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## A Hartree–Fock Program for Atomic Structure Calculations

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### *Abstract*

The Hartree–Fock equations for a general open shell atom are described. The matrix equations that result when the single particle orbitals are written in terms of a linear combination of analytic basis functions are derived. Attention is paid to the complexities that occur when open shells are present. The specifics of a working FORTRAN program which is available for public use are described. The program has the flexibility to handle either Slater-type orbitals or Gaussian-type orbitals.

### 1. Introduction

The restricted Hartree–Fock (HF) method is one of the standard methods for determining wave functions for atomic states (Froese-Fischer 1977). The word ‘restricted’ is used to denote the fact that the radial form of the orbitals are independent of the magnetic and spin projection quantum labels. HF wave functions can be used to compute atomic properties, or alternatively may serve as the starting point for a more sophisticated treatment such as the configuration interaction (CI) method (Hibbert 1975*a*). There are essentially two traditional methods by which HF calculations are carried out. In one, the radial wave functions are represented by a tabulation of numbers on a radial grid and finite difference techniques are used to integrate the potentials and solve the Schrödinger equation. In the other, the radial wave function is represented by linear superposition of functions with convenient analytic properties, e.g. Slater-type orbitals (STO) or Gaussian-type orbitals (GTO) (Roothaan 1951, 1960). Although programs based on the ‘numerical’ approach have been published (Froese-Fischer 1978, 1997), this is not true for the analytic approach. The only freely accessible HF program using basis functions is a program by Huzinaga *et al.* (1983) which uses GTOs. However, this program has limited usefulness since STOs are generally preferred for purely atomic calculations. Accordingly a program is presented that has been used to compute HF wave functions for a variety of atoms (mainly for use in scattering calculations) in the expectation that other workers in atomic physics might find it useful.

### 2. The Hartree–Fock Equations

While there are descriptions of the analytic HF method in the literature, it is desirable to recapitulate this information because a number of technicalities arise

for the open shell situation. Some understanding of the underlying theory will be valuable when attempting to get the HF equations to converge for open shell configurations. The theoretical development of the HF equations closely follows that given in the monograph by Hurley (1976).

In the restricted HF method the energy expression of an antisymmetrised single configuration wave function is minimised with respect to variations in the single particle orbitals. While the HF wave function for closed shell systems can be represented by a single Slater determinant, this is not generally true for open shell configurations. The wave function is usually restricted to be an eigenfunction of the orbital and spin angular momenta (although this is not always done).

The problem is to minimise the expectation value of the Hamiltonian

$$H = \sum_i \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}, \quad (1)$$

written more compactly as

$$H = \sum_i t(i) + \sum_{i < j} v(i, j), \quad (2)$$

with respect to variations in the orbital functions subject to the constraint that the orbitals be orthonormal, i.e.

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}. \quad (3)$$

For the purposes of the theoretical development, the possible configurations will be restricted to those containing at most two open shells of the same  $\ell$  value. The program can handle a configuration like  $(2p)^6(3p)^4(5p)$ , but cannot handle a configuration like  $(2p)^5(3p)^5(4p)$ .

The energy expectation can now be written

$$\begin{aligned} E = & \sum_k 2f_k + \sum_k \sum_l (2J_{kl} - K_{kl}) \\ & + \nu_1 \left( \sum_m 2f_m + \nu_1 \sum_m \sum_n (2aJ_{mn} - bK_{mn}) + \sum_k \sum_m (2J_{km} - K_{km}) \right) \\ & + \nu_2 \left( \sum_p 2f_p + \nu_2 \sum_p \sum_q (2cJ_{pq} - dK_{pq}) + \sum_k \sum_p (2J_{kp} - K_{kp}) \right) \\ & + \nu_1 \nu_2 \sum_p \sum_q (2eJ_{pq} - fK_{pq}). \end{aligned} \quad (4)$$

The sets of subscripts  $(k, l)$ ,  $(m, n)$  and  $(p, q)$  refer to the closed shell, and the first and second open shells respectively. When the subscripts  $(i, j)$  are used, these will be taken to refer to the set of both open and closed shell orbitals. The constants  $\nu_1$  and  $\nu_2$  are the fractional occupancies of the 1st and 2nd open shells. The constants  $a, b, c, d, e$  and  $f$  depend on the orbital and spin angular quantum numbers, and the specific element of the multipole expansion of the two-body interaction.

The expectation values  $f_i$ ,  $J_{ij}$  and  $K_{ij}$  are defined by

$$f_i = \langle \phi_i(1) | t(1) | \phi_i(1) \rangle, \quad (5)$$

$$\begin{aligned} J_{ij} &= \langle \phi_i(1)\phi_j(2) | v(1,2) | \phi_i(1)\phi_j(2) \rangle \\ &= \langle \phi_i(1) | J_j(1) | \phi_i(1) \rangle = \langle \phi_j(2) | J_i(2) | \phi_j(2) \rangle, \end{aligned} \quad (6)$$

$$\begin{aligned} K_{ij} &= \langle \phi_i(1)\phi_j(2) | v(1,2) | \phi_j(1)\phi_i(2) \rangle \\ &= \langle \phi_i(1) | K_j(1) | \phi_i(1) \rangle = \langle \phi_j(2) | K_i(2) | \phi_j(2) \rangle, \end{aligned} \quad (7)$$

where

$$J_j(1) | \phi(1) \rangle = \langle \phi_j(2) | v(1,2) | \phi_j(2) \rangle | \phi(1) \rangle, \quad (8)$$

$$K_j(1) | \phi_i(1) \rangle = \langle \phi_j(2) | v(1,2) | \phi(2) \rangle | \phi_j(1) \rangle. \quad (9)$$

The arbitrary variation of the orbital functions leads to the energy variation

$$\begin{aligned} \delta E &= \sum_k (\langle \delta \phi_k | F_0 | \phi_k \rangle + \langle \delta \phi_k^* | F_0^* | \phi_k^* \rangle) \\ &\quad + 2\nu_1 \sum_m (\langle \delta \phi_m | F_1 | \phi_m \rangle + \langle \delta \phi_m^* | F_1^* | \phi_m^* \rangle) \\ &\quad + 2\nu_2 \sum_p (\langle \delta \phi_p | F_2 | \phi_p \rangle + \langle \delta \phi_p^* | F_2^* | \phi_p^* \rangle), \end{aligned} \quad (10)$$

where

$$\begin{aligned} F_0 &= f + \sum_k (2J_k - K_k) + \nu_1 \sum_m (2J_m - K_m) + \nu_2 \sum_p (2J_p - K_p), \\ F_1 &= f + \sum_k (2J_k - K_k) + \nu_1 \sum_m (2aJ_m - bK_m) + \nu_2 \sum_p (2eJ_p - fK_p), \\ F_2 &= f + \sum_k (2J_k - K_k) + \nu_1 \sum_m (2eJ_m - fK_m) + \nu_2 \sum_p (2cJ_p - dK_p). \end{aligned} \quad (11)$$

When the orthogonality constraints are incorporated, the energy variation becomes

$$\delta \left( E - 2 \sum_i \sum_j \langle \phi_i | \phi_j \rangle \epsilon_{ij} \right) = 0, \quad (12)$$

which can be expanded as

$$\delta \left( E - 2 \sum_i \sum_j [\langle \delta \phi_i | \phi_j \rangle \epsilon_{ij} + \langle \delta \phi_i^* | \phi_j^* \rangle \epsilon_{ji}] \right) = 0. \quad (13)$$

Combining the equations gives a set of HF equations involving non-diagonal Lagrange multipliers,

$$\begin{aligned} F_0 | \phi_k \rangle &= \sum_j \epsilon_{kj} | \phi_j \rangle = \sum_l \epsilon_{kl} | \phi_l \rangle + \sum_n \epsilon_{kn} | \phi_n \rangle + \sum_q \epsilon_{kq} | \phi_q \rangle, \\ \nu_1 F_1 | \phi_m \rangle &= \sum_j \epsilon_{mj} | \phi_j \rangle = \sum_l \epsilon_{ml} | \phi_l \rangle + \sum_n \epsilon_{mn} | \phi_n \rangle + \sum_q \epsilon_{mq} | \phi_q \rangle, \\ \nu_2 F_2 | \phi_p \rangle &= \sum_j \epsilon_{pj} | \phi_j \rangle = \sum_l \epsilon_{pl} | \phi_l \rangle + \sum_n \epsilon_{pn} | \phi_n \rangle + \sum_q \epsilon_{pq} | \phi_q \rangle. \end{aligned} \quad (14)$$

