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Numerical Solution of General Hartree–Fock Equations for Atoms

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Two methods, M1 and $\widetilde{\text{M2}}$, for improving numerical Hartree-Fock (HF) radial functions during an SCF iteration are considered. It is shown that when rotations are introduced into the SCF process, functions can be improved one at a time, without direct concern over orthonormality conditions. Convergence characteristics for various classes of HF problems are considered. Generally M1 has the faster rate of convergence but when no exchange is present $\widetilde{\text{M2}}$ is preferable becoming, in effect, inverse iteration with a difference correction. In all cases, except the hydrogenic one, the asymptotic rate of convergence of the SCF process is linear.

1. INTRODUCTION

The Hartree–Fock (HF) approximation Ψ to the total wavefunction of a many-electron atomic system is a type of central-field approximation. However, instead of prescribing the field of force the Hartree–Fock method simply requires Ψ to be an antisymmetric configuration state function of central-field type with radial functions such that the energy is stationary with respect to variations in these functions [1]. This leads to a system of non-linear, integrodifferential equations known as the Hartree–Fock equations. For ground states or the lowest states with a given symemtry the energy is a minimum and the Hartree–Fock approximation may be viewed as the "best" approximation of central-field type. For this reason it is an important approximation in atomic structure theory, one often used as a standard for comparison purposes.

Hartree–Fock equations frequently are solved by an iterative process referred to as the *self-consistent field* (SCF) method. In an earlier paper [2] two numerical methods of solution, M1 and M2, were proposed which were shown to have far greater stability (and hence better convergence properties) than "standard" methods [3, 4] based on Hartree's procedure [1]. The instability of the latter, demonstrated by Griffin *et al.* [5], was often associated with several open shells of the same symmetry, such as Ti $3d^24s4d$, where an orthogonality constraint applies. In many cases, the first method (M1) converges rapidly even though it essentially ignores the orthogonality requirement.

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But in cases such as He $1s2s\,^1S$, where there is a strong orthogonality constraint, M1 generally fails whereas the second method (M2), which improves pairs of radial functions so as to retain orthogonality between them, performs satisfactorily. Considerable experience has been gained with these methods.

In this paper the Hartree–Fock calculations are classified according to the type of orthogonality constraint present and the role of M1 and M2 studied. When radial functions are constrained by orthogonality, the Hartree–Fock energy must be stationary to first order with respect to perturbations in the form of rotations. It will be shown that when the energy expression is invariant under rotations of a given pair of functions, the case may be treated as though the orthogonality requirement for that pair was not present. When the energy expression is not invariant, rotations may be introduced into the SCF process for finding the stationary energy. Then M1, which requires fewer computations per cycle, again has the better convergence characteristics, but a modified form of M2, which we denote by $\widetilde{\mathrm{M}2}$, is needed to deal with the special case where no exchange is present.

The classification of the various cases and the convergence characteristics of the methods will be illustrated primarily by a study of the two-eletron problem. We conclude with some general comments for more complex systems.

2. PROPERTIES OF THE HF EQUATIONS

The HF equations for $1snl\,^{1,3}L$ states of two-electron systems illustrate many of the properties of the HF equations. Let the *radial factor* for an nl electron be $R(nl;\,r) = (1/r)\,P(nl;\,r)$ where $P(nl;\,r)$ is the *radial function*. Furthermore, let us assume that

$$\begin{aligned}\langle nl \mid n'l\rangle &\equiv \int_0^\infty P(nl;\,r)\,P(n'l;\,r)\,dr \\ &= \delta_{nl,n'l} \qquad (1)\end{aligned}$$

where $\delta_{nl,n'l}$ is the Kronecker delta function. Then the energy for the state (assuming $nl \neq 1s$) is given by the well-known expression [2]

$$E(1snl\,^{1,3}L) = I(1s) + I(nl) + F^0(1s,\,nl) \pm \frac{1}{2l+1}\,G^l(1s,\,nl) \qquad (2)$$

where the "+" sign refers to the ^1L state, "−" to ^3L. Also,

$$I(nl) = -\frac{1}{2}\,\langle nl \mid L_l \mid nl\rangle, \qquad L_l = \frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2}$$

where Z is the atomic number,

$$\begin{aligned} Y^k(nl, n'l'; r) &= \int_0^r \left(\frac{s}{r}\right)^k P(nl; s)\, P(n'l'; s)\, ds \\ &\quad + \int_r^\infty \left(\frac{r}{s}\right)^{k+1} P(nl; s)\, P(n'l'; s)\, ds, \end{aligned}$$

$$F^k(nl, n'l') = \int_0^\infty P^2(nl; r) \left(\frac{1}{r}\right) Y^k(n'l', n'l'; r)\, dr$$

and

$$G^k(nl, n'l') = \int_0^\infty P(nl; r)\, P(n'l'; r) \left(\frac{1}{r}\right) Y^k(nl, n'l'; r)\, dr.$$

