

## 4 Dirac-Fock

### 4.1 The energy-expression

Subtracting the rest energy  $mc^2$  from  $E$ , the one-electron Dirac Hamiltonian

$$h_i = c\alpha_i \cdot \underline{p}_i + mc^2(\beta_i - I) - \frac{Z}{r_i} \quad (4.1)$$

and the **Dirac-Fock Hamiltonian**

$$H = \sum_i h_i + \sum_{i<j} r_{ij}^{-1} \quad (4.2)$$

The total wave function is the **Slater determinant**

$$\Psi = (N!)^{-1/2} |\psi_1(1)\psi_2(2)\dots\psi_N(N)|, \quad (4.3)$$

where the one-electron wave functions

$$\psi_{n\kappa m} = \begin{pmatrix} r^{-1}P_{n\kappa}(r)\chi_{\kappa}^m(\vartheta, \phi, \sigma) \\ ir^{-1}Q_{n\kappa}(r)\chi_{-\kappa}^m(\vartheta, \phi, \sigma) \end{pmatrix} \quad (4.4)$$

Then the total energy

$$\begin{aligned} E &= \langle \Psi | H | \Psi \rangle \\ &= \sum_i \langle \psi_i | h | \psi_i \rangle + \sum_{i<j} \left[ \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_j \psi_i \rangle \right] \\ &= \sum_i I_i + \sum_{i<j} [J_{ij} - K_{ij}], \end{aligned} \quad (4.5)$$

in terms of the one-electron integrals  $I$ , Coulomb integrals  $J$  and exchange integrals  $K$ .

Eq. (3.129)  $\Rightarrow$

$$\begin{aligned} I &= \langle \psi | h | \psi \rangle \\ &= \langle (g\chi_{\kappa}, -if\chi_{-\kappa}) | \times \\ &\left[ ic\left(\frac{\partial}{\partial r} + \frac{1 + \{\mp n\}}{r}\right) \begin{pmatrix} if\chi_{\kappa} \\ g\chi_{-\kappa} \end{pmatrix} + (\{ -2mc^2 \} + V) \begin{pmatrix} g\chi_{\kappa} \\ if\chi_{-\kappa} \end{pmatrix} \right] \rangle \end{aligned}$$

$$\begin{aligned}
&= \int_0^\infty r^2 dr \left\{ g \left[ c \left( -\frac{\partial}{\partial r} + \frac{\kappa-1}{r} \right) f + Vg \right] \right. \\
&\quad \left. + f \left[ c \left( \frac{\partial}{\partial r} + \frac{\kappa+1}{r} \right) g + (-2mc^2 + V)f \right] \right\} \\
&= \int_0^\infty dr \left\{ P \left[ c \left( -\frac{dQ}{dr} + \frac{f}{r} - \frac{f}{r} + \frac{\kappa}{r} Q \right) + VP \right] \right. \\
&\quad \left. + Q \left[ c \left( \frac{dP}{dr} - \frac{q}{r} + \frac{g}{r} + \frac{\kappa}{r} P \right) + (-2mc^2 + V)Q \right] \right\} \\
&= \int_0^\infty dr \left\{ c Q \left( \frac{dP}{dr} + \frac{\kappa}{r} P \right) - cP \left( \frac{dQ}{dr} - \frac{\kappa}{r} Q \right) + V(r)(P^2 + Q^2) - 2mc^2 Q^2 \right\} = 0
\end{aligned} \tag{4.6}$$

$$g = \frac{P}{r}, \quad g' = \frac{1}{r} P' - \frac{P}{r^2} = \frac{1}{r} \frac{dP}{dr} - \frac{1}{r} g \tag{4.7}$$

We see that  $I_{n\kappa}$  is independent of  $m$ .

Consider next the general two-electron integral

$$\begin{aligned}
\langle \psi_a \psi_b | \frac{1}{r_{12}} | \psi_c \psi_d \rangle &= \langle ab | v | cd \rangle \\
&= \int d\underline{r}_1 \int d\underline{r}_2 \psi_a^*(1) \psi_b^*(2) \frac{1}{r_{12}} \psi_c(1) \psi_d(2)
\end{aligned} \tag{4.8}$$

using the expansion

$$\begin{aligned}
\frac{1}{r_{12}} &= \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} C^k(1) \cdot C^k(2) \\
&= \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{q=-k}^k (-1)^q C_q^k(1) C_{-q}^k(2).
\end{aligned} \tag{4.9}$$

Here

$$C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_k^q, \quad -k \leq q \leq k. \tag{4.10}$$

Then the angular parts

$$\begin{aligned}
\langle \kappa m | C_q^k | \kappa' m' \rangle &= (-1)^{m+\frac{1}{2}} \left[ (2j+1)(2j'+1) \right]^{1/2} \times \\
&\quad \begin{pmatrix} j & k & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \delta(m, q+m') \\
&\equiv d^k(j'm', jm)
\end{aligned} \tag{4.11}$$

and the radial **Slater integrals**

$$\begin{aligned}
R^k(abcd) &= \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_1^k}{r_2^{k+1}} [P_a(1)P_c(1) + Q_a(1)Q_c(1)] \\
&\quad \times [P_b(2)P_d(2) + Q_b(2)Q_d(2)] \\
&= \int_0^\infty \frac{1}{r_2} Y_k(ac, r_2) [P_b(2)P_d(2) + Q_b(2)Q_d(2)] dr_2 \quad (4.12)
\end{aligned}$$

where

$$Y_k(ac, r_2) = r_2 \int_0^\infty \frac{r_1^k}{r_2^{k+1}} [P_a(1)P_c(1) + Q_a(1)Q_c(1)] dr_1 \quad (4.13)$$

