi_1\big]_{-\infty}^{\infty} \underline{- \int(\partial_k\psi_1^*)(\partial_kV)\psi_1} - \int \psi_1^*(\partial_k^2V)\psi_1 \\
&\qquad \underline{+ \int(\partial_k\psi_1)^*(\partial_kV)\psi_1}\Big\} \\
&= \frac{1}{2}\hbar^2\langle\psi_1|\nabla^2V|\psi_1\rangle \quad \Big|\psi(\infty)\to 0
\end{aligned} \tag{3.70}$$

Assembling the pieces in (3.65), (3.67), (3.69) and (3.70):

$$\begin{aligned}
\varepsilon &= \varepsilon_{\mathrm{nr}} - \frac{1}{4m^2c^2}\,\underline{\varepsilon_{\mathrm{nr}}\langle\psi_1|p^2|\psi_1\rangle} \\
&\quad + \frac{1}{4m^2c^2}\Big[\langle\psi_1|\hbar\underline{\sigma}\cdot(\nabla V\times\underline{p})|\psi_1\rangle \\
&\qquad + \underline{\varepsilon_{\mathrm{nr}}\langle\psi_1|p^2|\psi_1\rangle} - \frac{1}{2m}\langle\psi_1|p^4|\psi_1\rangle \\
&\qquad + \frac{1}{2}\hbar^2\langle\psi_1|\nabla^2V|\psi_1\rangle\Big] \\
&= \varepsilon_{\mathrm{nr}} + \langle h_m + h_{\mathrm{SO}} + h_{\mathrm{d}}\rangle + \mathcal{O}(c^{-4})
\end{aligned} \tag{3.71}$$

$$\begin{cases} \langle h_m \rangle = -\dfrac{1}{8m^3c^2}\langle\psi_1|p^4|\psi_1\rangle & \text{(mass-velocity)} \\ \langle h_{\rm SO} \rangle = \dfrac{\hbar}{4m^2c^2}\langle\psi_1|\underline{\sigma}\cdot(\nabla V\times\underline{p})|\psi_1\rangle & \text{(spin-orbit)} \\ \langle h_{\rm d} \rangle = \dfrac{\hbar^2}{8m^2c^2}\langle\psi_1|\nabla^2 V|\psi_1\rangle & \text{(Darwin)} \end{cases} \tag{3.72}$$

Returning to (3.65), in terms of ψ_2,

$$\varepsilon \cong \varepsilon_{\rm nr} - \varepsilon_{\rm nr} + \langle\psi_2|V|\psi_2\rangle \tag{3.73}$$

For the Coulomb potential of a point charge Z,

$$\nabla^2 V = -Z\nabla^2(\frac{1}{r}) = 4\pi Z \underbrace{\delta(\underline{r})}_{\text{3-D }\delta\text{-func}} \quad \Rightarrow \tag{3.74}$$

$$\begin{aligned} \langle h_{\rm d}\rangle &= \frac{\hbar^2}{8m^2c^2}\langle\psi_1|(4\pi Z)\delta(\underline{r})|\psi_1\rangle \\ &= \frac{\pi\hbar^2 Z}{2m^2c^2}|\psi_1(0)|^2 \end{aligned} \tag{3.75}$$

Example 1: For the 1s state of a hydrogenic atom, in a.u.,

$$\psi_{1\rm s} = \sqrt{\frac{Z^3}{\pi}}\mathrm{e}^{-Zr},$$

$$\begin{aligned} \langle h_{\rm d}\rangle &= \frac{\pi Z}{2c^2}\frac{Z^3}{\pi} = \frac{Z^4}{2c^2} \\ \langle h_m\rangle &= -\frac{1}{8m^3c^2}\langle p^4\rangle = -\frac{1}{2mc^2}\langle(\frac{p^2}{2m})^2\rangle \\ &= -\frac{1}{2mc^2}\langle(E-V)^2\rangle \\ &= -\frac{1}{2mc^2}\Big[(\frac{Z^2}{2})^2 - 2(-\frac{Z^2}{2})\langle V\rangle + \langle V^2\rangle\Big] \end{aligned}$$

As

$$\begin{aligned} \langle V\rangle &= \frac{Z^3}{\pi}(4\pi)\int_0^\infty \mathrm{e}^{-2Zr}\Big(\frac{-Z}{r}\Big)r^2\mathrm{d}r \\ &= -4Z^4\int_0^\infty \mathrm{e}^{-2Zr}r\mathrm{d}r = (-4Z^4)\frac{1!}{(2Z)^2} = -Z^2, \\ \langle V^2\rangle &= +4Z^3\int_0^\infty \mathrm{e}^{-2Zr}\Big(\frac{Z}{r}\Big)^2 r^2\mathrm{d}r = 4Z^5\frac{0!}{2Z} = 2Z^4, \\ \langle h_m\rangle &= -\frac{1}{2mc^2}Z^4\Big[\frac{1}{4} - 1 + 2\Big] = -\frac{5}{8c^2}Z^4 \\ \langle h_{\rm SO}\rangle &= 0 \end{aligned}$$

Summing up,

$$E_{\mathrm{rel}} = \langle h_m + h_{\mathrm{d}} \rangle = \frac{Z^4}{c^2}(-\frac{5}{8} + \frac{4}{8}) = \underline{-\frac{Z^4}{8c^2}} \tag{3.76}$$

3.5 Central fields

We now return to the full Dirac equation with a local potential $V(\underline{r}) = V(r)$. As

$$\left[\underline{l}, h_{\mathrm{D}}\right] = \mathrm{i}c\underline{\alpha} \times \underline{p} \neq 0 \tag{3.77}$$

$$\left[\underline{s}, h_{\mathrm{D}}\right] = -\mathrm{i}c\underline{\alpha} \times \underline{p} \neq 0 \tag{3.78}$$

neither $\underline{l}$ or $\underline{s}$ can have simultaneous eigenstates with h_{D} but their sum

$$\underline{j} = \underline{l} + \underline{s} \tag{3.79}$$

can because

$$[\underline{j}, \underline{h_{\mathrm{D}}}] = 0 \tag{3.80}$$

Details:

$$\underline{l} = \underline{r} \times \underline{p}$$

$$\left[\underline{l}, \beta\right] = 0, \quad \left[\underline{l}, V\right] = 0, \quad \left[\underline{l}, \underline{\alpha} \cdot \underline{p}\right] \neq 0$$

Consider the component l_1:

$$[l_1, \underline{\alpha} \cdot \underline{p}] = \alpha_1 \underbrace{[l_1, p_1]}_{=0} + \alpha_2 [l_1, p_2] + \alpha_3 [l_1, p_3]$$

$$\underline{l} = \underline{r} \times \underline{p} = -\mathrm{i} \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ x & y & z \\ \partial_x & \partial_y & \partial_z \end{vmatrix} \Rightarrow l_1 = -\mathrm{i}(y\partial_z - z\partial_y)$$

$$\begin{aligned}
[l_1, p_2] &= (-\mathrm{i})^2 [y\partial_z - z\partial_y, \partial_y] \\
&= -\Big(\underline{y\frac{\partial^2}{\partial y \partial z}} \underline{\underline{-z\frac{\partial^2}{\partial y^2}}} - \partial_z \underline{-y\frac{\partial^2}{\partial y \partial z}} \underline{\underline{+z\frac{\partial^2}{\partial y^2}}} \Big) \\
&= \frac{\partial}{\partial z} = \mathrm{i}p_3, \text{ cycl.} \Rightarrow \\
[l_1, \underline{\alpha} \cdot \underline{p}] = \alpha_2 \mathrm{i} p_3 - \alpha_3 \mathrm{i} p_2 &= \mathrm{i}(\underline{\alpha} \times \underline{p})_1, \text{ cycl.} \Rightarrow \\
[l, \underline{\alpha} \cdot \underline{p}] &= \mathrm{i}\ \underline{\alpha} \times \underline{p} \quad \square
\end{aligned}$$

Similarly for $[\underline{\sigma}, \underline{\alpha} \cdot \underline{p}]$ (=with spin),

$$\begin{aligned}
[\sigma_1, \underline{\alpha} \cdot \underline{p}] &= \begin{pmatrix} \sigma_1 & 0 \\ 0 & \sigma_1 \end{pmatrix} \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \\ \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \\ \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} \begin{pmatrix} \delta_1 & 0 \\ 0 & \delta_1 \end{pmatrix} \\
&= \begin{pmatrix} 0 & \sigma_1 \underline{\sigma} \cdot \underline{p} \\ \sigma_1 \underline{\sigma} \cdot \underline{p} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \underline{\sigma} \cdot \underline{p} \sigma_1 \\ \underline{\sigma} \cdot \underline{p} \sigma_1 & 0 \end{pmatrix} \\
&= \begin{pmatrix} 0 & [\sigma_1, \underline{\sigma} \cdot \underline{p}] \\ [\sigma_1, \underline{\sigma} \cdot \underline{p}] & 0 \end{pmatrix}
\end{aligned}$$