There is also a set of conjugate equations involving the conjugate operators  $F_0^*$ ,  $F_1^*$ , and  $F_2^*$ . These equations can be used to show that the matrix of Lagrange multipliers form a Hermitian matrix,  $\epsilon_{ij} = \epsilon_{ji}^*$ . Since the total energy is invariant to a unitary transformation of the closed shell orbitals amongst themselves, it is always possible to choose the closed shell orbitals so that the closed shell part of the Lagrange multiplier matrix is a diagonal matrix. It is also possible to transform the open-shell orbitals so that additional off-diagonal Lagrange multipliers can be set to zero. Using the notation,  $\epsilon_i = \epsilon_{ii}$ , the HF equations can be rewritten in a simpler form,

$$\begin{aligned} F_0 | \phi_k \rangle &= \epsilon_k | \phi_k \rangle + \sum_n \epsilon_{kn} | \phi_n \rangle + \sum_q \epsilon_{kq} | \phi_q \rangle, \\ \nu_1 F_1 | \phi_m \rangle &= \sum_l \epsilon_{ml} | \phi_l \rangle + \epsilon_m | \phi_m \rangle + \sum_q \epsilon_{mq} | \phi_q \rangle, \\ \nu_2 F_2 | \phi_p \rangle &= \sum_l \epsilon_{pl} | \phi_l \rangle + \sum_n \epsilon_{pn} | \phi_n \rangle + \epsilon_p | \phi_p \rangle. \end{aligned} \quad (15)$$

Multiplying on the left by  $\langle \phi_m |$  and integrating gives

$$\epsilon_{km} = \langle \phi_m | F_0 | \phi_k \rangle. \quad (16)$$

Other identities involving the Lagrange multipliers are easy to obtain,

$$\begin{aligned} \epsilon_{mk} &= \langle \phi_k | \nu_1 F_1 | \phi_m \rangle, \\ \epsilon_{kp} &= \langle \phi_p | F_0 | \phi_k \rangle, \quad \epsilon_{pk} = \langle \phi_k | \nu_2 F_2 | \phi_p \rangle, \\ \epsilon_{mp} &= \langle \phi_p | \nu_1 F_1 | \phi_m \rangle, \quad \epsilon_{pm} = \langle \phi_m | \nu_2 F_2 | \phi_p \rangle. \end{aligned} \quad (17)$$

The converged solutions of the HF equations obey the identity,  $\epsilon_{ij} = \epsilon_{ji}$ . Defining the coupling operators

$$\begin{aligned} F_{01} &= x_{01} F_0 + \nu_1 (1 - x_{01}) F_1, \\ F_{02} &= x_{02} F_0 + \nu_2 (1 - x_{02}) F_2, \\ F_{12} &= \nu_1 x_{12} F_1 + \nu_2 (1 - x_{12}) F_2, \end{aligned} \quad (18)$$

it is easy to see that these satisfy

$$\epsilon_{km} = \langle \phi_m | F_{01} | \phi_k \rangle, \quad \epsilon_{kp} = \langle \phi_p | F_{02} | \phi_k \rangle, \quad \epsilon_{mp} = \langle \phi_p | F_{12} | \phi_m \rangle. \quad (19)$$

The projection operators

$$Q_0 = \sum_k |\phi_k\rangle\langle\phi_k|, \quad Q_1 = \sum_m |\phi_m\rangle\langle\phi_m|, \quad Q_2 = \sum_p |\phi_p\rangle\langle\phi_p|, \quad (20)$$

can be used to project out solutions of the closed and open shell manifolds:

$$\begin{aligned} Q_0 | \phi_k \rangle &= | \phi_k \rangle; & Q_0 | \phi_m \rangle &= 0; & Q_0 | \phi_p \rangle &= 0, \\ Q_1 | \phi_k \rangle &= 0; & Q_1 | \phi_m \rangle &= | \phi_m \rangle; & Q_1 | \phi_p \rangle &= 0, \\ Q_2 | \phi_k \rangle &= 0; & Q_2 | \phi_m \rangle &= 0; & Q_2 | \phi_p \rangle &= | \phi_p \rangle. \end{aligned} \quad (21)$$

With these definitions the HF equations, can be rewritten

$$F_0 |\phi_k\rangle = \epsilon_k |\phi_k\rangle + \sum_n |\phi_n\rangle\langle\phi_n| F_{01} |\phi_k\rangle + \sum_q |\phi_q\rangle\langle\phi_q| F_{02} |\phi_k\rangle. \quad (22)$$

The  $\sum_n |\phi_n\rangle\langle\phi_n|$  and  $\sum_q |\phi_q\rangle\langle\phi_q|$  terms are projection operators, so this equation can be rewritten as

$$F_0 |\phi_k\rangle = \epsilon_k |\phi_k\rangle + Q_1 F_{01} |\phi_k\rangle + Q_2 F_{02} |\phi_k\rangle. \quad (23)$$

The projection and coupling operators are Hermitian operators, but their product is not. However, because

$$F_{01}(Q_1 |\phi_k\rangle) = 0 \quad \text{and} \quad F_{02}(Q_2 |\phi_k\rangle) = 0, \quad (24)$$

these terms can be added to (23) giving

$$F_0 |\phi_k\rangle = \epsilon_k |\phi_k\rangle + (F_{01} Q_1 + Q_1 F_{01}) |\phi_k\rangle + (F_{02} Q_2 + Q_2 F_{02}) |\phi_k\rangle, \quad (25)$$

which can be rewritten as

$$[F_0 - (F_{01} Q_1 + Q_1 F_{01}) - (F_{02} Q_2 + Q_2 F_{02})] |\phi_k\rangle = \epsilon_k |\phi_k\rangle. \quad (26)$$

Similar manipulations may be performed on the equations for the two open shell manifolds and the final form of the HF equations is

$$\begin{aligned} H_0 |\phi_k\rangle &= \epsilon_k |\phi_k\rangle, \\ H_1 |\phi_m\rangle &= \epsilon_m |\phi_m\rangle; \quad \eta_m = \frac{\epsilon_m}{\nu_1}, \\ H_2 |\phi_p\rangle &= \epsilon_p |\phi_p\rangle; \quad \eta_p = \frac{\epsilon_p}{\nu_2}. \end{aligned} \quad (27)$$

The effective Hamiltonians are

$$\begin{aligned} H_0 &= F_0 - (Q_1 F_{01} + F_{01} Q_1) - (Q_2 F_{02} + F_{02} Q_2), \\ H_1 &= F_1 - \frac{1}{\nu_1} [(Q_0 F_{01} + F_{01} Q_0) - (Q_2 F_{12} + F_{12} Q_2)], \\ H_2 &= F_2 - \frac{1}{\nu_2} [(Q_0 F_{02} + F_{02} Q_0) - (Q_1 F_{12} + F_{12} Q_1)]. \end{aligned} \quad (28)$$

Having obtained the solutions to these equations by the self-consistent field technique, the total energy of the HF single configuration wave function can be written as

$$E = \sum_k (4\ell_k + 2)(f_k + \epsilon_k) + \nu_1 (4\ell_m + 2)(f_m + \epsilon_m) + \nu_2 (4\ell_p + 2)(f_p + \epsilon_p). \quad (29)$$

This expression for the total energy is only true when the HF wave function has converged. The HF wave function also satisfies the virial theorem. The expectation value of the kinetic energy is

$$\begin{aligned} T &= \sum_k (4\ell_k + 2) \langle \phi_k | -\frac{1}{2} \nabla^2 | \phi_k \rangle + \nu_1 (4\ell_m + 2) \langle \phi_m | -\frac{1}{2} \nabla^2 | \phi_m \rangle \\ &\quad + \nu_2 (4\ell_p + 2) \langle \phi_p | -\frac{1}{2} \nabla^2 | \phi_p \rangle. \end{aligned} \quad (30)$$

The ratio of the potential energy to the kinetic energy should be equal to minus two, i.e.

$$\frac{V}{E} = \frac{E - T}{T} = -2. \quad (31)$$

Manipulations involving projection operators are not normally done when the finite difference techniques are applied to the HF equation. Under such circumstances it is customary to keep the off-diagonal Lagrange multipliers and solve Schrödinger-type equations with inhomogeneous terms.

### 3. The Basis Set Expansion

The HF equations are now in a form that is readily amenable to solution by expansion in terms of basis functions. A full derivation of the reduction of the HF equations need not be given since this has been covered adequately (Roothaan 1950, 1961; Hurley 1976). Only the essential definitions and results will be presented herein. In this section, matrix representations of operators will be designated as bold capitals,  $\mathbf{D}$ , column vectors will be denoted by lower case bold, e.g.  $\mathbf{c}$ , and row vectors designated by  $\mathbf{c}^\dagger$ .