$\Rightarrow$

$$\langle ab|v|cd\rangle = \sum_{kq} (-)^q R^k(abcd) \langle a|C_q^k|c\rangle \langle b|C_{-q}^k|d\rangle. \quad (4.14)$$

The **3- $j$  symbols** fulfil

$$|j_3 m_3\rangle = (2j_3 + 1)^{1/2} \sum_{m_1, m_2} (-)^{-j_1 + j_2 - m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} |j_1 m_1\rangle |j_2 m_2\rangle. \quad (4.15)$$

In other words,

$$C(j_1 j_2 j_3; m_1 m_2 m_3) = (-)^{-j_1 + j_2 - m_3} (2j_3 + 1)^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}, \quad (4.16)$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-)^{j_1 - j_2 - m_3} (2j_3 + 1)^{-1/2} C(j_1 j_2 j_3; m_1 m_2 - m_3). \quad (4.17)$$

The 3- $j$  symbols are tabulated by **Rotenberg et al.** For their *symmetries*, see p. 107 of Kvantkemi I. They can be calculated by a simple program.

In the special case  $j_1 = l$ ,  $j_2 = \frac{1}{2}$ ,  $C(l \frac{1}{2} j; m_l m_s m)$  is:

| $j$               | $m_s$                                  |                                       |
|-------------------|--|---------------------------------------|
|                   | $\frac{1}{2}$                          | $-\frac{1}{2}$                        |
| $l + \frac{1}{2}$ | $\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$  | $\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}$ |
| $l - \frac{1}{2}$ | $-\sqrt{\frac{l-m+\frac{1}{2}}{2l+1}}$ | $\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}$ |

$m_l = m - m_s.$

Returning to Eq. (4.11), if the quantum numbers  $m$  and  $m'$  are fixed, only one value  $q = m - m'$  survives.

From

$$\begin{aligned}
\langle ab|v|cd\rangle &= \sum_{kq} (-)^q R(abcd) \langle a|C_q^k|c\rangle \langle b|C_{-q}^k|d\rangle, & [4.14] \\
\langle ab|v|ab\rangle &= \sum_{kq} (-)^q R(abab) \langle a|C_q^k|a\rangle \langle b|C_{-q}^k|b\rangle \\
&\stackrel{q=0}{=} \sum_k d^k(j_a m_a, j_a m_a) d^k(j_b m_b, j_b m_b) F^k(a, b) \\
&= \sum_k a^k(j_a m_a, j_b m_b) F^k(a, b), & (4.18)
\end{aligned}$$

where

$$a^k(j_a m_a, j_b m_b) = d^k(j_a m_a, j_a m_a) d^k(j_b m_b, j_b m_b) \quad (4.19)$$

and

$$F^k(a, b) = R^k(abab) \quad (4.20)$$

This was the **Coulomb integral**. The **exchange part**

$$\begin{aligned}
\langle ab|v|ba\rangle &= \sum_{kq} (-)^q R(abba) \langle a|C_q^k|b\rangle \langle b|C_{-q}^k|a\rangle \\
&= \sum_k b^k(j_a m_a, j_b m_b) G^k(a, b) & (4.21)
\end{aligned}$$

with

$$b^k(j m; j' m') = [d^k(j m; j' m')]^2 \quad (4.22)$$

and

$$G^k(a, b) = R^k(abba). \quad (4.23)$$

Using the symmetry rules of the 3- $j$  symbols,

$$\begin{aligned}
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= (-)^J \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} \quad \left| \begin{array}{l} J = j_1 + j_2 + j_3 \\ \end{array} \right. \\
&= (-)^J \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} & (4.24)
\end{aligned}$$

and noting that  $q$  is fixed by  $q = m - m'$ ,

$$\begin{aligned}
d^k(j'm'; jm) &= (-)^{m+\frac{1}{2}} [(2j+1)(2j'+1)]^{1/2} \begin{pmatrix} j & k & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \\
&= (-)^{m+\frac{1}{2}} [(2j+1)(2j'+1)]^{1/2} \begin{pmatrix} j & k & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{pmatrix} j' & k & j \\ m' & q & -m \end{pmatrix} \\
&= (-)^{m+\frac{1}{2}} [(2j+1)(2j'+1)]^{1/2} \begin{pmatrix} j & k & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \\
&= (-)^{-m+m'} d^k(jm; j'm') \tag{4.25}
\end{aligned}$$

$\Rightarrow$

$$d^k(j_a m_a; j_b m_b) = (-)^q d^k(j_b m_b; j_a m_a). \tag{4.26}$$

For one electron outside a filled shell,  $j$ ,

$$\sum_m a^k(jm; j'm') = (2j+1)\delta(k, 0). \tag{4.27}$$

Thus the  $k > 0$  Coulomb terms vanish in case the potential is spherical. The exchange in this case,

$$\sum_m b^k(jm; j'm') = \frac{1}{2}(2j+1)\Gamma_{jkj'}, \tag{4.28}$$

with

$$\Gamma_{jkj'} = 2 \begin{pmatrix} j & k & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2. \tag{4.29}$$