Because Eq. (2) assumes the orthonormality conditions of Eq. (1) apply, Lagrange multipliers must be introduced into the variational process. Let $\epsilon_{nl,n'l} = \epsilon_{n'l,nl}$ be the Lagrange multiplier associated with Eq. (1). Then

$$\begin{aligned} W(1snl\,{}^{1,3}L) &= E(1snl\,{}^{1,3}L) + \epsilon_{1s,1s}\langle 1s \mid 1s\rangle \\ &\quad + \epsilon_{nl,nl}\langle nl \mid nl\rangle + \delta_{l,0}\epsilon_{1s,nl}\langle 1s \mid nl\rangle \end{aligned}$$

must be stationary with respect to variations in both $P(1s; r)$ and $P(nl; r)$. Applying calculus of variations to this expression we find radial functions satisfying the stationary condition are solutions of the equations

$$\begin{aligned} &\left\{L_0 - \frac{2}{r}\, Y^0(nl, nl; r) - \epsilon_{1s,1s}\right\} P(1s; r) \\ &\qquad = \pm \frac{1}{2l+1} \left(\frac{2}{r}\right) Y^l(1s, nl; r)\, P(nl; r) + \delta_{l,0}\epsilon_{1s,nl} P(nl; r) \\ &\left\{L_l - \frac{2}{r}\, Y^0(1s, 1s; r) - \epsilon_{nl,nl}\right\} P(nl; r) \\ &\qquad = \pm \frac{1}{2l+1} \left(\frac{2}{r}\right) Y^l(1s, nl; r)\, P(1s; r) + \delta_{l,0}\epsilon_{nl,1s} P(1s; r). \end{aligned}$$

The parameters $\epsilon_{nl,n'l}$ are referred to as *energy parameters* with $\epsilon_{nl,nl}$ a *diagonal* energy parameter and $\epsilon_{nl,n'l}$, $nl \neq n'l$ an *off-diagonal* parameter. For the $1s^2\,{}^1S$ state (where $nl \equiv 1s$) there is no exchange and the HF equation becomes

$$\left\{L_0 - \frac{2}{r}\, Y^0(1s, 1s; r) - \epsilon_{1s,1s}\right\} P(1s; r) = 0.$$

In each case the boundary conditions are

$$P(nl; 0) = 0 \qquad \text{and} \qquad P(nl; r) \to 0 \quad \text{as } r \to \infty,$$

and we adopt the phase convention $P(nl; r) > 0$, $r \to 0$.

Several cases can now be identified

(1) $1snl\,^{1,3}L$, $nl \neq ns$. In this case there are no off-diagonal neergy parameters and each equation is a *linear* integrodifferential equation of boundary value type *if* the other function is considered fixed or given.

(2) $1sns\,^3S$. In this case it readily can be shown that the wavefunction yielding the energy expression of Eq. (2) is invariant under a rotation of the radial basis. The wavefunction for $1sns\,^3S$ is a Slater determinant and can be written as

$$\Psi(1sns\,^3S) = (1/r_1r_2)\{P(1s;r_1)\,P(ns;r_2) - P(ns;r_1)\,P(1s;r_2)\}\,x\,|\,ss\,^3S\rangle$$

where $|\,ss\,^3S\rangle$ is a spin-angular factor independent of the radial functions. The factor depending directly on the radial functions may be expressed in matrix vector notation.

$$\mathbf{P}(r) = [P(1s;r), P(ns;r)]^T.$$

Then

$$P(1s;r_1)\,P(ns;r_2) - P(ns;r_1)\,P(1s;r_2) = \mathbf{P}(r_1)^T \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \mathbf{P}(r_2).$$

Now let us rotate the radial basis and define

$$\mathbf{P}^*(r) = \mathscr{O}\mathbf{P}(r)$$

where

$$\mathscr{O} = \begin{bmatrix} a & b \\ -b & a \end{bmatrix}, \qquad a^2 + b^2 = 1.$$

Then

$$\mathbf{P}(r) = \mathscr{O}^T\mathbf{P}^*(r)$$

Applying the transformation and performing the indicated matrix operation we find that the radial factor

$$[\mathbf{P}(r_1)]^T \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \mathbf{P}(r_2) = [\mathbf{P}^*(r_1)]^T\,\mathscr{O} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \mathscr{O}^T\mathbf{P}^*(r_2)$$

$$= [\mathbf{P}^*(r_1)]^T \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \mathbf{P}^*(r_2).$$

In other words the radial part of the total wavefunction remains unchanged when evaluated in terms of the rotated basis. Consequently for a given total energy the solutions to the Hartree–Fock equation are not unique.

The effect of such a rotation on the HF equations is a transformation of the energy parameters. Let $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}^*$ be matrices of energy parameters for $\mathbf{P}(r)$ and $\mathbf{P}^*(r)$ respectively. Then

$$\boldsymbol{\epsilon}^* = \mathscr{O}\boldsymbol{\epsilon}\mathscr{O}^T.$$

The *standard* solution from this set of possible solutions is the one suggested by Koopmans [6] which minimizes the energy of the ion. This solution is characterized by off-diagonal energy parameters equal to zero [6, 7] so that in our case $\epsilon^*_{1s,ns} = 0$. Thus the equations for this case are the same as those for (1) though a general method of solution should be able to detect when this representation applies and set certain off-diagonal energy parameters to zero. When all off-diagonal energy parameters are zero Slater [8] refers to this as the *diagonal* representation; however, mixed situations may also occur as in $1s^2 2s 3s\ {}^3S$, where $\epsilon_{2s,3s} = \epsilon_{3s,2s} = 0$ but all others are non-zero.

(3) $1sns\ {}^1S$, $ns \neq 1s$. Now the wavefunction is

$$\Psi(1sns\ {}^1S) = (1/r_1 r_2)\{P(1s; r_1)\, P(ns; r_2) + P(ns; r_1)\, P(1s; r_2)\} \mid ss\ {}^1S\rangle$$

which is *not* invariant under a rotation of the radial basis. The HF solutions are functions which leave the energy stationary with respect to all allowed perturbations. A possible perturbation is a rotation and so the energy must be stationary with respect to such rotations.