As $[\sigma_1, \sigma_2] = 2\mathrm{i}\sigma_3$, cycl.,

$$\begin{aligned}
[\sigma_1, \underline{\sigma} \cdot \underline{p}] &= \sigma_1(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3) \\
&\quad -(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)\sigma_1 \\
&= p_1 + \sigma_1\sigma_2 p_2 + \sigma_1\sigma_3 p_3 \\
&\quad -p_1 - \sigma_2\sigma_1 p_2 - \sigma_3\sigma_1 p_3 \\
&= \underbrace{[\sigma_1, \sigma_2]}_{2\mathrm{i}\sigma_3} p_2 - \underbrace{[\sigma_3, \sigma_1]}_{2\mathrm{i}\sigma_2} p_3 \\
&= 2\mathrm{i}[\sigma_3 p_2 - \sigma_2 p_3] = 2\mathrm{i}(p_2\sigma_3 - p_3\sigma_2) \\
&= 2\mathrm{i}(\underline{p} \times \underline{\sigma}), \text{ cycl.} \Rightarrow \\
[\underline{\sigma}, \underline{\alpha} \cdot \underline{p}] &= 2\mathrm{i}\underline{p} \times \underline{\alpha} = -2\mathrm{i}\underline{\alpha} \times \underline{p} \quad \square
\end{aligned}$$

Define

$$\underline{s} = \frac{1}{2}\hbar\underline{\sigma} \tag{3.81}$$

$\Rightarrow$ (3.79)

As a further detail, consider the operator

$$K = (V\sigma \cdot \underline{l} + 1)\beta \tag{3.82}$$

We shall show that

$$[K, \underline{j}] = 0 \tag{3.83}$$

$$[K, h_\mathrm{D}] = 0 \tag{3.84}$$

In other words, K, h_D, $\underline{j}^2$ and j_z can have simultaneous eigenstates.

Theorem *a*:

For two vectors $\underline{A}$ and $\underline{B}$ which commute with $\underline{\sigma}$ but not necessarily with each other,

$$(\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = \underline{A} \cdot \underline{B} + \mathrm{i}\underline{\sigma} \cdot (\underline{A} \times \underline{B}) \tag{3.85}$$

Proof:
The $\underline{\sigma}$ matrices simultaneously satisfy

$$\left.\begin{aligned}[\sigma_i, \sigma_k] = \sigma_i\sigma_k - \sigma_k\sigma_i = 2\mathrm{i}\delta_{ikl}\delta_l \\ \{\sigma_i, \sigma_k\} = \sigma_i\sigma_k + \sigma_k\sigma_i = 2\delta_{ik}\end{aligned}\right\} \Rightarrow$$

$$\sigma_i^2 = 1 \qquad (i = k) \tag{3.86}$$

$$\sigma_i\sigma_k = \mathrm{i}\delta_{ikl}\sigma_l \quad (i \neq k) \tag{3.87}$$

$$\begin{aligned}(\underline{\sigma}\cdot\underline{A})(\underline{\sigma}\cdot\underline{B}) &= \sigma_i A_i \sigma_j B_j \\ &\overset{[\underline{\sigma},\underline{A}]=0}{=} \underbrace{\sigma_i\sigma_i}_{=1} A_i B_i + \sum_{i\neq j} \sigma_i\sigma_j A_i B_j \\ &= \underline{A}\cdot\underline{B} + \sum_{i<j} \underbrace{\sigma_i\sigma_j}_{\mathrm{i}\delta_{ijk}\delta_k} \underbrace{(A_iB_j - A_jB_i)}_{(\underline{A}\times\underline{B})_k} \\ &= \underline{A}\cdot\underline{B} + \mathrm{i}\underline{\sigma}\cdot\underline{A}\times\underline{B} \quad \square\end{aligned} \tag{3.88}$$

The equation holds for both two- and four-component $\underline{\sigma}$

Theorem *b*:

$$(\underline{\alpha}\cdot\underline{A})(\underline{\alpha}\cdot\underline{B}) = (\underline{\sigma}\cdot\underline{A})(\underline{\sigma}\cdot\underline{B}) \tag{3.89}$$

Proof:

$$\begin{pmatrix} 0 & \underline{\sigma}\cdot\underline{A} \\ \underline{\sigma}\cdot\underline{A} & 0\end{pmatrix}\begin{pmatrix} 0 & \underline{\sigma}\cdot\underline{B} \\ \underline{\sigma}\cdot\underline{B} & 0\end{pmatrix} = \begin{pmatrix}\underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{B} & 0 \\ 0 & \underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{B}\end{pmatrix}$$
$$= (\underline{\sigma}^4\cdot\underline{A})(\underline{\sigma}^4\cdot\underline{B}) \quad \square$$

$\underline{\sigma}^4$ denotes a four dimensional σ.

Theorem *c*:

$$(\underline{\alpha}\cdot\underline{A})(\underline{\alpha}\cdot\underline{B}) = -\gamma_5\underline{A}\cdot\underline{B} + \mathrm{i}\underline{\alpha}\cdot(\underline{A}\times\underline{B}), \tag{3.90}$$

where

$$\gamma_5 = \gamma_1\gamma_2\gamma_3\gamma_4. \tag{3.91}$$

Proof:
We use the representation

$$\begin{aligned}\underline{\gamma} = \mathrm{i}\underline{\alpha}\beta &= \begin{pmatrix} 0 & -\mathrm{i}\underline{\sigma} \\ \mathrm{i}\underline{\sigma} & 0 \end{pmatrix} \\ \gamma_5 = \quad \beta &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\end{aligned}$$

Then, recalling that $\mathrm{i}^3 = -\mathrm{i}$,

$$\begin{aligned}\gamma_5 &= -\mathrm{i}\underbrace{\begin{pmatrix} 0 & -\sigma_1 \\ \sigma_1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -\sigma_2 \\ \sigma_2 & 0 \end{pmatrix}} \quad \underbrace{\begin{pmatrix} 0 & -\sigma_3 \\ \sigma_3 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} \\ &= -\mathrm{i}\begin{pmatrix} -\sigma_1\sigma_2 & 0 \\ 0 & -\sigma_1\sigma_2 \end{pmatrix} \qquad\qquad \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix} \\ &= \mathrm{i}\begin{pmatrix} 0 & \sigma_1\sigma_2\sigma_3 \\ \sigma_1\sigma_2\sigma_3 & 0 \end{pmatrix} \qquad \Big| \sigma_1\sigma_2 = \mathrm{i}\sigma_3 \\ &= -\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{aligned} \tag{3.92}$$

Then

$$\begin{cases} \gamma_5\underline{\alpha} = -\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = -\begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = -\underline{\sigma}^4 \\ \underline{\alpha}\gamma_5 = -\begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = -\underline{\sigma}^4, \end{cases} \tag{3.93}$$

$$\begin{cases} \gamma_5\underline{\sigma}^4 = -\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix} = -\begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = -\underline{\alpha} \\ \underline{\sigma}^4\gamma_5 = -\begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -\begin{pmatrix} 0 & \underline{\sigma} \\ \underline{\sigma} & 0 \end{pmatrix} = -\underline{\alpha}. \end{cases} \tag{3.94}$$

Multiplying **Theorem *a***, (3.85), from left by $-\gamma_5$:

$$(\underbrace{-\gamma_5\underline{\sigma}^4}_{-\underline{\alpha}} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = -\gamma_5 \underline{A} \cdot \underline{B} + \mathrm{i}(\underbrace{-\gamma_5\underline{\sigma}^4}_{\underline{\alpha}}) \cdot \underline{A} \times \underline{B} \quad \square$$

Theorem *d*:
Because

$$\begin{aligned}\underline{l} &= \underline{r} \times \underline{p} \quad (\perp \underline{p}), \\ \underline{p} \cdot \underline{l} &= \underline{l} \cdot \underline{p} = 0. \end{aligned} \tag{3.95}$$

Furthermore,

$$\underline{l} \times \underline{p} + \underline{p} \times \underline{l} = 2\mathrm{i}\underline{p} \tag{3.96}$$