The total energy for a closed-shell atom becomes

$$E = E^0 + E^C, \tag{4.30}$$

$$E^0 = \sum_A q_A I(A), \quad q_A = 2j_A + 1, \tag{4.31}$$

$$\begin{aligned}
E^C &= \sum_A \left\{ \underbrace{\frac{1}{2} q_A (q_A - 1) F^0(A, A)}_a \right. \\
&\quad \left. - \frac{1}{2} q_A \underbrace{\left( \frac{q_A - 1}{2j_A} \right)}_b \sum_{k>0} \underbrace{(2j_A + 1) \frac{1}{2} \Gamma_{j_A k j_A} F^k(A, A)}_c \right\} \\
&\quad + \frac{1}{2} \sum_{A, B \ A \neq B} q_A q_B \left\{ \underbrace{F^0(A, B)}_d - \sum_k \underbrace{\frac{1}{2} \Gamma_{j_A k j_B} G^k(A, B)}_e \right\} \tag{4.32}
\end{aligned}$$

- a.  $k = 0$  part of the intrashell repulsion
- b. 1 for a full shell, 0 for one electron
- c. Exchange of one  $j_A$  electron with the filled shell  $A$
- d.  $k = 0$  intershell part (the only Coulomb term)
- e. The exchange of one  $j_A$  electron with the average shell  $B$  electron

**Example 11** The intrashell interactions of one  $p_{3/2}$  shell:  
All radial integrals are identical. The angular parts ( $m m'$ ) become

$$\begin{aligned} \sum a = a^k \left( \frac{3}{2} \frac{1}{2} \right) &+ a^k \left( \frac{3}{2} - \frac{1}{2} \right) + a^k \left( \frac{3}{2} - \frac{3}{2} \right) \\ &+ a^k \left( \frac{1}{2} - \frac{1}{2} \right) + a^k \left( \frac{1}{2} - \frac{3}{2} \right) \\ &+ a^k \left( -\frac{1}{2} - \frac{3}{2} \right) \end{aligned} \quad (4.33)$$

$$\begin{aligned} \sum b = b^k \left( \frac{3}{2} \frac{1}{2} \right) &+ b^k \left( \frac{3}{2} - \frac{1}{2} \right) + b^k \left( \frac{3}{2} - \frac{3}{2} \right) \\ &+ b^k \left( \frac{1}{2} - \frac{1}{2} \right) + b^k \left( \frac{1}{2} - \frac{3}{2} \right) \\ &+ b^k \left( -\frac{1}{2} - \frac{3}{2} \right) \end{aligned} \quad (4.34)$$

Note that there are no self-interacting terms,  $a^k \left( \frac{3}{2} \frac{3}{2} \right)$  etc.

**Case a:**  $k = 0$

$k = 0 \Rightarrow q = 0 \Rightarrow m = m'$ . No self-interaction  $\Rightarrow$  the exchange term  $b^0(jm, jm') = 0$ .

There are six  $a^0(m, m')$  in (4.34). Their value equals 1. See I.P. Grant, *Proc. Roy. Soc. Lond. A* **262** (1961) 555, Tables 1-3 or use (4.19)+(4.25).

E.g.

$$\begin{aligned}
a^0\left(\frac{3}{2} \frac{1}{2}\right) &= d^0\left(\frac{3}{2} \frac{3}{2}, \frac{3}{2} \frac{3}{2}\right) a^0\left(\frac{3}{2} \frac{1}{2}, \frac{3}{2} \frac{1}{2}\right) \\
&= (-)^{\frac{3}{2}+\frac{1}{2}} \left(2\frac{3}{2} + 1\right) \begin{pmatrix} \frac{3}{2} & 0 & \frac{3}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{3}{2} & 0 & \frac{3}{2} \\ -\frac{3}{2} & 0 & \frac{3}{2} \end{pmatrix} \times \\
&\quad (-)^{\frac{1}{2}+\frac{1}{2}} \left(2\frac{3}{2} + 1\right) \begin{pmatrix} \frac{3}{2} & 0 & \frac{3}{2} \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{3}{2} & 0 & \frac{3}{2} \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \quad (4.35) \\
&= -16 \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}^2 \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} \frac{3}{2} & \frac{3}{2} & 0 \\ \frac{3}{2} & -\frac{3}{2} & 0 \end{pmatrix} \\
&= -16 \cdot \left(-\frac{1}{2}\right)^2 \left(-\frac{1}{2}\right) \frac{1}{2} \quad \left| \text{See KK I, p. 109} \right. \\
&= 1 \quad \square
\end{aligned}$$

(Grant, *op.cit.*, Table 2, same result).  $6 \times 1 = 6$ . The first term of  $E^C$ , eq. (4.32), gives

$$\frac{1}{2}q(q-1) = \frac{1}{2} \cdot 4(4-1) = 6 \Rightarrow 6F^0(A, A). \quad (4.36)$$

**Case b:**  $k = 2$

Similarly,

$$\begin{aligned}
\sum a^2 &= \\
&a^2\left(\frac{3}{2} \frac{1}{2}\right) + a^2\left(\frac{3}{2} - \frac{1}{2}\right) + a^2\left(\frac{3}{2} - \frac{3}{2}\right) + a^2\left(\frac{1}{2} - \frac{1}{2}\right) + a^2\left(\frac{1}{2} - \frac{3}{2}\right) + a^2\left(-\frac{1}{2} - \frac{3}{2}\right) \\
&= -\frac{1}{25} - \frac{1}{25} + \frac{1}{25} + \frac{1}{25} - \frac{1}{25} - \frac{1}{25} \\
&= -\frac{2}{25} \quad (4.37)
\end{aligned}$$