The orbital wave functions are expanded in terms of basis functions,

$$|\phi_i\rangle = \sum_{\alpha} c_{i\alpha} |\chi_{\alpha}\rangle. \quad (32)$$

The single particle orbital  $|\phi_i\rangle$  can be denoted in a compact vector notation as the column vector  $\mathbf{c}_i$ . The orthogonality constraint becomes

$$\langle\phi_i|\phi_j\rangle = \sum_{\alpha} \sum_{\beta} c_{i\alpha} \langle\chi_{\alpha}|\chi_{\beta}\rangle c_{j\beta} = \delta_{ij}. \quad (33)$$

Defining the overlap matrix  $\mathbf{S}$  by

$$\mathbf{S}_{\alpha\beta} = \langle\chi_{\alpha}|\chi_{\beta}\rangle, \quad (34)$$

the orthogonality constraint can now be written

$$\mathbf{c}_i^{\dagger} \mathbf{S} \mathbf{c}_j = \delta_{ij}. \quad (35)$$

The expectations of the energy with respect to the orbitals can be written in matrix notation

$$\begin{aligned} f_i &= \mathbf{c}_i^{\dagger} \mathbf{T} \mathbf{c}_i, \\ J_{ij} &= \mathbf{c}_i^{\dagger} \mathbf{J}_j \mathbf{c}_i = \mathbf{c}_j^{\dagger} \mathbf{J}_i \mathbf{c}_j, \\ K_{ij} &= \mathbf{c}_i^{\dagger} \mathbf{K}_j \mathbf{c}_i = \mathbf{c}_j^{\dagger} \mathbf{K}_i \mathbf{c}_j, \end{aligned} \quad (36)$$

where the Hermitian matrices have the following matrix elements

$$\begin{aligned} \mathbf{T}_{\alpha\beta} &= \langle\chi_{\alpha}|t|\chi_{\beta}\rangle, \\ \mathbf{J}_{i,\alpha\beta} &= \sum_{\gamma} \sum_{\delta} c_{i\gamma} c_{i\delta} \langle\chi_{\gamma} \chi_{\alpha} | v | \chi_{\delta} \chi_{\beta}\rangle, \\ \mathbf{K}_{i,\alpha\beta} &= \sum_{\gamma} \sum_{\delta} c_{j\gamma} c_{j\delta} \langle\chi_{\gamma} \chi_{\alpha} | v | \chi_{\delta} \chi_{\beta}\rangle. \end{aligned} \quad (37)$$

Defining the  $\mathbf{D}_i$  matrices as

$$\mathbf{D}_0 = \sum_k \mathbf{c}_k \mathbf{c}_k^{\dagger}, \quad \mathbf{D}_1 = \mathbf{c}_m \mathbf{c}_m^{\dagger}, \quad \mathbf{D}_2 = \mathbf{c}_p \mathbf{c}_p^{\dagger}, \quad (38)$$

it is easy to show that the products  $\mathbf{D}_0 \mathbf{S}$ ,  $\mathbf{D}_1 \mathbf{S}$  and  $\mathbf{D}_2 \mathbf{S}$  are the matrix representations of the projection operators  $Q_0$ ,  $Q_1$  and  $Q_2$ .

With these definitions, the HF equations become

$$\begin{aligned} \mathbf{H}_0 \mathbf{c}_k &= \epsilon_k \mathbf{S} \mathbf{c}_k, \\ \mathbf{H}_1 \mathbf{c}_m &= \eta_m \mathbf{S} \mathbf{c}_m; \quad \eta_m = \frac{\epsilon_m}{\nu_1}, \\ \mathbf{H}_2 \mathbf{c}_p &= \eta_p \mathbf{S} \mathbf{c}_p; \quad \eta_p = \frac{\epsilon_p}{\nu_2}, \end{aligned} \quad (39)$$



where

$$\begin{aligned}
 \mathbf{H}_0 &= \mathbf{F}_0 - [(\mathbf{S}\mathbf{D}_1\mathbf{F}_{01} + \mathbf{F}_{01}\mathbf{D}_1\mathbf{S}) + (\mathbf{S}\mathbf{D}_2\mathbf{F}_{02} + \mathbf{F}_{02}\mathbf{D}_2\mathbf{S})], \\
 \mathbf{H}_1 &= \mathbf{F}_1 - \frac{1}{\nu_1}[(\mathbf{S}\mathbf{D}_0\mathbf{F}_{01} + \mathbf{F}_{01}\mathbf{D}_0\mathbf{S}) + (\mathbf{S}\mathbf{D}_2\mathbf{F}_{12} + \mathbf{F}_{12}\mathbf{D}_2\mathbf{S})], \\
 \mathbf{H}_2 &= \mathbf{F}_2 - \frac{1}{\nu_2}[(\mathbf{S}\mathbf{D}_0\mathbf{F}_{02} + \mathbf{F}_{02}\mathbf{D}_0\mathbf{S}) + (\mathbf{S}\mathbf{D}_1\mathbf{F}_{12} + \mathbf{F}_{12}\mathbf{D}_1\mathbf{S})]. \quad (40)
 \end{aligned}$$

The HF equations are now written as a set of generalised matrix eigenvalue equations. These equations can be solved directly or a Cholesky factorisation of the overlap matrix can be made and the equations transformed into a set of standard eigenvalue equations. In the present program, a transformation to an orthogonal basis is used to turn the equation into a standard eigenvalue problem. The orthogonal basis is generated by diagonalising the overlap matrix. The overlap matrix can be written as

$$\mathbf{\Lambda}^T \mathbf{S} \mathbf{\Lambda} = \mathbf{U}, \quad (41)$$

where  $\mathbf{U}$  is a diagonal matrix, and  $\mathbf{\Lambda}$  is a unitary matrix containing the eigenvectors of  $\mathbf{S}$ . Each eigenvector is then divided by the square root of the eigenvalue, so that

$$(\mathbf{U}^{-\frac{1}{2}} \mathbf{\Lambda}^T) \mathbf{S} (\mathbf{\Lambda} \mathbf{U}^{-\frac{1}{2}}) = \mathbf{W}^T \mathbf{S} \mathbf{W} = \mathbf{I} \quad (42)$$

and

$$\mathbf{W}^T \mathbf{W} = \mathbf{U}^{-1}. \quad (43)$$

The generic matrix equation can now be written

$$\begin{aligned}
 \mathbf{H} \mathbf{U}^{-1} \mathbf{U} \mathbf{c} &= \epsilon \mathbf{S} \mathbf{U}^{-1} \mathbf{U} \mathbf{c} \\
 \Rightarrow \mathbf{H} \mathbf{W}^T \mathbf{W} \mathbf{U} \mathbf{c} &= \epsilon \mathbf{S} \mathbf{W}^T \mathbf{W} \mathbf{U} \mathbf{c} \\
 \Rightarrow \mathbf{W} \mathbf{H} \mathbf{W}^T (\mathbf{W} \mathbf{U} \mathbf{c}) &= \epsilon \mathbf{W} \mathbf{S} \mathbf{W}^T (\mathbf{W} \mathbf{U} \mathbf{c}) \\
 \Rightarrow \mathbf{G} \mathbf{d} &= \epsilon \mathbf{d}, \quad (44)
 \end{aligned}$$

where

$$\mathbf{G} = \mathbf{W} \mathbf{H} \mathbf{W}^T \text{ and } \mathbf{d} = \mathbf{W} \mathbf{U} \mathbf{c}. \quad (45)$$

The transformed problem has exactly the same eigenvalues as the original generalised eigenvalue problem. The eigenvectors for the original problem are obtained using

$$\mathbf{c} = \mathbf{W}^T \mathbf{d}. \quad (46)$$

There is a degree of arbitrariness about the effective Hamiltonians since no prescription has been given for the choice of the coupling parameters  $x_{01}$ ,  $x_{02}$  and  $x_{12}$ . When the open shell method was originally proposed (Roothaan 1960) for configurations containing one open shell, the parameter  $x_{01}$  was set to be

$$x_{01} = -\frac{\nu_1}{(1 - \nu_1)}i. \quad (47)$$

This choice makes a great deal of sense since all terms common to both  $F_0$  and  $F_1$  cancel, causing  $F_{01}$  to make only minor modifications to  $F_0$  and  $F_1$ . When two open shells are present it is possible to generalise the Roothaan prescription

$$x_{01} = -\frac{\nu_1}{(1 - \nu_1)}; \quad x_{02} = -\frac{\nu_2}{(1 - \nu_2)}; \quad x_{12} = -\frac{\nu_2}{(\nu_1 - \nu_2)}. \quad (48)$$

There is an obvious problem with this prescription when two open shells of the same symmetry, each containing the same number of electrons are present. However, other choices for these parameters exist (Adams 1978) (setting the coupling parameter,  $x_{12} = \frac{1}{2}$  is a sensible choice when  $\nu_1 = \nu_2$ ). Some of the choices of the parameters exhibit good convergence properties, other particularly inappropriate choices do not permit convergence to be attained at all (Moscardo and Alvarez-Collado 1979; Moscardo and Fernandez-Alonso 1978). An exhaustive discussion of the complications that can arise from the different schemes to choose the coupling parameters has been recently given (Krebs 1998). The discussion presented within has been restricted to presenting the information that is needed to run the program.