3. Effect of rotations

Let us consider the $1sns\ {}^{1,3}S$ case again and apply the perturbation

$$\begin{bmatrix} P(1s; r) \\ P(ns; r) \end{bmatrix} = \begin{bmatrix} 1 & \eta \\ -\eta & 1 \end{bmatrix} \begin{bmatrix} P^{\mathrm{HF}}(1s; r) \\ P^{\mathrm{HF}}(ns; r) \end{bmatrix} + \mathcal{O}(\eta^2)$$

which maintains orthogonality of the orbitals. Substituting into Eq. (2) we get

$$\begin{aligned} E(1sns\ {}^{1,3}S) = {} & E^{\mathrm{HF}}(1sns\ {}^{1,3}S) \\ & + 2(1 \pm 1)\{R^0(1s, ns; ns, ns) - R^0(1s, 1s; 1sns)\}\eta \\ & + \mathcal{O}(\eta^2) \end{aligned} \tag{3}$$

where $R^0(\alpha, \beta; \alpha', \beta')$ is a Slater integral defined as

$$R^0(\alpha, \beta; \alpha', \beta') = \int_0^\infty P(\alpha; r)\, P(\alpha'; r)(1/r)\, Y^0(\beta, \beta'; r)\, dr.$$

The stationary condition of the Hartree–Fock energy requires that

$$\begin{aligned} \left.\frac{dE}{d\eta}\right|_{\eta=0} & = (1 \pm 1)\{R^0(1s, ns; ns, ns) - R^0(1s, 1s; 1s, ns)\} \\ & = 0. \end{aligned}$$

We now see that for the ${}^3S$ state, where the "$-$" sign applies, this condition is satisfied for *all* radial functions. This corresponds to the case where the total wavefunction was invariant under a rotation of the radial basis and so this result may be used to characterize such cases. For the ^1S state the condition

$$R^0(1s, ns; ns, ns) - R^0(1s, 1s; 1s, ns) = 0 \tag{4}$$

must hold. We refer to this as the *stationary condition.*

Suppose now that at some intermediate stage of the SCF process we have orthogonal radial functions, $\bar{P}(1s; r)$, $\bar{P}(ns; r)$ such that

$$\bar{R}^0(1s, ns; ns, ns) - \bar{R}^0(1s, 1s; 1s, ns) = \bar{f} \tag{5}$$

where $\bar{R}^0$ is evaluated using radial functions $\bar{P}$. Clearly the stationary condition of Eq. (4) does not hold, that is, the stationary point with respect to rotations has not been reached, and a further rotation is required. Let

$$\begin{bmatrix} P(1s; r) \\ P(ns; r) \end{bmatrix} = (1 + \eta^2)^{-1/2} \begin{bmatrix} 1 & \eta \\ -\eta & 1 \end{bmatrix} \begin{bmatrix} \bar{P}(1s; r) \\ \bar{P}(ns; r) \end{bmatrix} \tag{6}$$

where η is to be determined such that Eq. (4) is satisfied to first order in η. Substituting Eqs. (5) and (6) into (4) and using the relations

$$F^0(\alpha, \beta) = R^0(\alpha, \beta; \alpha, \beta) = R^0(\beta, \alpha; \beta, \alpha)$$
$$G^0(\alpha, \beta) = R^0(\alpha, \beta; \beta, \alpha) = R^0(\alpha, \alpha; \beta, \beta)$$

we get

$$\bar{f} + \eta\{\bar{F}^0(1s, 1s) + \bar{F}^0(ns, ns) - 4\bar{G}^0(1s, ns) - 2\bar{F}^0(1s, ns)\} + \mathcal{O}(\eta^2) = 0$$

Neglecting the terms $\mathcal{O}(\eta^2)$ (and dropping the bars) we have

$$\eta = \frac{R^0(1s, ns; ns, ns) - R^0(1s, 1s; 1s, ns)}{2F^0(1s, ns) + 4G^0(1s, ns) - F^0(1s, 1s) - F^0(ns, ns)} \tag{7}$$

This expression, when applied iteratively, would define a sequence of rotations converging to functions satisfying Eq. (4). In fact, it is a Newton–Raphson iteration with respect to rotations for the stationary condition.

An exact expression for η can readily be obtained. Substituting (6) into (4), multiplying by $(1 + \eta^2)^2$ to eliminate the denominators and noting that Slater integrals involve products of *four* radial functions, we find η is the root of a *quartic* polynomial whose coefficients are sums of Slater integrals. In their paper on a natural orbital calculation for the helium atom, where a similar minimization problem arises, Reid and Ohrn [9] derive expressions for the five coefficients and then proceed to find a root of the polynomial by the Newton–Raphson method, starting with $\eta = 0$. Our procedure is equivalent to theirs except that we redefine the origin of the polynomial after each iteration so that only the condition and its first-order variation need be evaluated. For the general problem, where the conditions may be fairly complex, fewer expressions need be derived and incorporated into a computation by this approach.

4. Solution of the Radial Equations

The radial equation for a single electron in a fixed core is an integrodifferential equation of the form

$$y'' + \{f(r) - \epsilon\}\, y = \int_0^\infty K(r, t)\, y(t)\, dt \qquad (8)$$
$$y(0) = 0; \qquad y(r) \to 0, \qquad r \to \infty$$

where the integral equation part includes the exchange effect as well as the off-diagonal energy parameters, if any. Both M1 and M2 deal with discretized approximations to Eq. (8).