Symmetries:

$$\begin{aligned}
a^k(jm; j'm') &= a^k(j'm'; jm) = a^k(j-m; j'-m) \\
&= a^k(j-m; j'm') = a^k(jm; j'-m') \quad (4.38)
\end{aligned}$$

$$b^k(jm; j'm') = b^k(j'm'; jm) = b^k(j-m; j'-m') \quad (4.39)$$

The coefficients  $b^k$  are given in Table 4 of Grant. Here,

$$\begin{aligned}
& \sum b^2 = \\
& b^2\left(\frac{3}{2} \frac{1}{2}\right) + b^2\left(\frac{3}{2} - \frac{1}{2}\right) + b^2\left(\frac{3}{2} - \frac{3}{2}\right) + b^2\left(\frac{1}{2} - \frac{1}{2}\right) + b^2\left(\frac{1}{2} - \frac{3}{2}\right) + b^2\left(-\frac{1}{2} - \frac{3}{2}\right) \\
& = \frac{2}{25} + \frac{2}{25} + 0 + 0 + \frac{2}{25} + \frac{2}{25} \\
& = \frac{8}{25}
\end{aligned} \tag{4.40}$$

The radial parts  $R(abab) = R(abba) = R(aaaa)$ . Adding,

$$\sum a^2 - \sum b^2 = \left(-\frac{2}{25}\right) - \left(\frac{8}{25}\right) = -\frac{2}{5} \tag{4.41}$$

In eq. (4.32),

$$-\frac{1}{2}q\left(\frac{q-1}{2j}\right)(2j+1)\frac{1}{2}\Gamma_{\frac{3}{2}2\frac{3}{2}} = -\frac{1}{2} \cdot 4 \cdot \frac{4-1}{3} \cdot 4 \cdot \frac{1}{2} \cdot \underbrace{\frac{1}{10}}_{\text{Grant, Table 5, p. 570}} = -\frac{2}{5} \tag{4.42}$$

## 4.2 The Dirac-Fock equations

The two-electron energy (4.32) equals

$$\begin{aligned}
E^C &= \frac{1}{2} \sum_A q_A \int_0^\infty \frac{dr}{r} \left[ P_A^2(r) + Q_A^2(r) \right] \times \\
& \left\{ (q_A - 1)r \int_0^\infty \frac{1}{r_{>}} ds \left[ P_A^2(s) + Q_A^2(s) \right] \right. & \text{a.} \\
& + \sum_{B \neq A} q_B r \int_0^\infty \frac{1}{r_{>}} ds \left[ P_B^2(s) + Q_B^2(s) \right] & \text{b.} \\
& \left. - \sum_{k>0} \frac{q_A - 1}{2j_A} \frac{1}{2} (2j_A + 1) \Gamma_{j_A k j_A} r \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} \left[ P_A^2(s) + Q_A^2(s) \right] ds \right\} & \text{c.} \\
& - \frac{1}{2} \sum_{A \neq B} q_A q_B \sum_k \frac{1}{2} \Gamma_{j_A k j_B} \int_0^\infty dr \int_0^\infty ds \frac{r_{\leq}^k}{r_{>}^{k+1}} & \text{d.} \\
& \times \left[ P_A(s)P_B(s) + Q_A(s)Q_B(s) \right] \left[ P_A(r)P_B(r) + Q_A(r)Q_B(r) \right].
\end{aligned} \tag{4.43}$$

When introducing the variation,  $\Delta Q$ , a factor of 4 will appear in each of the four terms, from:

- a.  $\Delta(Q^2) = 2Q\Delta Q$ , both  $\Delta Q(r)$  and  $\Delta Q(s)$
- b.  $\Delta(Q^2) = 2Q\Delta Q$ ,  $A = i$  or  $B = i$

c. As a.

d.  $Q(r)$  or  $Q(s)$ ,  $A = i$  or  $B = i$

(4.44)

In terms of the variations  $\Delta P$  and  $\Delta Q$ , the variation of the two-electron energy becomes

$$\begin{aligned}
E^C = & 2q_A \int_0^\infty \frac{Dr}{r} \left[ P_A \Delta P_A + Q_A \Delta Q_A \right] \times \\
& \left\{ (q_A - 1)r \int_0^\infty \frac{1}{r_{>}} ds \left[ P_A^2(s) + Q_A^2(s) \right] \right. \\
& + \sum_{B \neq A} q_B r \int_0^\infty \frac{1}{r_{>}} ds \left[ P_B^2(s) + Q_B^2(s) \right] \\
& - \sum_{k>0} \frac{q_A - 1}{2j_A} \frac{1}{2} (2j_A + 1) \Gamma_{j_A k j_A} r \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} \left[ P_A^2(s) + Q_A^2(s) \right] ds \left. \right\} \\
& - \sum_{B \neq A} q_A q_B \sum_k \Gamma_{j_A k j_B} \int_0^\infty dr \int_0^\infty ds \\
& \times \left[ P_A(s) P_B(s) + Q_A(s) Q_B(s) \right] \left[ P_B(r) P \Delta P_A + Q_B(r) \Delta Q_A \right].
\end{aligned} \tag{4.45}$$

We introduce the auxiliary function

$$\begin{aligned}
Y_n(A, r) = & - (q_A - 1) Y_0(A, A; r) - \sum_{B \neq A} q_B Y_0(B, B; r) \\
& + \sum_{k>0} \frac{q_A - 1}{2j_A} \frac{1}{2} (2j_A + 1) \Gamma_{j_A k j_A} Y_k(A, A; r),
\end{aligned} \tag{4.46}$$

where

$$Y_k(ac; r) = r \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} \left[ P_a(s) P_c(s) + Q_a(s) Q_c(s) \right] ds \tag{4.13}$$

could be interpreted as an *effective electronic charge*, containing both inner and outer screening.