There is one particular choice for the coupling operators which is particularly useful for solving the HF equations within the fixed core (FC) approximation (Mitroy 1982). Consider a situation consisting of one open shell outside some closed shells. The HF equations are written

$$\begin{aligned} F_0|\phi_k\rangle &= \epsilon_k |\phi_k\rangle + \sum_n \epsilon_{kn} |\phi_n\rangle, \\ \nu_1 F_1|\phi_m\rangle &= \sum_l \epsilon_{ml} |\phi_l\rangle + \epsilon_m |\phi_m\rangle. \end{aligned} \quad (49)$$

Rather than use linear combinations of  $F_0$  and  $F_1$  to eliminate the Lagrange multipliers, equations (18) are used giving

$$\begin{aligned} F_0|\phi_k\rangle &= \epsilon_k |\phi_k\rangle + \sum_n \langle\phi_n|F_0|\phi_k\rangle|\phi_n\rangle, \\ \nu_1 F_1|\phi_m\rangle &= \sum_l \langle\phi_l|\nu_1 F_1|\phi_m\rangle |\phi_l\rangle + \epsilon_m |\phi_m\rangle. \end{aligned} \quad (50)$$

This can be written as

$$\begin{aligned} F_0|\phi_k\rangle &= \epsilon_k |\phi_k\rangle + Q_1 F_0 |\phi_k\rangle, \\ \nu_1 F_{10}|\phi_m\rangle &= \nu_1 Q_0 F_1 |\phi_m\rangle + \epsilon_m |\phi_m\rangle. \end{aligned} \quad (51)$$

The equation can be modified by subtracting terms such as  $F_0Q_1$ ,  $Q_1F_0Q_1$ ,  $\nu_1F_1Q_0$  and  $\nu_1Q_0F_1Q_0$  from both sides giving

$$\begin{aligned} (F_0 - Q_1F_0 - F_0Q_1 - Q_1F_0Q_0)|\phi_k\rangle &= \epsilon_k|\phi_k\rangle, \\ \nu_1(F_1 - Q_0F_1 - F_1Q_0 - Q_0F_1Q_0)|\phi_m\rangle &= \epsilon_m|\phi_m\rangle. \end{aligned} \quad (52)$$

The HF equations can now be written

$$\begin{aligned} H_0|\phi_k\rangle &= \epsilon_k|\phi_k\rangle, \\ H_1|\phi_m\rangle &= \epsilon_m|\phi_m\rangle; \quad \eta_m = \frac{\epsilon_m}{\nu_1}, \end{aligned} \quad (53)$$

where

$$H_0 = (1 - Q_1)F_0(1 - Q_1), \quad H_1 = (1 - Q_0)F_1(1 - Q_0). \quad (54)$$

Let the state vectors,  $|\phi_k^i\rangle$  and  $|\phi_m^i\rangle$  be the  $i$ th estimates of the HF orbitals obtained during the SCF iteration process. These estimates are not necessarily converged. Consider the action of the two operators upon these orbitals:

$$\begin{aligned} Q_1(H_0|\phi_k^i\rangle) &= Q_1(1 - Q_1)(F_0(1 - Q_1)|\phi_k^i\rangle) = 0, \\ Q_0(H_1|\phi_m^i\rangle) &= Q_0(1 - Q_0)(F_1(1 - Q_0)|\phi_m^i\rangle) = 0. \end{aligned} \quad (55)$$

A strong orthogonality constraint exists between the two manifolds of orbitals. This constraint causes the open shell orbitals of one iterate of the HF equations to be orthogonal to the closed shell orbitals even when the HF equations are far from convergence. This strong orthogonality condition is to be avoided in normal HF calculations since it can prevent convergence to the exact HF wave function. Consider for instance an attempt to solve the HF equations for the ground state configuration of Li,  $1s^22s^2S^e$  in a basis containing only two Slater-type orbitals. Provided the initial estimates of the  $1s$  and  $2s$  orbitals are orthogonal, there is no change in the specifics of the individual orbitals whatsoever. The  $2s$  orbital resulting from one iteration of the HF equations will be orthogonal to the  $1s$  orbital from the previous iteration. Since the space spanned by the basis set only contains two elements, this results in a new  $2s$  orbital which is identical to the previous estimate.

However, this strong orthogonality property can be sensibly used within the frozen core or fixed core (FC) approximation. Indeed, it is the preferred option for doing these calculations. Most versions of the open shell HF equations only satisfy a weak orthogonality condition, i.e. the open and closed shell orbitals are only guaranteed to be orthogonal once convergence of the full set of HF equations has been achieved. In fixed core calculations, the inability of the core orbitals to relax under the influence of the valence orbitals results in the valence orbitals having a small but finite overlap with the core orbitals. This non-orthogonality can be removed by a Schmidt orthogonalisation but using a coupling scheme that enforces strong orthogonality is the preferred approach.

#### 4. Matrix Elements for the STO and GTO Basis

The program has the inbuilt flexibility to handle either Slater-type orbitals (STO) or Gaussian-type orbitals (GTO). The ability to handle a GTO basis was a relatively recent addition. The single particle orbitals are written

$$\phi_i(\mathbf{r}) = \sum_{\alpha} \mathbf{c}_{i\alpha} \chi_{\alpha}(\mathbf{r}). \quad (56)$$

##### (4a) The STO Basis

The Slater-type orbitals are usually defined by

$$\chi_{\alpha}(\mathbf{r}) = \chi_{\alpha}(r) Y_{\ell m}(\mathbf{r}), \quad (57)$$

where

$$\chi_{\alpha}(r) = N_{\alpha} r^{n_{\alpha}-1} \exp(-\lambda_{\alpha} r), \quad (58)$$

where the normalisation constant is

$$N_{\alpha} = \sqrt{\frac{(2\lambda_{\alpha})^{2n_{\alpha}+1}}{(2n_{\alpha})!}}. \quad (59)$$

The matrix elements of the overlap matrix are

$$\mathbf{S}_{\alpha\beta} = N_{\alpha} N_{\beta} \frac{(n_{\alpha} + n_{\beta})!}{(\lambda_{\alpha} + \lambda_{\beta})^{n_{\alpha} + n_{\beta} + 1}}. \quad (60)$$

The one-body matrix elements of the non-relativistic Hamiltonian,  $T = -Z/r - \frac{1}{2}\nabla^2$ , are

$$\begin{aligned} \mathbf{T}_{\alpha\beta} = & N_{\alpha} N_{\beta} \frac{-\lambda_{\alpha}^2 (n_{\alpha} + n_{\beta})!}{2(\lambda_{\alpha} + \lambda_{\beta})^{n_{\alpha} + n_{\beta} + 1}} + N_{\alpha} N_{\beta} \frac{(\lambda_{\alpha} n_{\beta} - Z)(n_{\alpha} + n_{\beta} - 1)!}{(\lambda_{\alpha} + \lambda_{\beta})^{n_{\alpha} + n_{\beta}}} \\ & + N_{\alpha} N_{\beta} \frac{(\ell(\ell+1) - (n_{\beta} - 1)^2)(n_{\alpha} + n_{\beta} - 2)!}{2(\lambda_{\alpha} + \lambda_{\beta})^{n_{\alpha} + n_{\beta} - 1}}. \end{aligned} \quad (61)$$

The two-body matrix elements are more complicated since angular momentum considerations are involved. The matrix element for two electrons coupled to a total angular momentum of  $L$  is

$$\langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2); L | 1/r_{12} | \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2); L \rangle = \sum_k r_k(\ell_i, \ell_j, \ell_k, \ell_l) R^k(i, j, k, l). \quad (62)$$