Proof:

$$\underline{A} \times \underline{B} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$\begin{aligned} \underline{A} \times \underline{B} + \underline{B} \times \underline{A} = & \ \hat{\imath}\big([A_y, B_z] - [A_z, B_y]\big) \\ & + \hat{\jmath}\big(-[A_z, B_x] + [A_x, B_z]\big) \\ & + \hat{k}\big([A_x, B_y] - [A_y, B_x]\big) \end{aligned}$$

$$\begin{aligned} (\underline{l} \times \underline{p} + \underline{p} \times \underline{l})_x &= [l_y, p_z] - [l_z, p_y] \\ &= -\big[(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})(\frac{\partial}{\partial z}) - (\frac{\partial}{\partial z})(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})\big] \\ & \quad + \big[(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})(\frac{\partial}{\partial y}) - (\frac{\partial}{\partial y})(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})\big] \\ &= \frac{\partial}{\partial x} + \frac{\partial}{\partial x} = 2\mathrm{i}p_x, \quad \text{cycl.}\square \end{aligned}$$

Then the anticommutator

$$\begin{aligned} \{\underline{\sigma} \cdot \underline{l}, \underline{\alpha} \cdot \underline{p}\} &= (\underline{\sigma} \cdot \underline{l})(\underline{\alpha} \cdot \underline{p}) + (\underline{\alpha} \cdot \underline{p})(\underline{\sigma} \cdot \underline{l}) \\ &\overset{(3.90)}{=} -\gamma_5[\underbrace{\underline{l} \cdot \underline{p}}_{=0} + \underbrace{\underline{p} \cdot \underline{l}}_{=0} + \mathrm{i}\underline{\sigma}^4 \cdot \underbrace{(\underline{l} \times \underline{p} + \underline{p} \times \underline{l})}_{2\mathrm{i}\underline{p}}] \\ &= -2\underline{\alpha} \cdot \underline{p} \end{aligned} \tag{3.97}$$

Theorem *e*:

$$[K, \underline{\alpha} \cdot \underline{p}] = [\beta\underline{\sigma} \cdot \underline{l}, \underline{\alpha} \cdot \underline{p}] + [\beta, \underline{\alpha} \cdot \underline{p}]$$

Because

$$\begin{aligned} -\underline{\alpha}\beta &= \beta\underline{\alpha}, \\ -\underline{\alpha} \cdot \underline{p}\beta\underline{\sigma} \cdot \underline{l} &= \beta(\underline{\alpha} \cdot \underline{p})\underline{\sigma} \cdot \underline{l} \Rightarrow \\ [K, \underline{\alpha} \cdot \underline{p}] &= \beta \underbrace{\{\underline{\sigma} \cdot l, \underline{\alpha} \cdot \underline{p}\}}_{-2\underline{\alpha} \cdot \underline{p}} + 2\beta\underline{\alpha} \cdot \underline{p} = 0 \end{aligned} \tag{3.98}$$

Theorem *f*:
As

$$[\beta, \beta] = 0, \quad [K, \beta] = 0. \tag{3.99}$$

Theorem e+f $\Rightarrow$

$$[K, h_{\mathrm{D}}] = 0 \tag{3.100}$$

It remains to show that $[K, \underline{j}] = 0$.

Theorem *g*:

From theorem a, (3.85), taking $\underline{B}$ as an arbitrary vector, commuting with $\underline{A}$,

$$(\underline{\sigma} \cdot \underline{A})\underline{\sigma} = \underline{A} + \mathrm{i}\underline{\sigma} \times \underline{A}, \tag{3.101}$$

where we used

$$\underline{\sigma} \cdot \underline{A} \times \underline{B} = \underline{\sigma} \times \underline{A} \cdot \underline{B}.$$

Similarly, letting $\underline{A}$ be arbitrary,

$$\underline{\sigma}(\underline{\sigma} \cdot \underline{B}) = \underline{B} + \mathrm{i}\underline{B} \times \underline{\sigma}. \tag{3.102}$$

Letting then $\underline{A} = \underline{B} = \underline{l}$ and subtracting (3.101)-(3.102),

$$\begin{aligned}[\underline{\sigma} \cdot \underline{l}, \underline{\sigma}] &= \mathrm{i}\underline{\sigma} \times \underline{l} - \mathrm{i}\underline{l} \times \underline{\sigma} \\ &= 2\mathrm{i}\underline{\sigma} \times \underline{l}\end{aligned} \tag{3.103}$$

Theorem *h*:

Let $\underline{A}$ commute with $\underline{l}$. Then

$$\begin{aligned}[\underline{A} \cdot \underline{l}, \underline{l}] &= \sum_{i=1}^{3}\sum_{j=1}^{3}[A_i l_i l_j \hat{x}_j - l_j \hat{x}_j A_i l_i] \\ &= \sum_{i,j} A_i \hat{x}_j \underbrace{[l_i l_j - l_j l_i]}_{\delta_{ijk}\mathrm{i}l_k = -\mathrm{i}\delta_{jik} l_k} \\ &= -\mathrm{i}\underline{A} \times \underline{l}\end{aligned} \tag{3.104}$$

Letting $\underline{A} = \underline{\sigma}$,

$$[\underline{\sigma} \cdot \underline{l}, \underline{l}] = -\mathrm{i}\underline{\sigma} \times \underline{l} \tag{3.105}$$

Theorem *i*:

The desired commutator (note: $[K, \beta] = 0$)

$$\begin{aligned}[K, \underline{j}] &= [\beta\underline{\sigma} \cdot \underline{l}, \underline{l} + \frac{1}{2}\underline{\sigma}] \\ &= \beta[\underline{\sigma} \cdot \underline{l}, \underline{l}] + \frac{1}{2}\beta[\underline{\sigma} \cdot \underline{l}, \underline{\sigma}] \\ &= \beta(-\mathrm{i}\underline{\sigma} \times \underline{l}) + \frac{1}{2}\beta(2\mathrm{i}\underline{\sigma} \times \underline{l}) = 0 \quad \square\end{aligned} \tag{3.106}$$

Summarizing,

$$\boxed{[K,\underline{j}] = [K,h_{\mathrm{D}}] = [\underline{j},h_{\mathrm{D}}] = 0} \tag{3.107}$$

Denote the eigenvalues of K by $-\kappa$:

$$K\chi_\kappa^m = -\kappa\chi_\kappa^m, \tag{3.108}$$

where the $\underline{\sigma}$ (in K) are 2-component ones, and the 2-component spinors

$$\chi_\kappa^m \equiv |lsjm\rangle \tag{3.109}$$

The quantum number κ carries both j and l:

$$\kappa = \begin{cases} -l-1, & j = l+\frac{1}{2} \quad \text{(state '}l\text{')} \\ l, & j = l-\frac{1}{2} \quad \text{(state '}l^*\text{' or '}\bar{l}\text{').} \end{cases} \tag{3.110}$$

The lowest values are

$$\begin{array}{ccccccccc} \kappa & = & -1 & 1 & -2 & 2 & -3 & 3 & -4 & \ldots \\ & & s_{1/2} & p_{1/2} & p_{3/2} & d_{3/2} & d_{5/2} & f_{5/2} & f_{7/2} & \ldots \\ & & \mathrm{s} & \mathrm{p}^* & \mathrm{p} & \mathrm{d}^* & \mathrm{d} & \mathrm{f}^* & \mathrm{f} & \ldots \end{array} \tag{3.111}$$

From

$$\begin{aligned} \underline{j} &= \underline{l} + \underline{s}, \\ \underline{j}^2 &= \underline{l}^2 + 2\underline{l}\cdot\underline{s} + \underline{s}^2 \Rightarrow \\ \underline{l}\cdot\underline{s} &\equiv \frac{1}{2}[\underline{j}^2 - \underline{l}^2 - \underline{s}^2] \end{aligned} \tag{3.112}$$

Consequently

$$\begin{aligned} K &= \underline{\sigma}\cdot\underline{l} + 1 \\ &= \underline{j}^2 - \underline{l}^2 - \underline{s}^2 + 1 \\ K\chi_\kappa^m &= K|lsjm\rangle = [j(j+1) - l(l+1) - \underbrace{s(s+1)}_{\frac{3}{4}} + 1]\chi_\kappa^m \\ &= [(j+\frac{1}{2})^2 - l(l+1)]\chi_\kappa^m \\ &= -\kappa\chi_\kappa^m, \end{aligned}$$

whence

$$\kappa = l(l+1) - (j+\frac{1}{2})^2, \tag{3.113}$$

as can be verified from Table (3.111).