For simplicity, let the range $(0, r_M)$ for suitably large r_M be subdivided by equally spaced points $r_i = ih$, $i = 0,..., M$, $h = r_M/M$. Let y_i be the computed approximation to $y(r_i)$, let $\mathbf{y} = (y_1, y_2,..., y_{M-1})^T$ be the column vector of values, and let the boundary conditions be $y_0 = y_M = 0$. A direct discretization of Eq. (8) at each of the points r_i, $i = 1,..., M - 1$ would lead to a system of equations of the form

$$(\mathbf{T} - \epsilon \mathbf{I} - \mathbf{K})\mathbf{y} = 0$$

where $\mathbf{T}$ is a band matrix (the band width depending on the order of the discretization of y'') and $\mathbf{K}$ a full matrix. The above is now an eigenproblem and inverse iteration [10], for example, would require $\mathcal{O}(M^3)$ multiplications for its solution because of the denseness of the matrix $\mathbf{K}$. However, exchange terms can be evaluated efficiently as the solution of certain ordinary differential equations. (For the independent variable, $\rho = \log_e r$, these equations have an integrating factor and the solutions can be obtained through outward and inward integration [3]). As a result, it is possible to describe an iterative procedure requiring only $\mathcal{O}(M)$ multiplications per iteration.

Let $\{ y^{(k)}(r), K = 0, 1,...\}$ be a sequence of approximate solutions. Define

$$g^{(k)}(r) = \int_0^\infty K(r, t)\, y^{(k)}(t)\, dt$$

and

$$\left\{\frac{d^2}{dr^2} + f(r) - \epsilon\right\} y^{(k+1)}(r) = g^{(k)}(r). \qquad (9)$$

For the latter, the familiar Numerov method based on the discretization

$$\delta^2 y_i = h^2 \left(1 + \frac{\delta^2}{12}\right) y_i'', \qquad i = 1,..., M - 1$$

leads to a tridiagonal system of equations

$$(\mathbf{T} - \epsilon \mathbf{S})\, \mathbf{y}^{(k+1)} = \mathbf{c}^{(k)} \qquad (10)$$

where $\mathbf{T} = (t_{ij})$ and $\mathbf{S} = (s_{ij})$ are $(M-1) \times (M-1)$ tri-diagonal matrices with

$$t_{ij} = \begin{cases} -2 + \frac{10}{12}h^2 f_j, & i = j, \\ 1 + \frac{10}{12}h^2 f_j, & |i-j| = 1, \quad f_j \equiv f(r_j), \\ 0, & |i-j| > 1, \end{cases}$$

and

$$s_{ij} = \begin{cases} \frac{10}{12}h^2, & i = j, \\ \frac{1}{12}h^2, & |i-j| = 1, \\ 0, & |i-j| > 1. \end{cases}$$

The column vector $\mathbf{c} = (c_1, c_2, \ldots, c_{M-1})^T$ has components

$$c_i = \frac{h^2}{12}(g_{i+1} + 10g_i + g_{i-1}) + \tau_i^{(k)}, \qquad g_i \equiv g^{(k)}(r_i)$$

and $\tau_i^{(k)}$ is an estimate of the truncation error acting as a "deferred" difference correction [11].

Unlike Eq. (8), (9) is no longer an eigenvalue problem and unique solutions to the discretized approximations of Eq. (10) will exist for all values of ϵ provided the coefficient matrix $(\mathbf{T} - \epsilon\mathbf{S})$ is nonsingular. In order that solutions of Eq. (10) converge to solutions of Eq. (8) it is necessary to define $\epsilon = \epsilon^{(k)}$ so that the sequence $\epsilon^{(k)}$, $k = 0, 1, 2, \ldots$ converges to an eigenvalue. A natural choice is the Rayleigh quotient for $\mathbf{y}^{(k)}$. (In the case of one electron, the quotient can be shown to be the functional for which $y(r)$ is the stationary solution: when more than one electron is present and $f(r)$ also depends on $y(r)$, the quotient is no longer exactly stationary.) At the same time we would like to have the iterations converge to a normalized eigenfunction of Eq. (8) where normalization is defined in terms of numerical integration.

Define $(\mathbf{u}, \mathbf{v}) \doteq \int_0^\infty u(r)\, v(r)\, dr$ to be a computed approximation to the integral using only values of the vectors $\mathbf{u}$ and $\mathbf{v}$, and $\|\mathbf{u}\|^2 = (\mathbf{u}, \mathbf{u})$. The method M1 combines all these ideas as follows.

For $k = 0, 1, 2, \ldots$,

(1) $\epsilon^{(k)} = \mathbf{y}^{(k)T}[\mathbf{T}\mathbf{y}^{(k)} - \mathbf{c}^{(k)}]/\mathbf{y}^{(k)T}\mathbf{S}\mathbf{y}^{(k)}$,

(2) $[\mathbf{T} - \epsilon^{(k)}\mathbf{S}]\,\mathbf{z}^{(k+1)} = \mathbf{c}^{(k)}$,

(3.1) $\mathbf{y}^{(k+1)} = \mathbf{z}^{(k+1)}/\|\mathbf{z}^{(k+1)}\|$.

We will show later that M1 performs remarkably well in many cases. However, it breaks down when $\|\mathbf{c}^{(k)}\|$ is exceedingly small as, for example, when no exchange is present at all.

In the case of a single equation, method M2 also computes $\mathbf{z}^{(k+1)}$ as above, but rather than simply normalize the solution it solves a variational equation for $\partial\mathbf{z}^{(k+1)}/\partial\epsilon$, namely

$$[\mathbf{T} - \epsilon^{(k)}\mathbf{S}]\, \partial\mathbf{z}^{(k+1)}/\partial\epsilon = \mathbf{S}\mathbf{z}^{(k+1)} \tag{11}$$

and forms an intermediate function

$$\mathbf{v}^{(k+1)} = \mathbf{z}^{(k+1)} + \Delta\epsilon^{(k)} \partial \mathbf{z}^{(k+1)}/\partial\epsilon \tag{12}$$

which, when normalized, becomes $\mathbf{y}^{(k+1)}$. In Eq. (12), $\Delta\epsilon^{(k)}$ is chosen in such a way that

$$\| \mathbf{v}^{(k+1)} \| = 1 + \mathcal{O}([\Delta\epsilon^{(k)}]^2).$$

Only for certain values of ϵ will the solutions of Eq. (9) be normalized and Eq. (12) may be interpreted as the first two terms of in Taylor's series expansion about $\epsilon = \epsilon^{(k)}$ of a normalized solution.