Orthogonality leads to the Lagrange coefficients  $\varepsilon$ , whose variation

$$\Delta \varepsilon = \Delta \left[ E - \sum_A q_A \varepsilon_{AA} N_{AA} - \sum_{A \neq B} q_A q_B \varepsilon_{AB} N_{AB} \right], \tag{4.47}$$

where

$$N_{AB} = \int_0^\infty (P_A P_B + Q_A Q_B) dr. \tag{4.48}$$

Introducing  $\varepsilon_A = mc^2 - E_A$ , eq. (3.134) gives

$$\begin{cases} c(P' + \frac{\kappa}{r}P) + (-mc^2 + V - mc^2 - \varepsilon)Q = 0 & | + Q \times \\ c(Q' - \frac{\kappa}{r}Q) + (-mc^2 - V + mc^2 + \varepsilon)P = 0 & | - P \times \end{cases} \quad (4.49)$$

$$\begin{aligned} \varepsilon(P^2 + Q^2) &= c \left[ QP' + \frac{\kappa}{r}QP - PQ' + \frac{\kappa}{r}PQ \right] - 2mc^2Q^2 \\ &\quad + V[P^2 + Q^2] \\ &= c \left[ QP' - PQ' + \frac{2\kappa}{r}PQ \right] - 2mc^2Q^2 + V[P^2 + Q^2]. \end{aligned} \quad (4.50)$$

The variation of this one-electron term,

$$\begin{aligned} \Delta\varepsilon_A &= q_A \int_0^\infty \left\{ c \left[ \Delta QP' + Q\Delta P' - \Delta PQ' - P\Delta Q' + \frac{2\kappa}{r}(P\Delta Q + Q\Delta P) \right] \right. \\ &\quad \left. - 4c^2Q\Delta Q + 2V(P\Delta P + Q\Delta Q) \right\} dr. \end{aligned} \quad (4.51)$$

From  $\Delta P = \Delta Q = 0$  we get by partial integration

$$\begin{cases} \int_0^\infty Q\Delta P' dr = - \int_0^\infty Q'\Delta P dr \\ \int_0^\infty P\Delta Q' dr = - \int_0^\infty P'\Delta Q dr \end{cases} \quad (4.52)$$

Hence the variation of the one-electron energy

$$\begin{aligned} \Delta\varepsilon_A &= 2q_A c \int_0^\infty \left\{ \Delta Q_A P'_A + \Delta P'_A Q'_A + \frac{\kappa}{r}(P_A \Delta Q_A + Q_A \Delta P_A) \right. \\ &\quad \left. - 2cQ_A \Delta Q_A + \frac{1}{c}V(P_A \Delta P_A + Q_A \Delta Q_A) \right\} dr. \end{aligned} \quad (4.53)$$

Adding to this the variation of the two-electron energy,  $\Delta E^C$ , eq. (4.45), and subtracting the Lagrange multiplier terms for normalization and orthogonality, we get

$$\begin{aligned}
& \int_0^\infty 2q_A c \left\{ \Delta Q_A P'_A - \Delta P_A Q'_A + \frac{\kappa_A}{r} (P_A \Delta Q_A + Q_A \Delta P_A) \right. & (4.54) \\
& \quad \left. - 2c Q_A \Delta Q_A + \frac{1}{c} V_n (P_A \Delta P_A + Q_A \Delta Q_A) \right\} & \text{a.} \\
& -2q_A \int_0^\infty \frac{dr}{r} [P_A \Delta P_A + Q_A \Delta Q_A] Y_n(A, r) & \text{b.} \\
& - \sum_{B \neq A} q_A q_B \sum_k \Gamma_{j_A k j_B} \int_0^\infty \frac{dr}{r} Y_k(A, B; r) [P_B \Delta P_A + Q_B \Delta Q_A] & \text{c.} \\
& -2q_A \varepsilon_{AA} \int_0^\infty (P_A \Delta P_A + Q_A \Delta Q_A) dr & \text{d.} \\
& -2 \sum_{B \neq A} q_A q_B \varepsilon_{AB} \int_0^\infty (\Delta P_A P_B + \Delta Q_A Q_B) dr = 0. & \text{e.}
\end{aligned}$$

a. one-electron

b. use (4.46)

c. (4.45), inter-shell exchange

d. normalization

e. orthogonality

In the last term (e.), a factor of 2 comes from the possibilities "A" = A and "B" = A. Dividing (4.54) by  $2q_A c$  the coefficient of  $\Delta Q_A$  and  $-\Delta P_A$  become

$$\begin{aligned}
& P'_A + \frac{\kappa_A}{r} P_A + \frac{1}{c} [-2c^2 + V_n - \frac{1}{r} Y_n(A, r) - \varepsilon_{AA}] Q_A \\
& + \sum_{B \neq A} q_B \left[ - \sum_k \Gamma_{j_A k j_B} \frac{1}{2cr} Y_k(A, B; r) - \frac{1}{c} \varepsilon_{AB} \delta(\kappa_A, \kappa_B) \right] Q_B = 0 \\
& Q'_A + \frac{\kappa_A}{r} Q_A + \frac{1}{c} [-V_n + \frac{1}{r} Y_n(A, r) + \varepsilon_{AA}] P_A \\
& + \sum_{B \neq A} q_B \left[ \sum_k \Gamma_{j_A k j_B} \frac{1}{2cr} Y_k(A, B; r) + \frac{1}{c} \varepsilon_{AB} \delta(\kappa_A, \kappa_B) \right] P_B = 0
\end{aligned} \tag{4.55}$$

These are the Dirac-Fock equations for a closed-shell atom. We may set

$$\frac{1}{r} Y(A, r) = -V_n + \frac{1}{r} Y_n(A, r) = \frac{1}{r} [Z + Y_n(A, r)] \tag{4.56}$$