The multipole expansion derives from the multipole expansion of the electron-electron interaction  $1/r_{12}$ ,

$$\frac{1}{r_{12}} = \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} \frac{4\pi}{2k+1} \mathbf{Y}^k(\hat{\mathbf{r}}_1) \cdot \mathbf{Y}^k(\hat{\mathbf{r}}_2), \quad (63)$$

where

$$\mathbf{Y}^k(\hat{\mathbf{r}}_1) \cdot \mathbf{Y}^k(\hat{\mathbf{r}}_2) = \sum_m Y_{km}^*(\hat{\mathbf{r}}_1) Y_{km}(\hat{\mathbf{r}}_2), \quad (64)$$

$$r_< = \min(r_1, r_2) \text{ and } r_> = \max(r_1, r_2). \quad (65)$$

The angular matrix element is

$$r_k = (-1)^{\ell_i + \ell_j + L} \sqrt{(2\ell_i + 1)(2\ell_j + 1)(2\ell_k + 1)(2\ell_l + 1)} \\ \times \begin{pmatrix} \ell_i & k & \ell_k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_j & k & \ell_l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_i & \ell_j & L \\ \ell_l & \ell_k & k \end{Bmatrix} \quad (66)$$

and the radial matrix element is

$$H^k(i, j, k, l) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} c_{i\alpha} c_{j\beta} \langle \chi_{\alpha} \chi_{\beta} | r_{<}^k / r_{>}^{k+1} | \chi_{\gamma} \chi_{\delta} \rangle c_{k\gamma} c_{l\delta}, \quad (67)$$

where

$$\langle \chi_{\alpha} \chi_{\beta} | r_{<}^k / r_{>}^{k+1} | \chi_{\gamma} \chi_{\delta} \rangle = N_{\alpha} N_{\beta} N_{\gamma} N_{\delta} \left[ \frac{(n_{\alpha} + n_{\gamma} - k - 1)!}{(\lambda_{\alpha} + \lambda_{\gamma})^{n_{\alpha} + n_{\gamma} - k}} H_{\alpha\beta\gamma\delta}^k \right. \\ \left. + \frac{(n_{\beta} + n_{\delta} - k - 1)!}{(\lambda_{\beta} + \lambda_{\delta})^{n_{\beta} + n_{\delta} - k}} H_{\beta\alpha\delta\gamma}^k \right]. \quad (68)$$

The factor  $H_{\alpha\beta\gamma\delta}^k$  is

$$H_{\alpha\beta\gamma\delta}^k = \sum_{\nu=0}^{n_{\alpha} + n_{\gamma} - k - 1} \frac{(n_{\beta} + n_{\delta} + k + \nu)! (\lambda_{\alpha} + \lambda_{\gamma})^{\nu}}{(\lambda_{\alpha} + \lambda_{\beta} + \lambda_{\gamma} + \lambda_{\delta})^{n_{\beta} + n_{\delta} + k + \nu + 1} \nu!}. \quad (69)$$

One problem with the basis sets expansions in general is that the cusp condition as the origin is not automatically satisfied. The logarithmic derivative of the single particle orbitals should satisfy the following condition

$$\lim_{r \rightarrow 0} \frac{d\phi(r)/dr}{\phi(r)} = -\frac{Z}{\ell + 1}. \quad (70)$$

A high quality STO basis set will yield single particle orbitals for which the boundary conditions is almost satisfied. The condition can be exactly satisfied provided there is only one STO with  $n_{\alpha} = \ell + 1$  and the exponent is  $\lambda_{\alpha} = \frac{Z}{\ell + 1}$ .

All the other STOs should have  $n_{\alpha} \geq \ell + 3$ .

Most compilations of analytic HF wave functions do not use basis sets which automatically yield the correct cusp condition at the origin. It has been stated that the restrictions upon the basis sets can result in a larger STO basis set being needed to get a HF energy that is close to convergence. The experience of the author is that this is not necessarily the case and that it should be possible

to generate high quality basis sets that satisfy the exact boundary condition at the origin without too much extra computational effort.

The program also has the ability to use an additional types of basis function. At present, the program can also handle a Laguerre basis using functions that have proved popular in scattering calculations. To be precise, we define

$$\chi_\alpha(r) = N_\alpha r^\ell \exp(-\lambda_\alpha r) L_{n_\alpha - \ell - 1}^{(2\ell+2)}(2\lambda_\alpha r), \quad (71)$$

where the normalisation constant is

$$N_\alpha = \sqrt{\frac{(2\lambda_\alpha)^{2\ell+3} (n_\alpha - \ell - 1)!}{(\ell + n_\alpha + 1)!}}, \quad (72)$$

and  $L_{n_\alpha - \ell - 1}^{(2\ell+2)}(2\lambda_\alpha r)$  is an associated Laguerre polynomial that can be defined in terms of a confluent hypergeometric (Abramowitz and Stegun 1964) as

$$L_{n_\alpha - \ell - 1}^{(2\ell+2)}(2\lambda_\alpha r) = \frac{(n_\alpha + \ell + 1)!}{(n_\alpha - \ell - 1)!(2\ell + 2)!} M(-(n_\alpha - \ell - 1), 2\ell + 2, 2\lambda_\alpha r). \quad (73)$$

The matrix elements of this Laguerre basis are evaluated by expanding the basis functions as a sum of individual terms containing powers of  $r$  and exponential factors. Once the Laguerre functions have been expressed as a sum of the individual terms, the matrix elements collapse to sums over individual matrix elements which can be evaluated using the expressions developed for STOs. Because of this it is relatively easy to modify the program to use a slightly different Laguerre function.

#### (4b) The GTO Basis

Besides Laguerre functions, the program can also handle Gaussian-type orbitals. These are defined as

$$\chi_\alpha(r) = N_\alpha r^{n_\alpha - 1} \exp(-\lambda_\alpha r^2). \quad (74)$$

The GTO basis functions must satisfy the condition

$$n_\alpha = \ell_\alpha + 2i + 1; \quad i = 0, 1, 2, \dots \quad (75)$$

so that electron-electron matrix elements collapse to a simple analytic form. The normalisation constant is

$$N_\alpha = \sqrt{\frac{1}{(2n_\alpha - 1)!!} \sqrt{\frac{2(4\lambda_\alpha)^{2n_\alpha+1}}{\pi}}}, \quad (76)$$

and the overlap matrix is

$$\mathbf{S}_{\alpha\beta} = N_\alpha N_\beta (n_\alpha + n_\beta - 1)!! \sqrt{\frac{\pi}{2(2\lambda_\alpha + 2\lambda_\beta)^{n_\alpha + n_\beta + 1}}}. \quad (77)$$

The one-body matrix elements of the Hamiltonian are

$$\mathbf{T}_{\alpha\beta} = N_\alpha N_\beta \left\{ 2\lambda_\alpha \lambda_\beta X_{(n_\alpha+n_\beta+2)}^{(\lambda_\alpha+\lambda_\beta)} - (\lambda_\alpha n_\beta + \lambda_\beta n_\alpha) X_{(n_\alpha+n_\beta)}^{(\lambda_\alpha+\lambda_\beta)} \right. \\ \left. + \frac{(\ell(\ell+1) + n_\beta n_\alpha)}{2} X_{(n_\alpha+n_\beta-2)}^{(\lambda_\alpha+\lambda_\beta)} - \frac{Z \left( \frac{n_\alpha + n_\beta - 2}{2} \right)!}{2\sqrt{(\lambda_\alpha + \lambda_\beta)^{(n_\alpha+n_\beta)}}} \right\}, \quad (78)$$

where for even  $n$

$$X_n^\lambda = \int_0^\infty r^n \exp(-\lambda r^2) dr = (n-1)!! \sqrt{\frac{\pi}{2(2\lambda)^{n+1}}}. \quad (79)$$

Using the definition

$$p = \frac{n_\alpha + n_\beta + n_\gamma + n_\delta - 2}{2}, \quad (80)$$

the two-body matrix elements are

$$\langle \chi_\alpha \chi_\beta | r_{<}^k / r_{>}^{k+1} | \chi_\gamma \chi_\delta \rangle = N_\alpha N_\beta N_\gamma N_\delta \frac{\sqrt{\pi}}{2^{p+2} \sqrt{(\lambda_\alpha + \lambda_\beta + \lambda_\gamma + \lambda_\delta)^{(2p+1)}}} \\ \times \left[ \sum_{i=0}^{(n_\alpha+n_\gamma-k)/2} \frac{(2p-2i-1)!! \left( \frac{n_\alpha+n_\gamma-k}{2} \right)! 2^i (\lambda_\alpha + \lambda_\beta + \lambda_\gamma + \lambda_\delta)^i}{(n_\alpha + n_\gamma - i)! (\lambda_\alpha + \lambda_\gamma)^{(1+i)}} \right. \\ \left. + \sum_{i=0}^{(n_\beta+n_\delta-k)/2} \frac{(2p-2i-1)!! \left( \frac{n_\beta+n_\delta-k}{2} \right)! 2^i (\lambda_\alpha + \lambda_\beta + \lambda_\gamma + \lambda_\delta)^i}{(n_\beta + n_\delta - i)! (\lambda_\beta + \lambda_\delta)^{(1+i)}} \right]. \quad (81)$$

## 5. Program Details

The program that is being made available has existed in various incarnations since 1978 and some of this (awful) pre FTN77 code is still present in the most recent version. A considerable amount of work has been put into the program in the intervening years, for instance in the original version, all matrix diagonalisations were performed using the Jacobi algorithm. It was only recently, that this section was replaced by the Householder algorithm as taken from the EISPACK suite of subroutines (Smith *et al.* 1976). So while there are sections of the code that are relatively up to date and easy to read, there are also parts of the code that are poorly written and relatively opaque. However, the program has received a fair amount of exercise over the years, and has been ported to a variety of computers including Cyber, VAX, PRIME, SUN, IBM RS6000 and DEC ALPHA. So it is expected that the program should be easy to port to most

computers and furthermore it should be able to reliably handle all configurations involving at most two open shells outside a closed shell.