Again, numerical difficulties will occur as $\mathbf{c}^{(k)} \to 0$. If $\epsilon^{(k)}$ is not an exact eigenvalue of the matrix problem $(\mathbf{T} - \epsilon\mathbf{S})\mathbf{y} = 0$ (which is a reasonable assumption), then, in the limit when $\mathbf{c}^{(k)} = 0$, $\mathbf{z}^{(k+1)}$ also is zero; hence, by Eq. (11), $\partial\mathbf{z}^{(k+1)}\partial/\partial\epsilon = 0$ resulting in an undefined value of $\Delta\epsilon^{(k)}$ in Eq. (12). But with a slight modification of Eq. (11) whereby $\mathbf{z}^{(k+1)}$ on the right-hand side is replaced by $\mathbf{y}^{(k)}$, our method would make a smooth transition to inverse iteration for the matrix eigenvector problem. The latter has a *cubic* rate of convergence when the matrices **T** and **S** are symmetric and the Rayleigh quotient is used to define $\epsilon^{(k)}$, though rounding-errors reduce this rate once accurate solutions have been obtained [10]. This modification is the basis for our revised method $\widetilde{\text{M}}2$. More explicitly, step (3.1) of M1 is replaced by

(3.2) $[\mathbf{T} - \epsilon^{(k)}\mathbf{S}]\, \mathbf{w}^{(k+1)} = \mathbf{S}\mathbf{y}^{(k)}$,

(4.2) $\mathbf{y}^{(k+1)} = \mathbf{z}^{(k+1)} + \beta\mathbf{w}^{(k+1)}$; β such that $\| \mathbf{y}^{(k+1)} \| = 1$.

Our matrix **T** is not exactly symmetric, but inverse iteration can also be defined for a differential eigenvalue problem, and when the latter has an orthogonal set of eigenfunctions, convergence can be shown to be cubic. Therefore, as long as the iterations of our discretized problem reflect properties of the differential problem a similar rate of convergence should be observed.

When systems of equations are present, several additional factors must be considered. All functions could be iterated simultaneously but generally a *cyclic* iteration is preferable where for each equation the best current estimates of other functions are used. The analogy here is similar to the Jacobi iteration for linear equations versus Gauss–Seidel iteration where the latter has the better rate of convergence for certain classes of problems [12].

A more subtle question is that of orthogonality. As was shown in Section 2, the function for $1s2s\,^3S$ will be orthogonal when $\epsilon_{1s,2s} = 0$, but intermediate estimates may not be orthogonal. Some numerical experiments have shown that convergence is improved during initial stages by a Schmidt-orthogonalization process, (which changes the inner, more self-consistent functions the least), but that the asymptotic rate of convergence is decreased. A simple strategy orthogonalizes estimates at the end of every cycle.

When a pair of functions is constrained through an orthogonality requirement as in $1s2s\,^1S$, the method M2 described earlier [2] improves pairs of functions simultaneously in such a way as to maintain not only normalization but also orthogonality to first-order with respect to changes in the diagonal and off-diagonal energy parameters. This requires the additional computation of the variational equation for $\partial \mathbf{z}^{(k+1)}/\epsilon_{nl,n'l}$ and, in general, M2 becomes a far more complex algorithm than M1, particularly when combined with the concept of an *acceptable* solution to be described in the next section. But changing off-diagonal energy parameters indirectly introduces a rotation of the functions. As an alternative to M2 in this case, rotations can be introduced explicitly at the end of every cycle, following orthogonalization, and off-diagonal parameters can be computed directly. Suppose $\langle nl \mid n'l \rangle = 0$ and the Hartree–Fock equation for $P_{nl}(r)$ is written

$$\left\{L_l - \left(\frac{2}{r}\right) Y_{nl}(r) - \epsilon_{nl,nl}\right\} P_{nl}(r) = \left(\frac{2}{r}\right) X_{nl}(r) + \epsilon_{nl,n'l} P_{n'l}(r) \qquad (13)$$

where $2[Z - Y_{nl}(r)]/r$ is the *potential* function and $2X_{nl}(r)/r$ the *exchange* function. Multiplying the above equation by $P_{nl}(r)$, integrating and using the orthogonality property, we obtain the result

$$\epsilon_{nl,nl} = \langle nl \mid L_l \mid nl \rangle - 2 \int_0^\infty P_{nl}(r) \left(\frac{1}{r}\right) [Y_{nl}(r)\, P_{nl}(r) + X_{nl}(r)]\, dr$$

which is the Rayleigh quotient expression for the differential equation. Here we have assumed $\langle nl \mid nl \rangle = 1$. Similarly, the equation may be multiplied by $P_{n'l}(r)$ to yield the expression

$$\epsilon_{nl,n'l} = \langle n'l \mid L_l \mid nl \rangle - 2 \int_0^\infty P_{n'l}(r) \left(\frac{1}{r}\right) [Y_{nl}(r)\, P_{nl}(r) + X_{nl}(r)]\, dr$$

which can be used to obtain estimates of off-diagonal energy parameters. However, in the general case [7],