### 4.2.1 The relativistic Koopmans theorem

Multiply (4.55a) by  $cQ_A$ , (4.55b) by  $-cP_A$ , add, integrate and suppose  $\varepsilon_{AB} = 0$ :

$$\int_0^\infty \left[ cQ_A \left( P'_A + \frac{\kappa}{r} P_A \right) - cP_A \left( Q'_A - \frac{\kappa_A}{r} Q_A \right) - 2c^2 Q_A^2 \right. \quad (4.57)$$

$$\left. + V_n(P_A^2 + Q_A^2) - \varepsilon_{AA}(P_A^2 + Q_A^2) + (P_A^2 + Q_A^2) \left( -\frac{1}{r} Y_n(A, r) \right) \right.$$

$$\left. + c \sum_{B \neq A} q_B (Q_A Q_B + P_A P_B) \sum_k \Gamma_{j_A k j_B} \frac{1}{2cr} Y_k(A, B; r) \right] dr = 0.$$

$\Rightarrow$

$$\varepsilon_{AA} = \int_0^\infty \left[ cQ_A \left( P'_A + \frac{\kappa}{r} P_A \right) - cP_A \left( Q'_A - \frac{\kappa}{r} Q_A \right) - 2c^2 Q_A^2 + V_n \right] \Big|_{I_A}$$

$$+ \int_0^\infty dr (P_A^2 + Q_A^2) \left[ + \frac{q_A - 1}{r} Y_0(A, A; r) + \sum_{B \neq A} \frac{1}{r} q_B Y_0(B, B; r) \right] [4.46]$$

$$- \sum_{k > 0} \frac{q_A - 1}{2j_A r} \frac{1}{2} (2j_A + 1) \Gamma_{j_A k j_A} Y_k(A, A; r) \Big]$$

$$+ c \sum_{B \neq A} q_B (Q_A(r) Q_B(r) + P_A(r) P_B(r)) \sum_k \Gamma_{j_A k j_B} \frac{1}{2cr} \times$$

$$r \int_0^\infty \frac{r^k}{r^{k+1}} [P_A(s) P_B(s) + Q_A(s) Q_B(s)] ds \quad \Big| [4.13]$$

$$= I_A + (q_A - 1) F^0(A, A) + \sum_{B \neq A} q_B F^0(A, B)$$

$$- \sum_{k > 0} \frac{q_A - 1}{2j_A} \frac{1}{2} (2j_A + 1) \Gamma_{j_A k j_A} F^k(A, A)$$

$$- \sum_{B \neq A} \frac{q_B}{2} \sum_k \Gamma_{j_A k j_B} G^k(A, B). \quad (4.58)$$

A comparison with the total energy, (4.32) shows this to be the difference  $E(q_A) - E(q_A - 1)$   $\square$

### 4.2.2 Multiconfiguration treatment, a simple example

(C. Briançon, J.P. Desclaux, *Phys. Rev. A* **15** (1976) 2157)

The total energy for a  $p^4(J = 2)$  configuration. At the LS-limit,

$$\begin{cases} |^3P_2\rangle = \frac{1}{\sqrt{3}}[\sqrt{2}|\bar{p}^2p^2\rangle + |\bar{p}p^3\rangle] \\ |^2D_2\rangle = \frac{1}{\sqrt{3}}[|\bar{p}^2p^2\rangle - \sqrt{2}|\bar{p}p^3\rangle] \end{cases} \quad (4.59)$$

Generally,

$$|J = 2\rangle = a|\bar{p}^2p^2\rangle + \sqrt{1 - a^2}|\bar{p}p^3\rangle, \quad (4.60)$$

with the total energy

$$\begin{aligned} E_T &= a^2 E_{av}(\bar{p}^2p^2) + (1 - a^2) E_{av}(\bar{p}p^3) \\ &\quad - \frac{4}{75} a^2 F^2(p, p) + \frac{3}{50} (1 - a^2) G^2(\bar{p}, p) \\ &\quad + \frac{8}{50} \sqrt{2} a \sqrt{1 - a^2} R^2(\bar{p}, \bar{p}, p, p). \end{aligned} \quad (4.61)$$

### 4.2.3 "Average-of-configuration" treatment

Assume that all  $|jm\rangle$  states of the one-electron states are equally probable in the many-electron wave function.

**Example 21** Iodine,  $5p^5$ .

The hole can be in the  $5p$  or the  $5\bar{p}$  shell. They have 4 and 2  $m_j$ -states, respectively. Therefore the statistical weights are  $\frac{4}{6}$  and  $\frac{2}{6}$ , respectively.

**Example 32** Ground state of uranium,  $5f^36d$ .

a)  $f$ -configuration.

$$\begin{aligned} l = 3, \quad f : j = 3 + \frac{1}{2} = \frac{7}{2}, \quad 2j + 1 = 8 \\ \bar{f} : j = 3 - \frac{1}{2} = \frac{5}{2}, \quad 2j + 1 = 6 \end{aligned}$$

| config | $\bar{f}^3$   | $\bar{f}^2 f$  | $\bar{f} f^2$  | $f^3$  | $\Sigma$ |
|--------|---|--|--|--|----------|
| weight | $\frac{6 \cdot 5 \cdot 4}{3!} = 20$<br>$= \frac{5}{91}$ | $\frac{6 \cdot 5}{2!} \cdot \frac{8}{1!} = 120$<br>$= \frac{30}{91}$ | $\frac{6}{1!} \cdot \frac{8 \cdot 7}{2!} = 168$<br>$= \frac{42}{91}$ | $\frac{8 \cdot 7 \cdot 6}{3!} = 56$<br>$= \frac{14}{91}$ | 364      |