In spite of the revisions that the program has been put through recently, there are still numerous examples of inefficiencies present in the program. The amount of memory required could be reduced, and the program could certainly be speeded up. However, in most circumstances the demands that the program places on most computational systems are not large and the desire to make the program available for general use has outweighed the benefits (and drawbacks) associated with a revised version specifically for general usage.

### (5a) Input

All of the program input is read from unit *IRD* (= 5) and is in free format.

#### 1. Card 1. (*KTL*(14), *I* = 1,14)

The array *KTL*(*I*) contains a number of parameters which control the flow of the program and determines the extent of the screen output.

<i>KTL</i> (1)	> 0	The program jumps to subroutine <i>OUT</i> after reading in and orthogonalising the orbitals. Mainly used to Schmidt orthogonalise a set of orbitals or to check the input stream.
<i>KTL</i> (2)	> 0	A strong orthogonality conditions is maintained between the open and closed shell orbitals during the iterative process.
<i>KTL</i> (3)	> 0	Details of the STO basis are printed out.
	> 10	The one-body matrix elements of the STO basis are printed.
	> 100	A diagnostic message is printed whenever the program enters the more important subroutines.
<i>KTL</i> (4)	> 0	Some statistics about the size of the two electron STO tables are printed.
<i>KTL</i> (5)	> 0	Details of the SCF iterations are printed. In particular the single particle energies and the orbital coefficients are printed.
	> 10	All the single particle energies, from all the open and closed shell manifolds are printed.
	> 20	This prints out the single electron Hamiltonians. A lot of output is produced.
<i>KTL</i> (6)	> 0	An alternate value of <i>x</i> coefficient used to couple the open and closed shell orbitals can be set manually. The coupling coefficient is set to $x = DBLE(KTL(6))/DBLE(100)$ .
<i>KTL</i> (7)		Not used.
<i>KTL</i> (8)	> 0	Damping is used to stabilise the convergence of the SCF process. The new orbital is updated according to $\mathbf{c}_i^{new} = y\mathbf{c}_i^{new} + (1 - y)\mathbf{c}_i^{old}$ , where $y = KTL(8)/100$ .
<i>KTL</i> (9)	> 2	Aitken's acceleration method is used to increase the rate of convergence of the SCF process. The extrapolation is used for iterations $i = 1 + KTL(9) * J$ where $J = 1, 2, 3, \dots$ . This facility is rarely used.
<i>KTL</i> (10)	> 0	The configuration is one for which the angular momentum information is not computed automatically. When this option is set, the angular coefficients are those of the 'average energy'



- configuration.  $KTL(10)$  should be set to  $100 + NMIN$ , where  $NMIN$  is the minimum  $N$  value value for which  $AK$  and  $BK$  Slater integrals need to be input.
- $KTL(11) > 0$  Angular coefficients for direct Slater integrals are needed. The number of coefficients input is  $KTL(11)$ .
- $KTL(12) > 0$  Angular coefficients for exchange Slater integrals are needed. The number of coefficients input is  $KTL(12)$ .
- $KTL(13) > 0$  Determines the amount of diagnostic output printed during the non-linear optimisation of the exponents.
- $KTL(13) > 10$  The energy and floating exponents are output after the completion of each HF calculation.
- $KTL(14) > 0$  The program will diagonalise the Hamiltonian for the hydrogenic  $-Z/r$  field.

## 2. Card 2. *RMASS,RNE,ZZZZ*

*RMASS*. This is the mass of the atom (not used).

*RNE*. This is the number of electrons (not used).

*ZZZZ*. This is the nuclear charge (read in as a positive number).

## 3. Card 3. *NDIM, NWF*

*NDIM*. This denotes the total number of basis functions.

*NWF*. This is the number of single particle orbitals.

## 4. Card 4. *NIT,LT,IST,LMAX,IDAVID,IVA04A*

*NIT*. This the maximum number of permissible SCF iterations.

*LT*. This is (twice) the total orbital angular momentum.

*IST*. This is (twice) the total spin angular momentum.

*LMAX*. The maximum  $\ell$ -value of any single particle orbital.

*IDAVID*. This determines whether non-linear optimisation of the exponential parameters of the basis is performed with the Davidson–Powell routine, *MODDAV*.

If  $IDAVID = 0$ , then *MODDAV* is not called. If  $IDAVID = 1$ , then *MODDAV* is called. If  $IDAVID = 2$ , *IDAVID* is set to zero after *MODDAV* has been called once.

*IVA04A*. If  $IVA04A = 1$ , non-linear optimisation of the STOs is performed using a quasi-Newton method.

## 5. Card 5. *MAXIT1,ECOMM2,FTOLER,FACTOR,DIFF* and Card 6. *MAXIT2,ECOMM2,FTOLER,ESCALE*

These cards deal with the non-linear optimisation of the basis functions. The data in card 5 refer to Davidson–Powell routine *MODDAV*, and the data in card 6 refer to the quasi-Newton algorithm *VA04A*. These routines were taken from the program *CIV3* and so more detail about the non-linear optimisation can be obtained elsewhere (Hibbert 1975*b*).

*MAXIT1* and *MAXIT2* refer to the maximum number of iterations

*ECOMM2* is the accuracy to which the exponents are to be optimised. A reasonable value for *ECOMM2* is an existing exponent multiplied by  $10^{-3}$  (it is assumed that rough estimates of the exponent are known).

*FTOLER* is the accuracy to which the energy is to be determined. This tolerance also determines the convergence criteria of the overall SCF process.

*DIFF* is an estimate of the expected improvement in the energy.

*FACTOR*. When estimating the gradient vector in *MODDAV*, the following step size is chosen

$$\delta\lambda = \text{FACTOR} \times \lambda \text{ if } \lambda \neq 0, \quad \delta\lambda = \text{FACTOR} \text{ if } \lambda = 0. \quad (82)$$

A value of  $10^{-4}$  should be reasonable.

*ESCALE* is the initial step length for parameter variation in *VA04A*. The bigger the number, the larger the initial step length. The step-length is

$$\delta\lambda = 0.1 \times \text{ESCALE} \times \text{ECOMM2}. \quad (83)$$

A reasonable estimate of the initial step length would be about 0.1 to 0.01 and once *ECOMM2* has been set, *ESCALE* should be adjusted to get an appropriate initial step length.

#### 6. Card 7. *IVPOL,ALPHAD,RCPOL*

When dealing with situations involving a couple of electrons outside a closed core it is often advantageous to allow for the polarisation of the core by using a semi-empirical polarisation potential. The matrix elements of this potential are computed by numerical integration.

$$V_{pol}(r) = -\frac{\alpha_d}{2r^4} [1 - \exp(-r^6/r_0^6)]. \quad (84)$$

*IVPOL*. When *IVPOL* > 0, the open-shell the polarisation potential is included in the one-electron part of the Hamiltonian. This option can only be used sensibly in the context of a frozen-core calculation.

*ALPHAD* is the value of the static dipole polarisability,  $\alpha_d$  in  $a_0^3$ .

*RCPOL* is the cutoff parameter,  $r_0$  in the polarisation potential.

The present program has been used to compute the frozen-(polarised)-core HF wave functions used in a number of calculations of electron scattering from  $\text{Be}^+$ , Na,  $\text{Al}^{2+}$ , K and  $\text{Ca}^+$ .

#### 7. Card 8. *NV(I),LV(I),GV(I),IVY(I),ITP(I)*

This card type defines the analytic basis and  $I = 1, \text{NDIM}$  cards are input.

*NV(I)*. The power of  $n_\alpha$  in  $r^{n_\alpha-1}$  for the STOs and GTOs. Also specifies the values of  $n_\alpha$  in  $L_{n_\alpha-\ell-1}^{(2\ell+2)}(2\lambda_\alpha r)$ .

*LV(I)*. This is the  $\ell$ -value of the STO. The STOs should be read in a sequence of increasing *LV*. Those with *LV* = 0, should precede those with *LV* = 1, those with *LV* = 1 should precede those with *LV* = 2, and so on.

*GV(I)*. This is the exponential parameter,  $\lambda_\alpha$  of the STO or GTO.

*IVY(I)*. If *IVY(I)* > 0, then the exponent of the STO is can be adjusted in a non-linear optimisation of the basis.

*ITP(I)*. There is a facility built into the program to use more than one type of basis function. Set *ITP(I)* = 0 for STOs, *ITP(I)* = 1 for LTOs, and

$ITP(I) = 10$  for GTOs. It is possible to include STOs and LTOs in the same calculation.