For the 4-component case we introduce the Ansatz

$$\Psi = \Psi_\kappa^m = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} g(r)\chi_\kappa^m \\ \mathrm{i}f(r)\chi_{-\kappa}^m \end{pmatrix} = \frac{1}{r}\begin{pmatrix} P(r)\chi_\kappa^m \\ \mathrm{i}Q(r)\chi_{-\kappa}^m \end{pmatrix} \tag{3.114}$$

for which, indeed

$$K\Psi_\kappa^m = \begin{pmatrix} \underline{\sigma}\cdot\underline{l}+1 & 0 \\ 0 & -\underline{\sigma}\cdot\underline{l}-1 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = -\kappa\Psi_\kappa^m. \tag{3.115}$$

This Ψ is an eigenfunction to $h_\mathrm{D}, K, \underline{j}^2$ and j_z.

3.5.1 The radial Part

From

$$\begin{aligned} \underline{A}\times(\underline{B}\times\underline{C}) &= (\underline{A}\cdot\underline{C})\underline{B} - (\underline{A}\cdot\underline{B})\underline{C}, \\ (\underline{A}\cdot\underline{B})\underline{C} &= (\underline{A}\cdot\underline{C})\underline{B} - \underline{A}\times(\underline{B}\times\underline{C}), \end{aligned} \tag{3.116}$$

with

$$\begin{aligned} \underline{A} &= \underline{B} = \underline{\hat{r}} = (\hat{\imath},\hat{\jmath},\hat{k}), \quad \underline{C} = \nabla, \\ \nabla &= \underline{\hat{r}}(\hat{r}\cdot\nabla) - \underline{\hat{r}}\times(\underline{\hat{r}}\times\nabla) \\ &= \hat{e}_r\frac{\partial}{\partial r} - \mathrm{i}\frac{\hat{e}_r}{r}\times\underline{l}. \end{aligned} \tag{3.117}$$

Here $\hat{e}_r$ is the unit vector along the radius (and $\underline{l} = \underline{r}\times\underline{p}$). Consequently the kinetic energy term

$$\underline{\alpha}\cdot\underline{p} = -\mathrm{i}\alpha_r\frac{\partial}{\partial r} - \frac{1}{r}\underline{\alpha}\cdot\hat{r}\times\underline{l}. \tag{3.118}$$

Denoting

$$\underline{\sigma} = \underline{\sigma}^4 = \begin{pmatrix} \underline{\sigma} & 0 \\ 0 & \underline{\sigma} \end{pmatrix}$$

and using

$$\underline{\alpha}\cdot\underline{A}\,\underline{\alpha}\cdot\underline{B} = \underline{A}\cdot\underline{B} + \mathrm{i}\underline{\sigma}\cdot\underline{A}\times\underline{B} \qquad [3.88\text{-}3.89]$$

for $\underline{A} = \underline{\hat{r}}$ and $\underline{B} = \underline{l}$,

$$\underbrace{(\underline{\alpha}\cdot\underline{\hat{r}})}_{\alpha_r}(\underline{\alpha}\cdot\underline{l}) = \underbrace{\underline{\hat{r}}\cdot\underline{l}}_{=0} + \mathrm{i}\underline{\sigma}\cdot\underline{\hat{r}}\times\underline{l} \tag{3.119}$$

($\underline{\hat{r}}\cdot\underline{l} = 0$ as the angular momentum has no radial components.) Multiplying by $\mathrm{i}\gamma_5$ and recalling that $\underline{\alpha} = -\gamma_5\underline{\sigma}$,

$$\begin{aligned} \mathrm{i}\gamma_5\alpha_r(\underline{\alpha}\cdot\underline{l}) &= -\gamma_5\underline{\sigma}\cdot\underline{r}\times\underline{l} \\ \mathrm{i}\gamma_5\sigma_r(\underline{\sigma}\cdot\underline{l}) &= \underline{\alpha}\cdot\underline{r}\times\underline{l}. \end{aligned} \tag{3.120}$$

$$\begin{aligned}\underline{\alpha}\cdot\underline{p} &= \mathrm{i}\gamma_5\sigma_r\frac{\partial}{\partial r}-\frac{1}{r}\mathrm{i}\gamma_5\sigma_r(\underline{\sigma}\cdot\underline{l}) \\ &= \mathrm{i}\gamma_5\sigma_r[\frac{\partial}{\partial r}-\frac{1}{r}\underline{\sigma}\cdot\underline{l}]. \end{aligned} \tag{3.121}$$

Thus the Dirac Hamiltonian

$$\begin{aligned} h_\mathrm{D} &= c\underline{\alpha}\cdot\underline{p}+\beta mc^2+V(r) \\ &= \mathrm{i}c\gamma_5\sigma_r\Big[\frac{\partial}{\partial r}-\frac{1}{r}\underline{\sigma}\cdot\underline{l}\Big]+\beta mc^2+V(r). \end{aligned} \tag{3.122}$$

with

$$\begin{aligned} K=\beta(\underline{\sigma}\cdot\underline{l}+1), &\quad \beta^2=1\Rightarrow \\ \underline{\sigma}\cdot\underline{l}=\beta K-1, & \end{aligned} \tag{3.123}$$

$$\boxed{h_\mathrm{D}=\mathrm{i}c\gamma_5\sigma_r\Big[\tfrac{\partial}{\partial r}+\tfrac{1}{r}-\tfrac{\beta K}{r}\Big]+\beta mc^2+V(r)} \tag{3.124}$$

Theorem *a*:

$$\sigma_r^2=1 \tag{3.125}$$

(like in the cartesian case, $\sigma_i^2=1$)

Proof:

$$\begin{aligned} \sigma_r &= \underline{\sigma}\cdot\hat{r}=\sum_i\sigma_i\frac{1}{r}(\sigma_x x+\sigma_y y+\sigma_z z) \\ \sigma_r^2 &= frac1r^2\Big[\sum_i\underbrace{\sigma_i^2}_{=1}x_i^2+\sum_{i>j}x_ix_j\underbrace{(\sigma_i\sigma_j+\sigma_j\sigma_i)}_{=0}\Big]=1 \quad \square \end{aligned}$$

Theorem *b*:

$$\{K,\sigma_r\}=0 \tag{3.126}$$

Proof:

$$\begin{aligned} K &= \beta(\underline{\sigma}\cdot\underline{l}+1) \\ [\beta,\underline{\sigma}\cdot\underline{l}] &= 0 \\ [\beta,\sigma_r] &= 0 \end{aligned}$$

(3.85) $\Rightarrow$

$$\left.\begin{array}{l}(\underline{\sigma}\cdot\underline{l})(\underline{\sigma}\cdot\hat{\underline{r}})=\underline{l}\cdot\hat{\underline{r}}+\mathrm{i}\underline{\sigma}\cdot(\underline{l}\times\hat{\underline{r}})\\(\underline{\sigma}\cdot\hat{\underline{r}})(\underline{\sigma}\cdot\underline{l})=\hat{\underline{r}}\cdot\underline{l}+\mathrm{i}\underline{\sigma}\cdot(\hat{\underline{r}}\times\underline{l})\end{array}\right\}\Rightarrow$$

$$\begin{aligned}\{K,\sigma_r\}&=\{\beta(\underline{\sigma}\cdot\underline{l}+1),\underline{\sigma}\cdot\hat{\underline{r}}\}\\&=\beta\mathrm{i}\underline{\sigma}\cdot\underbrace{(\underline{l}\times\hat{\underline{r}}+\hat{\underline{r}}\times\underline{l})}_{2\mathrm{i}\hat{\underline{r}}}+2\beta\underline{\sigma}\cdot\hat{\underline{r}}\\&=0\quad\square\end{aligned}$$

Theorem *c*:

$$\sigma_r\chi_\kappa^m=-\chi_{-\kappa}^m\tag{3.127}$$

Proof:

$$\begin{aligned}K(\sigma_r\chi_\kappa^m)&=-\sigma_r(K\chi_\kappa^m)\\&=\kappa(\sigma_r\chi_\kappa^m)\end{aligned}\tag{3.128}$$

Thus the eigenvalue of $\sigma_r\chi_\kappa^m$ is κ, while

$$K\chi_\kappa^m=-\kappa\chi_\kappa^m\qquad[3.108]$$

whence

$$\sigma_r\chi_\kappa^m=-\chi_{-\kappa}^m\quad\square$$

Recalling now that

$$\gamma_5=-\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad\beta=\begin{pmatrix}1&0\\0&-1\end{pmatrix},$$