$$q_{nl}\epsilon_{nl,n'l} = q_{n'l}\epsilon_{n'l,nl}$$

where q_{nl} is the occupation number for the nl subshell, and it is desirable that our estimates also have this property. When $q_{nl} = q_{n'l}$, we use an average of the two expressions. When $q_{nl} \neq q_{n'l}$ we let $\epsilon_{nl,n'l} = \lambda/q_{nl}$, $\epsilon_{n'l,nl} = \lambda/q_{n'l}$, subtract the two expressions and use the fact that $\langle n'l \mid L_l \mid nl \rangle = \langle nl \mid L_l \mid n'l \rangle$ to obtain the result,

$$\lambda = \left[\frac{2q_{nl}q_{n'l}}{q_{n'l} - q_{nl}}\right] \int_0^\infty \left(\frac{1}{r}\right) \{P_{nl}(r)[Y_{n'l}(r) - Y_{nl}(r)]\, P_{n'l}(r) \\ + P_{nl}(r)\, X_{n'l}(r) - P_{n'l}X_{nl}(r)\}\, dr.$$

With the introduction of expressions for the potential and exchange functions, the expression for λ may be simplified further [7], but for our purposes here it is sufficient to know that off-diagonal energy parameters can be computed given the radial functions.

5. The SCF Iteration

With these comments, the basic stages in an SCF iteration for the general Hartree–Fock equations can be described.

(1) Set $\epsilon_{nl,n'l} = 0$ for all nl, $n'l$.

(2) Estimate the radial functions.

(3) Orthogonalize the radial functions.

(4) Rotate pairs of functions according to Eq. (7).

(5) Compute off-diagonal energy parameters but leave $\epsilon_{nl,n'l} = 0$ whenever the wavefunction is invariant under rotations.

(6) For each equation, in turn, starting with the innermost:

(a) Compute the potential and exchange functions.

(b) Compute $\epsilon_{nl,nl}$ as a Rayleigh quotient.

(c) Solve the differential equation using either M1 or $\widetilde{\mathrm{M2}}$ for a *single* equation.

(d) Test if the solution is acceptable. If so, replace or improve the current estimate. Otherwise adjust $\epsilon_{nl,nl}$ and repeat (6c)–(6d).

(7) Test for convergence of the SCF iteration. If self-consistency has not been achieved repeat (3)–(7).

Simple estimates for radial functions are screened hydrogenic functions with an effective nuclear charge, $Z_{\mathrm{eff}} = Z - \sigma_{nl}$, where σ_{nl} is a screening parameter. Scaled functions from other atoms or even functions from other terms of the same atom may be used. More elaborate estimates are functions from other methods such as Thomas–Fermi or Cowan's statistical exchange [13].

An *acceptable* solution of a radial equation is one for which $P(nl; r) > 0$, $r \rightarrow 0$ (our phase convention) and one which has the required number of nodes, not counting the small maxima or minima in the tail of a radial function arising from the persistence of the exchange effect or the rotation of the radial functions by the orthogonality constraint. After the first or second iteration (depending on the accuracy of the [redacted] and $1s3s\ {}^3S$ where the energy is only *stationary*.

Normally, an acceptable solution replaces the current estimate of a radial function. However, when several electrons of the same type are present as in $1s^2\ {}^1S$, the potential function $f(r)$ of Eq. (8) also depends on $y(r)$. If, for example, the current estimate of the radial function is too diffuse, then the nuclear charge will not be screened enough and the solution of Eq. (9) will be too contracted. In this way, oscillations are introduced. These can be damped by the use of accelerating parameters, α. Let the functions of step (3.1) for M1 (or (4.2) for $\widetilde{\mathrm{M2}}$) be denoted by $\bar{\mathbf{y}}^{(k+1)}$ and define

$$\bar{\bar{\mathbf{y}}}^{(k+1)} = (1 - \alpha)\, \bar{\mathbf{y}}^{(k+1)} + \alpha \mathbf{y}^{(k)}$$

with

$$\mathbf{y}^{(k+1)} = \bar{\bar{\mathbf{y}}}^{(k+1)}/\| \bar{\bar{\mathbf{y}}}^{(k+1)} \|.$$

When $\alpha = 0$, the solution of the differential equation replaces the current estimate, but for $0 < \alpha < 1$, a normalized linear combination of the solution and the current estimate form the new estimate. This "averaging" process has the effect of damping the oscillations.

No optimum methods are known for determining α. When the same equation is solved repetitively, values of $\epsilon^{(k)}$ could be extrapolated using, say, Steffensen's iteration [14]. If written as

$$\hat{\epsilon}^{(k+1)} = (1 - \alpha)\, \epsilon^{(k+1)} + \alpha\epsilon^{(k)}$$

this leads to

$$\alpha = 1/(1 - \rho^{-1}), \qquad \rho = (\epsilon^{(k+1)} - \epsilon^{(k)})/(\epsilon^{(k)} - \epsilon^{(k-1)}) \tag{11}$$

and requires that the equation be solved *three* times prior to extrapolation. Actually extrapolation should not be used until a linear rate of convergence is observed which requires *four* successive values [14]. For tightly bound electrons, the rate of convergence is sufficiently rapid that acceleration is not worthwhile. Also, in complex atoms changes in one function may occur because of changes in another. Such coupling can only be taken into account by extrapolating *cycles* of the SCF iteration, a process with a considerable amount of overhead, in general.

A simple expedient that does remarkably well is to end each SCF cycle with three or more iterations each time selecting the least self-consistent equation. If one function is converging much more slowly than another and is selected three times consecutively, a value of ρ can be computed according to Eq. (12), and $\alpha = \alpha^{(k)}$ adjusted as follows.

$$\begin{aligned} \alpha^{(k+1)} &= 1/4 + (3/4)\, \alpha^{(k)}, \qquad & \rho < 0 \\ &= (3/4)\, \alpha^{(k)}, & \rho > 0. \end{aligned}$$

In this way the accelerating parameter is increased when oscillations occur, and decreased otherwise. Clearly other values could also be used for the constants.