Note that you have to include the permutation of electrons,  $n!$ , in the weight calculation.

b)  $d$ -configuration

$$\begin{aligned} l = 2, \quad d : j = 2 + \frac{1}{2} = \frac{5}{2}, \quad 2j + 1 = 6 \\ \bar{d} : j = 2 - \frac{1}{2} = \frac{3}{2}, \quad 2j + 1 = 4 \end{aligned}$$

|        |                 |                 |          |
|--------|-----------------|-----------------|----------|
| config | $\bar{d}$       | $d$             | $\Sigma$ |
| weight | 4               | 6               | 10       |
|        | $= \frac{2}{5}$ | $= \frac{3}{5}$ |          |

Altogether eight  $jj$ -coupled configurations:

|                     |                                  |                                   |                                   |                                   |
|---------------------|----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| config              | $\bar{d}\bar{f}^3$               | $\bar{d}\bar{f}^2f$               | $\bar{d}\bar{f}f^2$               | $\bar{d}f^3$                      |
| weight              | $\frac{2}{5} \cdot \frac{5}{91}$ | $\frac{2}{5} \cdot \frac{30}{91}$ | $\frac{2}{5} \cdot \frac{42}{91}$ | $\frac{2}{5} \cdot \frac{14}{91}$ |
| weight $\times 455$ | 10                               | 60                                | 84                                | 28                                |
| config              | $d\bar{f}^3$                     | $d\bar{f}^2f$                     | $d\bar{f}f^2$                     | $df^3$                            |
| weight              | $\frac{3}{5} \cdot \frac{5}{91}$ | $\frac{3}{5} \cdot \frac{30}{91}$ | $\frac{3}{5} \cdot \frac{42}{91}$ | $\frac{3}{5} \cdot \frac{14}{91}$ |
| weight $\times 455$ | 15                               | 90                                | 126                               | 42                                |

### 4.3 Numerical solution of the Dirac-Fock equations

Choosing the variable

$$t = \ln r \quad (4.62)$$

and the step length  $h = \Delta t = 0.05$ , one usually obtains a precision of about 9 figures (for  $E_T$ ). About 200 radial grid points,  $r_i$ , are needed between the first point and the practical infinity. All wave functions  $P_A, Q_A$  and potentials  $\frac{1}{r}Y(A, r)$  and  $\frac{1}{r} \sum_{B \neq A} q_B \sum_k \Gamma_{j_A k j_B} Y_k(A, B; R)$  are expressed at the  $r_i$ .

The integrations outwards are started by the series expansion

$$\begin{cases} P(r) = r^\gamma(p_0 + p_1 r + p_2 r^2 + \dots) \\ Q(r) = r^\gamma(q_0 + q_1 r + q_2 r^2 + \dots). \end{cases} \quad (4.63)$$

After sufficiently many points are obtained, a five-point **Adams predictor-corrector method** or some other numerical method is used. Consider

$$y' = \frac{dy}{dt} = f(y)y(t) + g(t) \quad (4.64)$$

The new,  $(n + 1)$ :th point is obtained by combining the *predictor*

$$p_{n+1} = y_n + \frac{h}{720} [1901y'_n - 2774y'_{n-1} + 2616y'_{n-2} - 1274y'_{n-3} + 251y'_{n-4}] \quad (4.65)$$

and the *corrector*

$$c_{n+1} = y_n + \frac{h}{720} [251p'_{n+1} + 646y'_n - 264y'_{n-1} + 106y'_{n-2} - 19y'_{n-3}] \quad (4.66)$$

to

$$y_{n+1} = \frac{1}{502} [473c_{n+1} + 29p_{n+1}] + \mathcal{O}(h^7) \quad (4.67)$$

The outwards integration becomes unstable after the (effective, radial) potential,  $V(r) = -\frac{1}{r}Y(A, r)$  crosses the eigenvalue,  $\varepsilon$

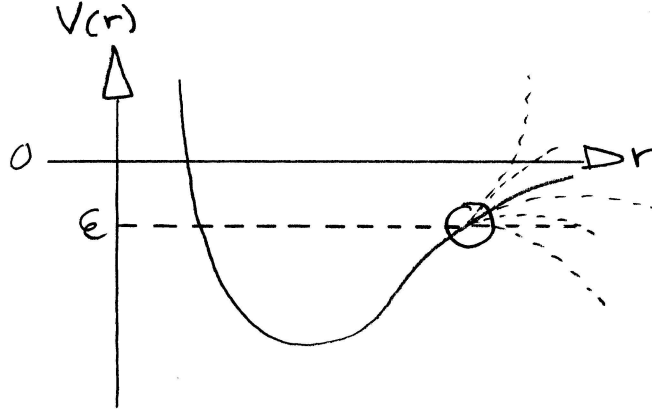


Figure 4.1: The instability of the integration depicted

Similarly, the inwards integration becomes unstable after this point. The solution is to fit the two integrations at this point.

In "Method 2" one solves both the original inhomogeneous differential equations and the homogeneous ones with  $\sum_{B \neq A} = 0$ . Then every linear combination of the two solutions is a solution.

The coefficients of the homogeneous solution,  $\alpha$ , follow from

$$\begin{cases} P_L^i(r_I) + \alpha_L P_L^h(r_I) = P_R^i(r_I) + \alpha_R P_R^h(r_I) \\ Q_L^i(r_I) + \alpha_L Q_L^h(r_I) = Q_R^i(r_I) + \alpha_R Q_R^h(r_I), \end{cases} \quad (4.68)$$

at the matching point,  $r_I$ . Here i=inhomogeneous, h=homogeneous, L="left" ( $r < r_I$ ), R="right" ( $r > r_I$ ).