(3.124) becomes

$$\left[\mathrm{i}c(-)\begin{pmatrix}0&1\\1&0\end{pmatrix}\sigma_r\left(\frac{\partial}{\partial r}+\frac{1}{r}-\frac{1}{r}\begin{pmatrix}1&0\\0&-1\end{pmatrix}K^4\right)+\begin{pmatrix}1&0\\0&-1\end{pmatrix}mc^2+V-E\right]\begin{pmatrix}g\chi_\kappa^m\\\mathrm{i}f\chi_{-\kappa}^m\end{pmatrix}=0.$$

where K^4 denotes the four-dimensional K-operator. Recalling

$$K^4\begin{pmatrix}g\chi_\kappa\\\mathrm{i}f\chi_{-\kappa}\end{pmatrix}=(-\kappa)\begin{pmatrix}g\chi_\kappa\\\mathrm{i}f\chi_{-\kappa}\end{pmatrix},$$

$$-\mathrm{i}c\begin{pmatrix}0&1\\1&0\end{pmatrix}\sigma_r\left[\Big(\frac{\partial}{\partial r}+\frac{1}{r}\Big)\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}-\frac{1}{r}\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}\right]$$
$$+mc^2\begin{pmatrix}g\chi_\kappa\\ -\mathrm{i}f\chi_{-\kappa}\end{pmatrix}+(V-E)\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}=0.$$

Then operate with σ_r using (3.127):

$$-\mathrm{i}c\begin{pmatrix}0&1\\1&0\end{pmatrix}\left[-\Big(\frac{\partial}{\partial r}+\frac{1}{r}\Big)\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}+\frac{1}{r}\begin{pmatrix}g\chi_{-\kappa}\\ \mathrm{i}f\chi_{\kappa}\end{pmatrix}\right]$$
$$+mc^2\begin{pmatrix}g\chi_\kappa\\ -\mathrm{i}f\chi_{-\kappa}\end{pmatrix}+(V-E)\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}=0,$$

$$\mathrm{i}c\Big(\frac{\partial}{\partial r}+\frac{1}{r}\Big)\begin{pmatrix}\mathrm{i}f\chi_\kappa\\ g\chi_{-\kappa}\end{pmatrix}-\frac{\mathrm{i}c}{r}\begin{pmatrix}\mathrm{i}f\kappa\chi_\kappa\\ -g\kappa\chi_{-\kappa}\end{pmatrix}$$
$$+mc^2\begin{pmatrix}g\chi_\kappa\\ -\mathrm{i}f\chi_{-\kappa}\end{pmatrix}+(V-E)\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}=0.$$

For the two components

$$\mathrm{i}c\left(\frac{\partial}{\partial r}+\big(1\{\mp\}\kappa\big)\frac{1}{r}\right)\begin{pmatrix}\mathrm{i}f\chi_\kappa\\ g\chi_{-\kappa}\end{pmatrix}+\Big[\{\pm\}mc^2+V-E\Big]\begin{pmatrix}g\chi_\kappa\\ \mathrm{i}f\chi_{-\kappa}\end{pmatrix}=0 \quad (3.129)$$

Dividing by the angular part and i we get

$$\begin{cases}-c\Big(\dfrac{\partial}{\partial r}+\dfrac{1-\kappa}{r}\Big)f+(mc^2+V-E)g &=0\\ c\Big(\dfrac{\partial}{\partial r}+\dfrac{1+\kappa}{r}\Big)g+(-mc^2+V-E)f &=0\end{cases} \quad (3.130)$$

Introducing

$$\begin{cases}P=rg\\ Q=rf\end{cases}, \quad (3.131)$$

$$\begin{cases}\dfrac{\mathrm{d}P}{\mathrm{d}r}=g+r\dfrac{\mathrm{d}g}{\mathrm{d}r}\\ \dfrac{\mathrm{d}Q}{\mathrm{d}r}=f+r\dfrac{\mathrm{d}f}{\mathrm{d}r}\end{cases}\Rightarrow\begin{cases}\dfrac{\mathrm{d}g}{\mathrm{d}r}=\dfrac{1}{r}\dfrac{\mathrm{d}P}{\mathrm{d}r}-\dfrac{P}{r^2}\\ \dfrac{\mathrm{d}f}{\mathrm{d}r}=\dfrac{1}{r}\dfrac{\mathrm{d}Q}{\mathrm{d}r}-\dfrac{Q}{r^2}\end{cases} \quad (3.132)$$

$$\begin{cases}\dfrac{1}{r}\Big(\dfrac{\mathrm{d}Q}{\mathrm{d}r}-\dfrac{Q}{r}+(1-\kappa)\dfrac{Q}{r}\Big)+\Big(-mc+\dfrac{E-V}{c}\Big)\dfrac{P}{r}=0\\ \dfrac{1}{r}\Big(\dfrac{\mathrm{d}P}{\mathrm{d}r}-\dfrac{P}{r}+(1+\kappa)\dfrac{P}{r}\Big)+\Big(-mc+\dfrac{V-E}{c}\Big)\dfrac{Q}{r}=0\end{cases} \quad (3.133)$$

$$\boxed{\begin{cases} \dfrac{\mathrm{d}P}{\mathrm{d}r} + \kappa\dfrac{P}{r} + \Big(-mc + \dfrac{V-E}{c}\Big)Q = 0 \\ \dfrac{\mathrm{d}Q}{\mathrm{d}r} - \kappa\dfrac{Q}{r} + \Big(-mc + \dfrac{E-V}{c}\Big)P = 0 \end{cases}} \tag{3.134}$$

3.5.2 Non-relativistic limit

Let the potential $|V| \ll E \approx mc^2$. For the $E > 0$ states

$$-mc + \frac{V-E}{c} \approx -2mc \Rightarrow$$

$$Q \approx \frac{1}{2mc}\Big(\frac{\mathrm{d}P}{\mathrm{d}r} + \kappa\frac{P}{r}\Big) \Rightarrow \tag{3.135}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}r} = \frac{1}{2mc}\Big(P'' + \frac{\kappa}{r}P' - \frac{\kappa}{r^2}P\Big) \tag{3.136}$$

Denoting $E = mc^2 + \varepsilon$, for bound states $\varepsilon < 0$,

$$P'' + \underline{\frac{\kappa}{r}P'} - \frac{\kappa}{r^2}P - \frac{\kappa}{r} \times \Big(\underline{P'} + \kappa\frac{P}{r}\Big) + (2mc)\Big(-mc + \frac{mc^2 + \varepsilon - V}{c}\Big)P = 0.$$

$$P'' - \frac{\kappa(\kappa+1)}{r^2}P + 2m(\varepsilon - V)P = 0. \tag{3.137}$$

$$\kappa = \begin{cases} -l-1 \\ l \end{cases} \Rightarrow \kappa(\kappa+1) = \begin{cases} (-l-1)(-l) \\ l(l+1) \end{cases} = l(l+1) \tag{3.138}$$

$\Rightarrow$

$$P'' - \frac{l(l+1)}{r^2}P + 2m(\varepsilon - V)P = 0, \tag{3.139}$$

the usual non-relativistic equation.

3.6 The Dirac-Coulomb Problem

(Darwin 1928, Gordon 1928). Consider

$$V = -\frac{Z}{r} \tag{3.140}$$

For normalized bound states

$$\int_0^\infty r^2\mathrm{d}r(f^2 + g^2) = \int_0^\infty \mathrm{d}r(P^2 + Q^2) = 1 \tag{3.141}$$

(3.134) $\Rightarrow$

$$\begin{cases} \dfrac{\mathrm{d}P}{\mathrm{d}r} + \kappa\dfrac{P}{r} + \Big(-mc - \dfrac{Z}{c}\dfrac{1}{r} - \dfrac{E}{c}\Big)Q = 0 \\ \dfrac{\mathrm{d}Q}{\mathrm{d}r} - \kappa\dfrac{Q}{r} + \Big(-mc + \dfrac{Z}{c}\dfrac{1}{r} + \dfrac{E}{c}\Big)P = 0 \end{cases} \tag{3.142}$$

So far $\hbar = 1$. Let now $m = c = 1$, as well. Then the unit charge $e = \alpha = 1/137.036$. Furthermore denote

$$\lambda = \sqrt{(1 - E^2)} \tag{3.143}$$

$$x = 2\lambda r \tag{3.144}$$

and introduce the new functions ϕ_1 and ϕ_2 for which

$$\begin{cases} P = \sqrt{1+E}\,\mathrm{e}^{-\lambda r}(\phi_1 + \phi_2) \\ Q = \sqrt{1-E}\,\mathrm{e}^{-\lambda r}(\phi_1 - \phi_2) \end{cases} \tag{3.145}$$