A measure of self-consistency is the maximum absolute change in a function from one cycle to the next. Let

$$\mathbf{P}_{nl}^{(k)} = (P_{nl}^{(k)}(r_1), P_{nl}^{(k)}(r_2) \cdots P_{nl}^{(k)}(r_{M-1}))^T$$

be the vector of function values after the k'th solution of the equation for $P_{nl}(r)$. Let $\bar{\mathbf{P}}_{nl}^{(k+1)}$ be a similar vector at stage $(k + 1)$ but prior to acceleration, if any. Then

$$\Delta P_{nl}^{(k)} = \max \mid \bar{P}_{nl}^{(k+1)}(r_i) - P_{nl}^{(k)}(r_i) \mid.$$

In going from the k'th to $(k + 1)$st stage it should be remembered that the potential and exchange function are recomputed and it is this variation which accounts for the linear convergence of the overall SCF iteration, as shown by the numerical results presented in the next section.

6. Numerical Results

The convergence of these procedures for the different cases mentioned in Section 2 has been studied using a modified version of MCHF72 [15].

In Fig. 1, the rate of convergence of M1 for $1s2p\ ^3P$ of He is compared with that of $\widetilde{\text{M}}2$, by plotting $-\log_{10}(\Delta P_{nl}^{(k)})$ versus the number of iterations. (In this case, since there is no orthogonality constraint, M2 and $\widetilde{\text{M}}2$ produce similar results.) The initial estimates were screened hydrogenic functions with $\sigma_{1s} = 0$ and $\sigma_{2p} = 1$. Clearly M1 has the faster rate of convergence. In both cases, convergence is linear after about four iterations.

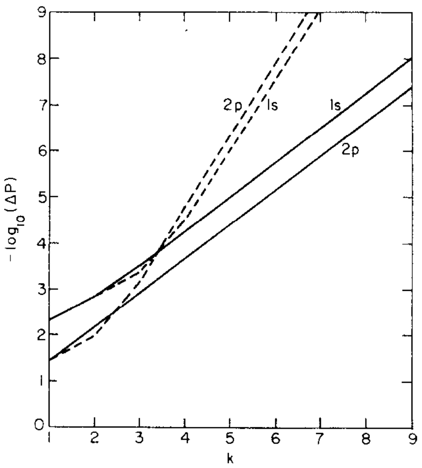

FIG. 1. A comparison of the rate of convergence of M1 (dashed line) with $\widetilde{\text{M}}2$ (solid line) for He $1s2p\ ^3P$.

The $1s2p\ ^3P$ case is a particularly simple one in that no orthogonality requirements are present. In Fig. 2, convergence for the most difficult state, $1s2s\ ^1S$ of He, is shown with initial estimates being the functions for $1s2s\ ^3S$. In one case, M1 is used along with orthogonalization and rotations at the end of very cycle. In the other, M2 improves pairs of functions simultaneously so as to maintain orthogonality to first order. Again, M1 has the better convergence characteristics, but the rate of convergence is not as fast as for the $1s2p\ ^3P$ state. We conclude that, with the introduction of rotations, M2 need not be used to deal with orthogonality constraints.

The $1s2s\ ^3S$ case again has no off-diagonal energy parameters, but the final functions should be orthogonal. Figure 3 shows the rate of convergence for two different SCF strategies. In both, the initial estimates are screened hydrogenic with $\sigma_{1s} = 0$ and $\sigma_{2s} = 1$; M1 was used exclusively. In the first strategy, the functions are improved in turn, and then orthogonalized. Note that the $1s$ function does not begin to improve significantly until the $2s$ function has similar accuracy. Then both improve rapidly. Note also the leveling off of ΔP_{2s}. Though the HF equations have orthogonal

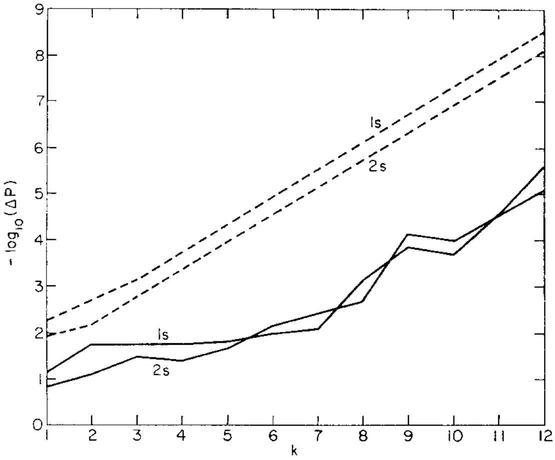

FIG. 2. A comparison of the rate of convergence of M1 (dashed line) with M2 (solid line) for He $1s2s\,{}^1S$.