This LTO function has received extensive use in scattering calculations. Since only relatively few runs have been performed with Laguerre-type orbitals, the accuracy of this option cannot be guaranteed.

8. Card 9.  $N(I), NE(I), L(I), NOC(I), NFR(I)$  and

Card 10.  $(C(J, I), J=1, NML(I))$

Cards 9 and 10 are read in together for each orbitals from  $I = 1, NWF$ . For each single particle state an initial estimate of the orbital coefficients is required.

$N(I)$  is simply an integer label for the orbital. This label is only used for the storage of the  $AK$  and  $BK$  Slater integral coefficients.

$NE(I)$  designates which eigensolution (in terms of increasing energy) of the effective single particle Hamiltonian should be used to describe for the orbital.

$L(I)$  is the  $\ell$  value of the single particle orbital.

$NOC(I)$  designates the number of electrons occupying the single particle state.

$NFR(I)$ . This denotes the whether the orbital is ‘frozen’ during the SCF iterative process. If  $NFR(I) > 0$ , then this orbital is not updated during the SCF process.

$C(J, I)$ . These are the linear expansion coefficients of the STO basis set. After the orbital coefficients are read in, the set of orbitals are then normalised and orthogonalised. The number of coefficients must be equal the number of basis functions for that  $\ell$  value. For any orbital this is equal to  $NML(I)$  (which is computed internally).

9. Card 11.  $(I1, I2, KV, AAK)$  and Card 12.  $(I1, I2, KV, AAK)$

Cards 11 and 12 are concerned with the detailed specification of the HF energy. The HF energy can be written in the general form

$$E = \sum_i q_i \langle \phi_i | T | \phi_i \rangle + \sum_{i,j} \sum_k q_i q_j f_k(i, j) F^k(i, j) + \sum_{i,j} \sum_k q_i q_j g_k(i, j) G^k(i, j), \quad (85)$$

where the  $q_i$  are the orbital occupancies, and the  $f_k$  and  $F^k$  factors are the angular and direct Slater integrals, and the  $g_k$  and  $G^k$  factors are the exchange integrals. The HF equations determine the set of orbitals that minimise this energy function. For situations involving fully closed shells, or one or two electrons outside a closed shell, the  $f_k$  and  $g_k$  angular factors are computed automatically. In other situations the coefficients need to be input.

Card 11 is read a total of  $I = 1, KTL(11)$  times. This reads in the angular coefficients for the direct-type Slater integrals. The coefficient is stored in the array  $AK(N(I1), N(I2), KV/2)$ .

Card 12 is read a total of  $I = 1, KTL(12)$  times. This reads in the angular coefficients for the exchange-type Slater integrals. The coefficient is stored in the array  $BK(N(I1), N(I2), KV/2)$ .

The coefficients that are read in and stored in the arrays  $AK(I, J, K)$  and  $BK(I, J, K)$  are not the  $f_k$  and  $g_k$  coefficients, rather they are the differences

from the coefficients for the ‘average energy of the configuration’. This feature of the program was modeled on a similar feature in the *MCHF77* program (Froese-Fischer 1978).

The generation of *LS* dependent energy expressions for arbitrary configurations is quite complicated. That is why the original *MCHF77* approach of leaving this to the user has been adopted! A number of atomic physics textbooks discuss the angular momentum algebra associated with the generation of energy expressions in a lot of detail and also include tabulated energy expressions for a number of configurations (Condon and Odabsai 1980).

In addition there have been programs published that generate energy expressions for general atomic configurations (Hibbert 1970, 1971, 1982; Lima 1991).

### (5b) Array Dimensions

Most of the program dimensions are set using parameter statements. These parameters are:

*IMAN*. The number of manifolds for which single particle orbitals can be constrained to be orthogonal. At present, this is set to 3.

*IYG*. The number of separate groups of two-electron radial Slater integrals.

*ITX*. The maximum number of iterations.

*LDM*. The maximum number of basis functions for a particular  $\ell$ -value.

*LU*. The maximum  $\ell$  value of any individual single particle orbital.

*NORB*. The maximum number of single particle orbitals

*NSTO*. The total number of basis functions.

*NYK*. The maximum number of raw Slater integrals for a given  $(\ell_i, \ell_j, \ell_k, \ell_l)$  combination.

There are also a number of arrays that store precomputed factorial tables.

*FS(I)* contains  $(I-1)!$ . Storage is allowed for 80 elements. The array is initialised in *COMBIN*.

*DFT(I, J)* contains  $(I-1)!/(J-1)!$ . Storage is allocated for  $80 \times 80$  elements. The array is initialised in *COMBIN*.

*FL(I)* contains  $\log(I!)$ . Storage is allocated to 100 elements. The array is initialised in *GAMMA*. These values are used by the  $3j$  and  $6j$  routines *W3J* and *W6J*.

*FACT2(I)* contains  $(I-1)!!$  ( $I!! = 1 \cdot 3 \cdot 5 \dots I$  for  $I$  odd and  $I!! = 2 \cdot 4 \cdot 6 \dots I$  for  $I$  even). Storage is allowed for 100 elements. The array is initialised in *COMBIN*.

### (5c) Open Files

A number of files are used in the course of any calculation. These files are written to units *IRD*, *IWR*, *IKP*, *IDISK1* and *IDISK2* which are defined in routine *RHF*.

*RHFIN.DAT*. This file is identified with unit *IRD* = 5 and contains the input stream for the program.

The screen output is written to the unit *IWR* = 6.

*SLATER1.DAT*. This file, written to *IDISK1* = 11, contains the table of two electron direct and exchange radial integrals. This used to be a ‘SCRATCH’ file until the program was ported to an IBM RS6000 and the vagaries of the AIX operating system were encountered. At present the file is deleted manually or by using operating system commands after the completion of the program.

*SLATER2.DAT*. This file, written to  $IDISK2 = 21$ , contains the table of two electron direct and exchange radial integrals. This file is only used when a non-linear optimisation of the STO or GTO exponents is being performed.

*RHFOUT.DAT*. This file is designed to act as a clone of the *RHFIN.DAT* file and utilises unit,  $IKP = 12$ . This file can therefore serve as an input file to the program. The orbital coefficients written to it are those retained in the computer memory after the SCF cycle has completed or halted. In those cases where the SCF process converged slowly, and had to be halted because the maximum number of iterations was exceeded, the wave function file *RHFOUT.DAT* can be copied to *RHFIN.DAT* and used to restart the program.

#### (5d) Structure of the Program

The view has been taken that an exhaustive description of the program is not warranted. Most of the program is adequately commented, so only a brief description of the more important parts of the program is detailed here.

##### 1. RHF

This is the initial entry point for the program. The routines initialising the factorial tables, *GAMMA* and *COMBIN* and the routine *SETZER* which fills some arrays with zeros are called. The subroutine *SLATER* which reads in the input stream is also called. The files, *RHFIN.DAT*, *SLATER1.DAT*, *SLATER2.DAT* and *RHFOUT.DAT* are opened as required.

Some of the important decisions that determine the type of calculation are taken here.

When  $KTL(14) > 0$ , the program calls *ZHYD* to compute hydrogenic eigenstates and stops.

When  $(IDAVID + IVA04A) > 0$ , then *ZEOPT* is called and a non-linear optimisation of selected exponents is performed. Otherwise, the program just keeps iterating the SCF cycle for the input basis set until convergence is obtained. Convergence is achieved when the  $L_2$  norm of the difference between the orbital vectors satisfies

$$DELI = \max_{i=1,2,3,..} |\mathbf{c}_i^{j+1} - \mathbf{c}_i^j| < DPS \quad (86)$$

for two successive iterations.  $DPS$  is set in the subroutine *SCF*.

##### 2. SLATER

This routine reads in all the input data. The routine *CLOP*, which organises the individual orbitals into the open and closed shell manifolds is called here. If  $KTL(1) > 0$ , then the routines, *NWBAS*, *OUT*, *SPE* and *VPOL* are called to evaluate certain matrix elements and the program halts.

##### 3. NWBAS

The purpose of this routine is to compute quantities associated with the analytic basis and the single particle orbitals. The basis set is normalised so that the diagonal elements of the overlap matrix  $\mathbf{S}$  are 1, and the non-diagonal elements of  $\mathbf{S}$  are computed. The overlap matrix is diagonalised in *SDAG* and the transformation matrix  $\mathbf{W}$  to the orthogonal basis stored. The single particle

orbitals,  $\mathbf{c}_i$  are normalised and then orthogonalised in *ORTHOG*. The matrix elements of the one body Hamiltonian, and optionally the polarisation potential are computed in *SPE* and *VPOL* respectively.

#### 4. *ORTHOG*

This routine performs a Schmidt orthogonalisation of the single particle orbitals. The orthogonalisation is performed in the order in which the orbitals are input.