Then

$$\begin{cases} \dfrac{\mathrm{d}P}{\mathrm{d}r} = \sqrt{1+E}\,\mathrm{e}^{-\lambda r}\Big[-\lambda(\phi_1 + \phi_2) + \dfrac{\mathrm{d}\phi_1}{\mathrm{d}r} + \dfrac{\mathrm{d}\phi_2}{\mathrm{d}r}\Big] \\ \dfrac{\mathrm{d}Q}{\mathrm{d}r} = \sqrt{1-E}\,\mathrm{e}^{-\lambda r}\Big[-\lambda(\phi_1 - \phi_2) + \dfrac{\mathrm{d}\phi_1}{\mathrm{d}r} - \dfrac{\mathrm{d}\phi_2}{\mathrm{d}r}\Big] \end{cases} \tag{3.146}$$

Straightforward algebra on Eq. (3.142) gives:

$$\begin{cases} \sqrt{1+E}\,\mathrm{e}^{-\lambda r}\Big[-\lambda(\phi_1 + \phi_2) + \dfrac{\mathrm{d}\phi_1}{\mathrm{d}r} + \dfrac{\mathrm{d}\phi_2}{\mathrm{d}r}\Big] = \\ \qquad -\dfrac{\kappa}{r}\sqrt{1+E}\,\mathrm{e}^{-\lambda r}(\phi_1 + \phi_2) + \Big[E + \dfrac{Z}{r} + 1\Big]\sqrt{1-E}\,\mathrm{e}^{-\lambda r}(\phi_1 - \phi_2) \end{cases}$$

Dividing the top equation by $\sqrt{1+E}\mathrm{e}^{-\lambda r}$ and the bottom one by $\sqrt{1-E}\mathrm{e}^{-\lambda r}$ and noting that $\frac{\partial}{\partial r} = 2\lambda\frac{\partial}{\partial x}$ we get

$$\begin{cases} -\lambda(\phi_1 + \phi_2) + 2\lambda\Big(\dfrac{\mathrm{d}\phi_1}{\mathrm{d}x} + \dfrac{\mathrm{d}\phi_2}{\mathrm{d}x}\Big) = \\ \qquad -\dfrac{\kappa}{r}(\phi_1 + \phi_2) + \Big[E + \dfrac{2\lambda Z}{x} + 1\Big]\sqrt{\dfrac{1-E}{1+E}}(\phi_1 - \phi_2) \\ -\lambda(\phi_1 - \phi_2) + 2\lambda\Big(\dfrac{\mathrm{d}\phi_1}{\mathrm{d}x} - \dfrac{\mathrm{d}\phi_2}{\mathrm{d}x}\Big) = \\ \qquad \dfrac{\kappa}{r}(\phi_1 - \phi_2) - \Big[E + \dfrac{2\lambda Z}{x} - 1\Big]\sqrt{\dfrac{1+E}{1-E}}(\phi_1 + \phi_2) \end{cases}$$

Dividing now by 2λ, gives

$$\begin{cases} \phi_1' + \phi_2' = & \frac{1}{2}(\phi_1+\phi_2) - \frac{\kappa}{x}(\phi_1+\phi_2) \\ & + \left[E + \frac{2\lambda Z}{x} + 1\right]\frac{1}{2\sqrt{(1+E)(1-E)}}\sqrt{\frac{1-E}{1+E}}(\phi_1-\phi_2) \\ \phi_1' - \phi_2' = & \frac{1}{2}(\phi_1-\phi_2) + \frac{\kappa}{x}(\phi_1-\phi_2) \\ & - \left[E + \frac{2\lambda Z}{x} - 1\right]\frac{1}{2\sqrt{(1+E)(1-E)}}\sqrt{\frac{1+E}{1-E}}(\phi_1+\phi_2) \end{cases}$$

Now, remembering the definition of λ, (3.143), the above can be reorganized to

$$\begin{cases} \phi_1' + \phi_2' = & \phi_1\left[\frac{1}{2} - \frac{\kappa}{x} + \frac{E + \frac{2\lambda Z}{x} + 1}{2(1+E)}\right] \\ & + \phi_2\left[\frac{1}{2} - \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} + 1}{2(1+E)}\right] \\ \phi_1' - \phi_2' = & \phi_1\left[\frac{1}{2} + \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} - 1}{2(1-E)}\right] \\ & + \phi_2\left[-\frac{1}{2} - \frac{\kappa}{x} - \frac{E + \frac{2\lambda Z}{x} - 1}{2(1-E)}\right] \end{cases}$$

Writing down the sum and difference of the above { (sum at top, difference at bottom):

$$\begin{cases} 2\phi_1' = & \phi_1\left[1 + \left(E + \frac{2\lambda Z}{x}\right)\frac{1}{2}\left(\frac{1}{1+E} - \frac{1}{1-E}\right) + \frac{1}{2}\left(\frac{1}{1+E} + \frac{1}{1-E}\right)\right] \\ & + \phi_2\left[-\frac{2\kappa}{x} + \left(E + \frac{2\lambda Z}{x}\right)\frac{-1}{2}\left(\frac{1}{1+E} + \frac{1}{1-E}\right) - \frac{1}{2}\left(\frac{1}{1+E} - \frac{1}{1-E}\right)\right] \\ 2\phi_2' = & \phi_1\left[-\frac{2\kappa}{x} + \left(E + \frac{2\lambda Z}{x}\right)\frac{1}{2}\left(\frac{1}{1+E} + \frac{1}{1-E}\right) + \frac{1}{2}\left(\frac{1}{1+E} - \frac{1}{1-E}\right)\right] \\ & + \phi_2\left[1 - \left(E + \frac{2\lambda Z}{x}\right)\frac{1}{2}\left(\frac{1}{1+E} - \frac{1}{1-E}\right) - \frac{1}{2}\left(\frac{1}{1+E} + \frac{1}{1-E}\right)\right] \end{cases} \tag{3.147}$$

As

$$\begin{aligned} \frac{1}{1+E} - \frac{1}{1-E} &= \frac{-2E}{1-E^2} = \frac{-2E}{\lambda^2} \\ \frac{1}{1+E} + \frac{1}{1-E} &= \frac{2}{1-E^2} = \frac{2}{\lambda^2}, \end{aligned} \tag{3.148}$$

$$\begin{cases} 2\phi_1' = & \phi_1\Big[1 + \Big(E + \dfrac{2\lambda Z}{x}\Big)\Big(\dfrac{-E}{\lambda^2}\Big) + \dfrac{1}{\lambda^2}\Big] \\ & + \phi_2\Big[-\dfrac{2\kappa}{x} - \Big(E + \dfrac{2\lambda Z}{x}\Big)\dfrac{1}{\lambda^2} + \dfrac{E}{\lambda^2}\Big] \\ 2\phi_2' = & \phi_1\Big[-\dfrac{2\kappa}{x} + \Big(E + \dfrac{2\lambda Z}{x}\Big)\dfrac{1}{\lambda^2} - \dfrac{E}{\lambda^2}\Big] \\ & + \phi_2\Big[1 - \Big(E + \dfrac{2\lambda Z}{x}\Big)\Big(\dfrac{-E}{\lambda^2}\Big) - \dfrac{1}{\lambda^2}\Big] \end{cases} \tag{3.149}$$

$$\begin{cases} \phi_1' = \phi_1\Big[1 - \dfrac{ZE}{x\lambda}\Big] + \phi_2\Big[-\dfrac{\kappa}{x} - \dfrac{Z}{x\lambda}\Big] \\ \phi_2' = \phi_1\Big[-\dfrac{\kappa}{x} + \dfrac{Z}{x\lambda}\Big] + \phi_2\Big[\dfrac{ZE}{x\lambda}\Big] \end{cases} \tag{3.150}$$

Introducing the series

$$\begin{cases} \phi_1 = x^\gamma \displaystyle\sum_{m=0}^{\infty} \alpha_m x^m \\ \phi_2 = x^\gamma \displaystyle\sum_{m=0}^{\infty} \beta_m x^m \end{cases} \tag{3.151}$$

$$\begin{cases} \phi_1' = x^\gamma \displaystyle\sum_{m=0}^{\infty} (\gamma+m)\alpha_m x^{m-1} \\ \quad = x^\gamma \displaystyle\sum_{m=0}^{\infty} \Big[\alpha_m x^m\Big(1 - \dfrac{ZE}{x\lambda}\Big) - \beta_m x^m\Big(\dfrac{\kappa}{x} + \dfrac{Z}{x\lambda}\Big)\Big] \\ \phi_2' = x^\gamma \displaystyle\sum_{m=0}^{\infty} (\gamma+m)\beta_m x^{m-1} \\ \quad = x^\gamma \displaystyle\sum_{m=0}^{\infty} \Big[\alpha_m x^m\Big(-\dfrac{\kappa}{x} + \dfrac{Z}{x\lambda}\Big) + \beta_m x^m \dfrac{ZE}{x\lambda}\Big] \end{cases} \tag{3.152}$$