This solution fulfills the boundary conditions but may not be normalized. Normalization by a constant is not allowed because the equation is inhomogeneous  $\Rightarrow$  the eigenvalue of  $\varepsilon_{AA}$  is chosen to obtain normalization.

Actually it suffices if we converge towards a normalized solution. Let  $\varepsilon = \varepsilon_{AA}$ . Then

$$\int_0^\infty (P^2 + Q^2)dr + 2\delta\varepsilon \int_0^\infty \left( P \frac{\partial P}{\partial \varepsilon} + Q \frac{\partial Q}{\partial \varepsilon} \right) dr = 1. \quad (4.69)$$

By first differentiating the original Dirac-Fock equations,

$$\begin{cases} \frac{d}{dt} \left( \frac{\partial P}{\partial \varepsilon} \right) + \kappa \frac{\partial P}{\partial \varepsilon} + f(r) \frac{\partial Q}{\partial \varepsilon} = \frac{1}{2c} Q \\ \frac{d}{dt} \left( \frac{\partial Q}{\partial \varepsilon} \right) - \kappa \frac{\partial Q}{\partial \varepsilon} + g(r) \frac{\partial P}{\partial \varepsilon} = -\frac{1}{2c} P, \end{cases} \quad (4.70)$$

these derivatives can be solved by the same subroutines as  $P$  and  $Q$  themselves. Then (4.69)  $\Rightarrow$

$$\delta\varepsilon_A = \frac{1 - \int_0^\infty (P_A^2 + Q_A^2)dr}{2 \int_0^\infty \left( P_A \frac{\partial P_A}{\partial \varepsilon_A} + Q_A \frac{\partial Q_A}{\partial \varepsilon_A} \right) dr}. \quad (4.71)$$

In the old Dirac-Fock One-Center Expansion (DF-OCE) method, four numerical methods could be used:

1.
  - Calculate only  $\psi_R^h$ , put  $P_L = P_R^i + \alpha_R P_R^h$ .
  - Fit  $Q$  by changing  $\varepsilon$ .
  - Finally normalize by force (inner shells) or by using  $\partial P/\partial \varepsilon$  (molecules).
2. Previous method. Normalize by adding to  $P$  some amount of  $\delta\varepsilon \times (\partial P/\partial \varepsilon)$ . If the number of nodes requires it, change  $\varepsilon$ . The continuity is guaranteed.
  - Fit  $\varepsilon$  by (4.71)
3. Use both  $\alpha_L$  and  $\alpha_R$ . Use (4.71). For wrong number of nodes,
4. change  $\varepsilon$  to get the right number of nodes.

#### 4.3.1 Specific features of the DF-OCE method

- Each MO consists of a *dominant* AO and other AOs. **Example:** For the  $\Gamma_7$  MO of  $\text{CH}_4$ ,  $2\bar{p}_{3/2} + 4d + 4f$ .
- Use for the dominant component Method 1 and for the others Method 3 or, if necessary, Method 4.
- Then the dominant component fixes  $\varepsilon$  (which is not changed in Method 3 for the other components).

- After treating the entire MO, set the common

$$\varepsilon_{\text{MO}} = \sum_{\text{AO}} N(\text{AO})\varepsilon_{\text{AO}} \quad (4.72)$$

(SOLDMO, lines 175-177)

Then correct it by setting

$$\varepsilon_{\text{MO}} \rightarrow \varepsilon_{\text{MO}} + \frac{1 - \sum_i N_i}{\sum_i 2 \int_0^\infty (P_i p_i + Q_i q_i)} \bigg| p_i = \frac{\partial P_i}{\partial \varepsilon_i} \quad (4.73)$$

(SOLDMO, lines 178, 180)

- After treating the entire MO, normalize it by the coefficient  $[\sum_i N_i]^{-1/2}$ .  
(SOLDMO, lines 157, 204-211)

Some results:

Desclaux and Pyykkö (1974): the bond-length contraction

D&P (1976): the Ag/Au difference

D&P (1976):  $\bar{p}$  bonding in TiH.

D&P (1977a): TiH<sub>4</sub>-(104)H<sub>4</sub>. Trends.

D&P (1977b): (114)H<sub>4</sub>  $\gtrsim$  PbH<sub>4</sub>.

D&P (1978): MoH<sub>6</sub>/WH<sub>6</sub>.  $R_e, D_e, k_2$ ; oxidation state.

P (1979b): MH<sup>+</sup>, MH<sub>2</sub>, Groups 2 and 12.

P (1979c): LnH, AnH.

[See Table 7.3 of RTAM I.]

The iterations can be speeded up (by roughly a factor of 2) by using a *convergence factor*  $\alpha$ .

Let  $P_n^i, Q_n^i$  and  $P_n^f, Q_n^f$  be the initial and final values during the  $n$ :th iteration. Choose

$$\begin{cases} P_{n+1}^i(r) = \beta[\alpha P_n^f + (1 - \alpha)P_n^i] \\ Q_{n+1}^i(r) = \beta[\alpha Q_n^f + (1 - \alpha)Q_n^i] \end{cases} \quad (4.74)$$

Here  $\beta$  is a normalization factor and  $\alpha$  is restricted to

$$0.1 \leq \alpha \leq 0.9$$

and is calculated every time from the change

$$\Delta R_n = \max[P_n^i(r) - P_n^f(r), Q_n^i(r) - Q_n^f(r)].$$