#### 5. *BASME*

The subroutine *BASME* organises the generation of the matrix elements of the electron-electron interaction. The two-body matrix elements are written to disk by a call to the routine *OUTPUT*. The matrix elements are put to disk in this manner, because at one time the program was located on a computer with very limited disk space, and the only place the matrix elements could be stored was another computer on the network. There were limitations on the size of individual records that could be written across the network.

#### 6. *Direct*

This routine computes the elements of the matrices  $\mathbf{F}_0$ ,  $\mathbf{F}_1$  and  $\mathbf{F}_2$  for the direct part of the electron-electron interaction. The routine *COUPLE* which computes the exchange contributions to the single particle Hamiltonian is called from here.

#### 7. *COUPLE*

This routine computes the elements of the matrices  $\mathbf{F}_0$ ,  $\mathbf{F}_1$  and  $\mathbf{F}_2$  for the exchange part of the electron-electron interaction.

#### 8. *EIGEN*

This routine controls the formation and diagonalisation of the effective Hamiltonians once the matrix representation of all necessary operators have been constructed. The coupling operators are formed, the projection operators are included, the Hamiltonian is transformed to the orthogonal basis. The matrix is diagonalised in *HAMDAG*, the correct eigenvectors are selected in *SORT* and then transformed back to the original basis. The eigenvectors are normalised in *NORM*, iteration damping is done in *DAMP*, the energy estimate is computed in *EHF*, the convergence test is also computed in *EHF*, and the updating and replacement of the eigenvectors is performed in *SET*.

The complicated structure of this subroutine is a result of history. The options to handle the various open shell situations were developed in an incremental manner, and not as part of a single formalism to handle the different open shell cases.

#### 9. *OUT*

The purpose of *OUT* is to print the eigenvalues and eigenvectors of the converged solution. For each single particle orbital, the orbital vector  $\mathbf{c}_i$ , the Koopman energy  $\epsilon_i$ , and the cusp condition at the origin are printed (the cusp conditions are meaningless for GTOs). As well, it is possible to compute the expectation values,  $r^k$  for  $k = -1, 1, 2$  and  $3$  and  $\nabla$ . The total energy and the

ratio  $\frac{V}{E} = \frac{E-T}{T}$  are also printed. The file *RHFOUT.DAT*, which contains the latest estimates of the orbitals coefficients and can be used as an input stream to the program is also written to disk.

#### (5e) Running the Program

The program as it stands cannot be used all the time as a black box. Generating converged solutions by the SCF procedure can be quite an involved procedure, especially for situations involving open shells or excited states. For closed shell atoms and a lot of ground state configurations, the default options built into the program generally result in converged solutions being obtained without any problems. For instance, when it has been necessary to use wave functions from the Clementi and Roetti (1974) tabulation for a scattering calculation, it is generally quicker to type in the STO basis, and run the HF program to generate the linear expansion coefficients rather than typing these coefficients in manually.

Unlike some finite difference HF programs, the present program does not have a ‘self-starting’ option. The initial estimate of the HF orbitals are input by the user. Since the HF orbitals are a linear combination of a relatively few basis functions, it has never been too onerous a chore to input the initial starting  $\mathbf{c}_i$  vectors. In addition, one can use existing tabulations of analytic HF functions to furnish the initial starting vector.

One useful feature of the program is the production of the file *RHFOUT.DAT*. This file writes out the wave function details when the program terminates. The file *RHFOUT.DAT* has exactly the same form as the input data stream *RHFIN.DAT* and so the latest results from a not quite converged calculation can be used to restart another calculation.

It is envisaged that the program will mostly be used to generate excited states since extensive tabulations of ground state HF functions already exist. The calculations involving open shell configurations are the most difficult to converge. The following tricks should permit convergence to be obtained in most circumstances.

- The first thing that should be done is to turn damping on. This is often the difference between convergence and non-convergence. Some times, damping factors as high as 0.90 have been used.
- The output file *RHFOUT.DAT* contains the last estimate of the wave function in a format that is compatible with *RHFIN.DAT*. It is possible to copy *RHFOUT.DAT* onto *RHFIN.DAT* and restart the calculation when the SCF process is converging very slowly.
- Most often it is the failure for the valence orbitals to converge that causes problems. It can be advantageous to run the calculation with the valence orbitals omitted to get reasonable initial estimates of the core orbitals. Once, reasonable descriptions for the core orbitals have been obtained, the valence electrons can be included and convergence should be easier to achieve.
- It is often a good idea to scan through the eigenvalues resulting from the matrix diagonalisation. For instance, suppose the state of interest is the  $3p\ ^2P^0$  state of sodium. When using the default choice of the coupling operators due to Roothaan, the second lowest eigenvalue would represent

the  $3p$  orbital. However, when the strong orthogonality condition is set, it is the lowest eigenvalue that represents the  $3p$  orbital. In general, the use of the Roothaan choice for the coupling operators results in an eigenvalue spectrum in which the orbitals are ordered in a natural manner. However, other choices of the coupling operators result in the eigenvalues being shuffled around and it is sometimes useful to dump the eigenvalue spectrum from each individual effective Hamiltonian to output. This can be done by setting  $KTL(5) > 10$ .

- This program has been primarily used in investigations that have concerned the behaviour of the valence electrons. Accordingly, it cannot be guaranteed to behave well for situations involving inner shell vacancies.
- The program may crash if a closed shell orbital is frozen, while other closed shell orbitals of the same  $\ell$  symmetry are not frozen.
- Configurations with one or two electrons missing from a closed p or d shell seem to converge the slowest. Damping factors almost always have to be used in these situations.

It might be tempting to use this program to generate orbitals computed with the one-body terms of the Breit-Pauli Hamiltonian to take into account relativistic modifications of the orbitals. It is strongly recommended that this not be done. The diagonalisation of the Breit-Pauli Hamiltonian for a hydrogenic ion with  $Z = 60$  gives ridiculous energies.

#### (5f) Basis Set Selection

The analytic approach to the HF method has one additional layer of complexity that is not present in the numerical approach. This is the detailed specification of the basis set. The level to which complexities can intrude into what should be a rather simple business is best exemplified by the present environment in quantum chemistry which has seen acronyms proliferate to a great extent. Fortunately, the situation in atomic physics is rather simpler and there are a number of tabulations of analytic HF wave functions that provide reasonable starting points for the calculations of excited state wave functions. The following discussion assumes that the program will be used to generate orbitals for excited state configurations.

The first point to be made is that the existing basis functions that are used to describe the core orbitals should be adequate for a description of the inner parts of the valence orbitals. To a large extent, the behaviour of the radial wave functions for core and excited state orbitals close to the origin are quite similar apart from an overall normalising factor (Connerade 1998).

An important point to stress is the extent to which small differences in the energy can lead to major differences in the wave functions. This is especially true for highly excited levels. A reasonable initial estimate for the exponential parameter is  $\lambda = \sqrt{2\epsilon}$ , where  $\epsilon$  is the ionisation energy (or Koopman energy) of the state.

When doing a non-linear optimisation for the basis set parameters for excited states, it is often best to do the optimisation within the framework of a frozen core model. Besides having less equations to solve, frozen core calculations often take fewer SCF iterations to converge, and this can lead to major time savings. There is another advantage to a frozen core calculation. If the effect of the



optimisation will only be an energy decrease of 0.0001 Hartree, this small change in the energy will be swamped by the total HF energy which is  $-1000$  Hartree around  $Z = 20$ . Making the relative change in the energy as large as possible has obvious benefits when performing an optimisation. When an optimisation run is performed, the options giving the enhanced printout [i.e.  $KTL(13) > 0$ ] should be turned on.

Many compilations of basis functions and wave functions already exist in the literature. The compilation of Clementi and Roetti (1974) gives STO basis wave functions for every ground state of every ion for  $Z \leq 54$  while MacLean and MacLean (1982) provide tabulations for heavier atoms (which really should be treated with a relativistic formulation). More accurate STO basis sets for neutral atom ground states have recently been published by Bunge *et al.* (1993) and Koga *et al.* (1993a, 1993b, 1994). The situation with GTO basis sets is not as satisfactory despite the enormous efforts expended in creating basis sets for molecular calculations. Most of the GTO basis sets use contracted basis functions constructed from linear combinations of GTOs. However, Partridge (1987, 1989a, 1989b), Huzinaga and Miguel (1990) and Huzinaga *et al.* (1993) have published basis sets of uncontracted GTOs that are suitable for this program.

## 6. Availability of the Program

The program can be obtained over the internet at

<http://lacebark.ntu.edu.au/j-mitroy/research/atomic.htm>.

Alternatively email can be sent to [j-mitroy@banks.ntu.edu.au](mailto:j-mitroy@banks.ntu.edu.au) (regular mail also accepted). This document is also available as a RevTEX file. The results of a number of sample calculations (and associated input streams) exist at this site.

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