The coefficients for every power, $x^{\gamma+m-1}$, must vanish for the expansion to be true:

$$\begin{cases} \alpha_m(\gamma+m) = \alpha_{m-1} - \alpha_m \dfrac{ZE}{\lambda} - \beta_m\Big(\kappa + \dfrac{Z}{\lambda}\Big) \\ \beta_m(\gamma+m) = \alpha_m\Big(-\kappa + \dfrac{Z}{\lambda}\Big) + \beta_m \dfrac{ZE}{\lambda}. \end{cases} \tag{3.153}$$

If α_{m-1} is known, these equations gives (α_m, β_m) For $m = 0$ ($\alpha_{-1} = 0$ is assumed),

$$\begin{cases} \gamma\alpha_0 = \alpha_0\Big(-\dfrac{ZE}{\lambda}\Big) - \beta_0\Big(\kappa + \dfrac{Z}{\lambda}\Big) \\ \gamma\beta_0 = \alpha_0\Big(-\kappa + \dfrac{Z}{\lambda}\Big) + \beta_0 \dfrac{ZE}{\lambda}. \end{cases} \tag{3.154}$$

This linear, homogenous pair has solutions if

$$\begin{aligned}
\begin{vmatrix} \gamma + ZE/\lambda & \kappa + Z/\lambda \\ \kappa - Z/\lambda & \gamma - ZE/\lambda \end{vmatrix} &= 0 && (3.155) \\
\gamma^2 - \left(\frac{ZE}{\lambda}\right)^2 - \kappa^2 + \left(\frac{Z}{\lambda}\right)^2 &= 0 \\
\gamma_2 + \left(\frac{Z}{\lambda}\right)^2 (1 - E^2) - \kappa^2 &= 0 \\
\gamma^2 &= \kappa^2 - Z^2. && (3.156)
\end{aligned}$$

It turn out that

$$\gamma = +\sqrt{\kappa^2 - Z^2} \tag{3.157}$$

is the acceptable solution and

$$\gamma = -\sqrt{\kappa^2 - Z^2}$$

the irregular one (which can't be normalized). Recall that Z included the proton charge $e_{\mathrm{p}} = \alpha = 1/137.036$. For integer Z',

$$\gamma = +\sqrt{\kappa^2 - (\alpha Z')^2} \tag{3.158}$$

The Eq. (3.153b) $\Rightarrow$

$$\frac{\beta_m}{\alpha_m} = \frac{-\kappa + Z/\lambda}{m + \gamma - ZE/\lambda} = \frac{\kappa - Z/\lambda}{n' - m}, \tag{3.159}$$

In terms of a new quantity

$$n' = \frac{ZE}{\lambda} - \gamma. \tag{3.160}$$

A substitution to (3.153a) gives

$$\alpha_m \left[\gamma + m + \frac{ZE}{\lambda} + \left(\kappa + \frac{Z}{\lambda}\right) \frac{\kappa - Z/\lambda}{n' - m} \right] = \alpha_{m-1} \tag{3.161}$$

Here

$$
\begin{aligned}
&\left[\gamma + m + \frac{ZE}{\lambda} + \Big(\kappa + \frac{Z}{\lambda}\Big)\frac{\kappa - Z/\lambda}{n' - m}\right] \\
&= \gamma + m + \frac{ZE}{\lambda} + \frac{\kappa^2 - (Z/\lambda)^2}{n' - m} \\
&= \frac{1}{n' - m}\left[\Big(\gamma + m + \frac{ZE}{\lambda}\Big)\Big(-\gamma - m + \frac{ZE}{\lambda}\Big) + \kappa^2 - (Z/\lambda)^2\right] \\
&= \frac{1}{n' - m}\left[-\Big(\gamma^2 + 2\gamma m + m^2\Big) + (ZE/\lambda)^2 + \kappa^2 - (Z/\lambda)^2\right] \\
&= \frac{1}{n' - m}\left[-\kappa^2 + Z^2 - 2\gamma m - m^2 + \kappa^2 + Z^2\underbrace{\frac{E^2 - 1}{\lambda^2}}_{=-1}\right] \\
&= -m\frac{2\gamma + m}{n' - m} \Rightarrow
\end{aligned}
$$

$$
\alpha_m = -\frac{n' - m}{m(2\gamma + m)}\alpha_{m-1}. \tag{3.162}
$$

$$
\begin{aligned}
\alpha_m &= (-)^m \frac{(n' - m)\ldots(n' - 1)}{m!(2\gamma + m)\ldots(2\gamma + 1)}\alpha_0 \\
&= \frac{(1 - n')(2 - n')\ldots(m - n')}{m!(2\gamma + 1)\ldots(2\gamma + m)}\alpha_0.
\end{aligned} \tag{3.163}
$$

(3.159) $\Rightarrow$

$$
\left.\begin{aligned}
\frac{\beta_m}{\alpha_m} &= \frac{\kappa - Z/\lambda}{n' - m} \\
\frac{\beta_{m-1}}{\alpha_{m-1}} &= \frac{\kappa - Z/\lambda}{n' - m + 1}
\end{aligned}\right\} \Rightarrow
$$

$$
\begin{aligned}
\frac{\beta_m}{\beta_{m-1}} &= \frac{n' - m + 1}{n' - m}\frac{\alpha_m}{\alpha_{m-1}} \Rightarrow \\
\beta_m &= (-)^m \frac{(n' - m + 1)\ldots(n')}{m!(2\gamma + 1)\ldots(2\gamma + m)}\beta_0.
\end{aligned} \tag{3.164}
$$

(3.154b) $\Rightarrow$

$$
\begin{aligned}
\alpha_0\Big(-\kappa + \frac{Z}{\lambda}\Big) &= \beta_0\Big(\gamma - \frac{ZE}{\lambda}\Big) \Rightarrow \\
\frac{\alpha_0}{\beta_0} = \frac{\gamma - ZE/\lambda}{-\kappa + Z/\lambda} &= \frac{n'}{\kappa - Z/\lambda}.
\end{aligned} \tag{3.165}
$$

Comparing the coefficients (3.163)-(3.164) with those of a confluent hypergeometrical function,

$$ {}_1F_1(a;c;x) = 1 + \frac{a}{c}x + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \cdots \,, \tag{3.166} $$

$$ \begin{cases} \phi_1 = \alpha_0 x^\gamma {}_1F_1(1-n';2\gamma+1;x) \\ \phi_2 = \beta_0 x^\gamma {}_1F_1(-n';2\gamma+1;x) \\ \quad = \dfrac{\kappa - Z/\lambda}{n'}\alpha_0 x^\gamma {}_1F_1(-n';2\gamma+1;x). \end{cases} \tag{3.167} $$

For $x \to \infty$, ${}_1F_1(a;c;x) \to \mathrm{e}^x$ because

$$ \lim_{m\to\infty}\frac{\alpha_m}{\alpha_{m-1}} = \lim_{m\to\infty}\frac{-n'+m}{m(2\gamma+m)} \to \frac{1}{m}. \tag{3.168} $$

Therefore the series must terminate, That happens for ϕ_2 with

$$ n' = 0, 1, 2, \ldots \tag{3.169} $$

($n' = 0$ is the ground state, $n' = 1$ the 1$^{\mathrm{st}}$ excited state, etc.) Thus n' is the number of nodes in ϕ_2 (or in g)

For $n'1 = 0$, the coefficients of ϕ_1 have

$$ \begin{aligned} \alpha_m &= \frac{(1-n')\ldots(m-n')}{m!(2\gamma+1)\ldots(2\gamma+m)}\alpha_0 \\ &= \frac{1}{m!(2\gamma+1)\ldots(2\gamma+m)}\alpha_0, \end{aligned} $$

which converges.

Introduce the principal quantum number

$$ n = n' + |\kappa|. \tag{3.170} $$

Then the definition of n', (3.160), gives

$$ \begin{aligned} \frac{ZE_{n\kappa}}{\lambda} &= n' + \gamma \\ E^2 = \frac{\lambda^2}{Z^2}(n'+\gamma)^2 &= \frac{(1-E^2)(n'+\gamma)^2}{Z^2} \Rightarrow \\ E^2\left[1 + \frac{(n'+\gamma)^2}{Z^2}\right] &= \frac{(n'+\gamma)^2}{Z^2} \Rightarrow \end{aligned} $$

$$ \boxed{E_{n\kappa} = \left[1 + \tfrac{Z^2}{(n'+\gamma)^2}\right]^{-1/2}} \tag{3.171} $$

The κ occurs only in $\gamma = \sqrt{\kappa^2 - Z^2}$, $+|\kappa|$ and $-|\kappa|$ are degenerate for the same n! For instance for $n = 2$,

$$E_{2s_{1/2}} = E_{2p_{1/2}} < E_{2p_{3/2}}. \tag{3.172}$$

(Note though that with QED accounted for $E_{2s_{1/2}} > E_{2p_{1/2}}$!) An expansion in powers of Z^2 gives (we still have $c = 1$)

$$E_{n\kappa} - 1 = \varepsilon_{n\kappa} = -\frac{1}{2}\frac{Z^2}{n^2} + \frac{Z^4}{n^3}\left[\frac{3}{8n} - \frac{1}{2|\kappa|}\right] + \mathcal{O}(Z^6) \tag{3.173}$$

Qualitative conclusions:

a. Largest stabilization for $|\kappa| = 1$.

b. States with same l (and n) but different j are *spin-orbit* split.

c. For $|\kappa| = 1$, both f and g diverge at the origin like $r^{\gamma-1}$. They remain normalized. The isomer or isotope shifts, proportional to $\rho(0)$, grow by a factor of 13 for U.

d. The radial density, $P^2 + Q^2$, has no nodes.

e. The radial electron density suffers a relativistic contraction.

f. Normalization is no problem

g. Continuum, also positron-like can be solved.

h. Integrals, properties, solvable.

i. Literature: See Table 2.3 of RTAM I-III (1986, 1993, 2000)

3.7 Virial theorems

Literature: See RTAM I-III, Table 2.5.

Fock (1930b), Gupta (1932), Rose & Welton (1952), March (1953), Kim (1967), McKinley (1971), M. Brack (1983).

3.7.1 Non-relativistic case

Let

$$\underline{r} \to \underline{r}' = \lambda \underline{r} \quad | \underline{r} = \frac{\underline{r}'}{\lambda} \tag{3.174}$$

$$\begin{aligned} H = T + V &= -\frac{1}{2}\nabla^2 + Cr^n \\ &\to \lambda^2\Big(-\frac{1}{2}\nabla'^2\Big) + C\lambda^{-n}(r')^n \end{aligned} \tag{3.175}$$

$$E(\lambda) = \lambda^2\langle T\rangle + \lambda^{-n}\langle V\rangle \tag{3.176}$$

$$\frac{\partial E}{\partial \lambda} = \Big[2\lambda\langle T\rangle - n\lambda^{-n-1}\langle V\rangle\Big]_{\lambda=1} = 0 \tag{3.177}$$

$\Rightarrow$

$$\boxed{2\langle T\rangle = n\langle V\rangle} \quad \text{Coulomb: } n = 1 \tag{3.178}$$

Because $E(\lambda)$ has to be a minimum at $\lambda = 1$,

$$\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=1} = \Big[2\langle T\rangle + n(n+1)\lambda^{-n-2}\langle V\rangle\Big]_{\lambda=1} > 0 \tag{3.179}$$

$\Rightarrow$

$$\begin{aligned} n\langle V\rangle + n(n+1)\langle V\rangle &> 0, \quad \langle V\rangle < 0 \\ (2+n)n\langle V\rangle &> 0 \end{aligned}$$

$$\boxed{-2 < n < 0} \tag{3.180}$$

3.7.2 Dirac

$$h_{\rm D}\Phi = E\Phi \tag{3.181}$$
$$h_{\rm D} = c\underline{\alpha}\cdot\underline{p}0\beta mc^2 + V(r), \tag{3.182}$$
$$V(r) = Cr^n \tag{3.183}$$

Bound states considered:

$$\Phi = \begin{pmatrix}\phi_A \\ \phi_B\end{pmatrix}, \quad \langle\phi|\phi\rangle = 1, \quad \langle A|A\rangle + \langle B|B\rangle = 1 \tag{3.184}$$

Again, let $\underline{r} \to \underline{r}' = \lambda\underline{r}$, $\mathrm{d}\underline{r} \to \lambda^{-1}\mathrm{d}r'$.

$$\Phi(\underline{r}) \to \lambda^{3/2}\Phi(\underline{r}') \tag{3.185}$$
$$h_{\rm D} \to c\lambda\underline{\alpha}\cdot\underline{p} + \beta mc^2 + \lambda^{-n}V(r). \tag{3.186}$$

$$\begin{cases} \langle\Phi'|c\underline{\alpha}\cdot\underline{p}|\Phi'\rangle = \lambda\langle\Phi|c\underline{\alpha}\cdot\underline{p}|\Phi\rangle \\ \langle\Phi'|\beta mc^2|\Phi'\rangle = mc^2(N_A - N_B) \\ \langle\Phi'|r^{-n}|\Phi'\rangle = \lambda^{-n}\langle\Phi|r^{-n}|\Phi\rangle \end{cases} \tag{3.187}$$

$$E(\lambda) = \lambda\langle c\underline{\alpha}\cdot\underline{p}\rangle + \lambda^{-n}\langle V\rangle + mc^2(N_A - N_B) \tag{3.188}$$
$$\left(\frac{\partial E}{\partial\lambda}\right)_{\lambda=1} = 0 \quad \Rightarrow \boxed{\langle T\rangle = n\langle V\rangle} \tag{3.189}$$

For $n = -1$,

$$\langle T\rangle + \langle V\rangle = c\langle\underline{\alpha}\cdot\underline{p}\rangle + \langle V\rangle = 0 \tag{3.190}$$

$$\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=1} \Rightarrow$$
$$\left[n(n+1)\lambda^{-n-2}\langle V\rangle\right]_{\lambda=1} > 0 \qquad (3.191)$$

$$\langle V\rangle < 0 \Rightarrow n(n+1) < 0 \Rightarrow$$
$$-1 < \; n \; < 0. \qquad (3.192)$$

For $n = -1$,

$$E = \langle T\rangle + \langle V\rangle + mc^2(N_A - N_B)$$
$$E = mc^2(N_A - N_B). \qquad (3.193)$$

$$\boxed{E = mc^2\langle\beta\rangle} \qquad (3.194)$$

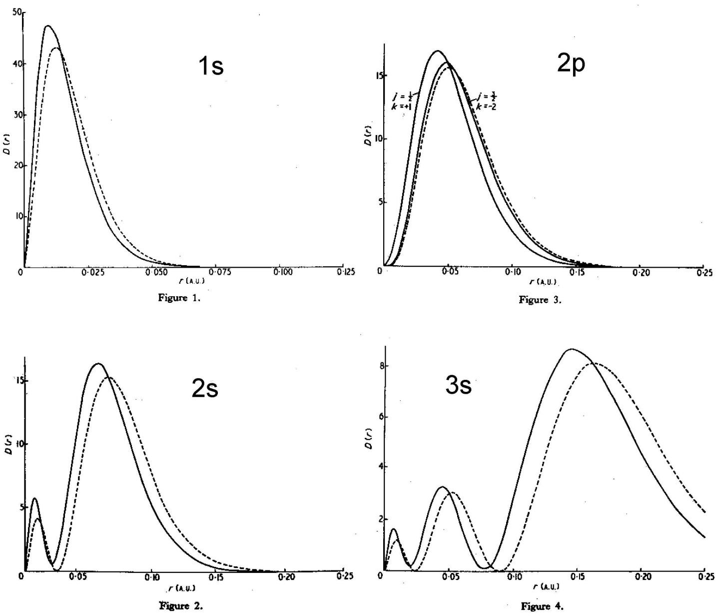

Figure 3.1: Radial electron densities for the 1s, 2s, 2p and 3s states in a hydrogen-like atom with $Z = 80$. The dotted curve denotes the non-relativistic density and the solid curve the relativistic density. Reproduced with permission from V.M. Burke and I.P. Grant, *Proc. Phys. Soc. (London)* **90** (1967) 297-314.

From Figure (3.1) it is seen that the relativistic contraction is of the order for the states 1s, 2s, $2p_{1/2}$ and 3p, whereas the contraction of $2p_{3/2}$ is considerably lesser. The figures 2 and 4 (inside (3.1)) show that 2s and 3s are procentually contracted as much as 1s is. The same conclusion can be drawn for all s-electrons up to the valence shell in a many-electron atom. The p-shells also contract in the same way, but not as much.