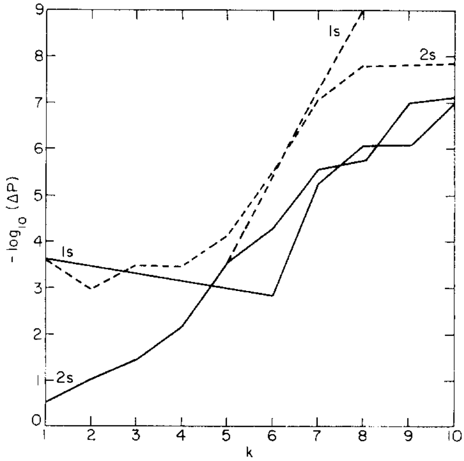

FIG. 3. A comparison of two strategies for orthogonalization for He $1s2s\,{}^3S$ using M1. In the first (dashed line), each function is improved in a cycle, then $2s$ orthogonalized to $1s$. In the second (solid line) after every improvement the least self-consistent function is orthogonalized to the other and a cycle is followed by *four* improvements of the least self-consistent function.

solutions in the diagonal representation, the self-consistent solutions of the discretized problem have an overlap integral of about 10^{-8} and so the orthogonalization process at the end of the cycle prevents further convergence of P_{2s}. In the second strategy, the equations are each solved in turn, followed by four improvements of the least self-consistent equation. After each improvement, the least self-consistent function is orthogonalized to the other. With this strategy, the solution of the $1s$ equation is avoided until the self-consistency of $2s$ is comparable. Note however, that ΔP_{1s} for $k = 6$ is now *larger* than at $k = 1$ because of the considerable change in P_{2s}

during the intervening iterations. The self-consistency for P_{1s} improves rapidly and at $k = 7$ the functions have similar self-consistency as those at $k = 6$ for the first strategy, yet the former required the solution of only 10 equations, whereas the latter required 12. The erratic convergence after $k = 7$ is due to the orthogonalization process. In fact, the second strategy performs similar to the first (with fewer equations solved) if P_{1s} is improved when $k = 5$ and orthogonalization turned off as soon as the overlap is less than 10^{-5}.

When no exchange is present, $\widetilde{\mathrm{M2}}$ is the preferred method. Figure 4 shows the very rapid convergence for $1s\,{}^2S$ of He$^+$ where the potential function $f(r)$ does not depend on the solution. The initial estimate in this case was a screened hydrogenic function with $\sigma = 0.5$. By contrast, the convergence of $1s^2\,{}^1S$ of He is much slower since $f(r)$ now also depends on the solution. Furthermore, with $\alpha = 0$ a linear rate of convergence is observed, a rate which improved appreciably by the simple acceleration strategy described earlier.

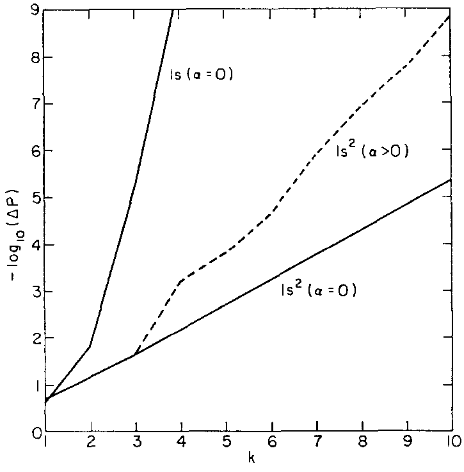

FIG. 4. Convergence of $\widetilde{\mathrm{M2}}$ without accelerating parameters (solid line) for He$^+$ $1s\,{}^2S$ and He $1s^2\,{}^1S$ compared with convergence with accelerating parameters (dashed line) for He $1s^2\,{}^1S$.

In complex atoms, the systems of equations are strongly coupled, but converge even with crude initial estimates, at least when no off-diagonal energy parameters are present. For example, when unscreened hydrogenic functions are used as initial estimates for Ra $7s^2$ ($Z = 88$), virtually no convergence is observed in the first two cycles except electrons appear to "sort themselves out." After that convergence begins with $\Delta P = \max\{\Delta P_{nl}\}$ on the average reduced by a factor of about 0.156 per cycle. In these calculations, each cycle of the SCF process was appended with eight improvements of the least self-consistent function. No function was ever selected three times in a row for acceleration to be introduced.

In Table I, some values of ΔP are tabulated for various atoms or ions with initial estimates as indicated. The computation (CPU) times in seconds on an IBM System

TABLE I

CPU Time in Seconds for Several Calculations Using an IBM System 370/168

Atom/ion	Z	Number of functions	Configuration	Initial estimates	Maximum ΔP	Time (seconds)
Be	4	2	$1s^2 2s^2\ {}^1S$	$\sigma = 0$	1.2×10^{-8}	2.04
W^{+70}	74	2	$1s^2 2s^2\ {}^1S$	$\sigma = 0$	7.0×10^{-14}	1.05
La	57	13	$4f6s^2\ {}^2F$	$\sigma = c$	4.8×10^{-8}	51.69
W^{+17}	74	13	$4f6s^2\ {}^2F$	$\sigma = c$	3.6×10^{-9}	41.36
Ra	88	16	$7s^2\ {}^1S$	$\sigma = c$	1.0×10^{-7}	74.74
Ra	88	16	$7s^2\ {}^1S$	$\sigma = 0$	9×10^{-8}	82.82

370/168 are also reported. Note that convergence is more rapid for highly ionized systems. For W^{+70} $1s^2 2s^2$, convergence is especially rapid. For neutral Be, ΔP is limited to about 10^{-8} by the orthogonalization process in the same way as for the [redacted] to a subshell closer to the nucleus. Let the number of electrons in the ith subshell be q_i. In the first case, a simple screening law was applied, namely,

$$\sigma_i \equiv c_i = \sum_{j<i} q_j + \tfrac{1}{2} q_i .$$

In the second,

$$\sigma_i \equiv 0.$$

As expected, the first required less computer time, but an inherent difficulty lies in knowing in advance which group is "closer." Fortunately, this factor does not seem to be a critical one. It may be that an optimum ordering can be determined though it could depend on the degree of ionization. In Table II, the initial screening parameters for the first case are compared with the final screening parameter, defined so that

$$\langle r_{nl} \rangle^{\mathrm{HF}} = \langle r_{nl} \rangle^{\mathrm{H}} / (Z - \sigma_{nl})$$

where $\langle r_{nl} \rangle^{\mathrm{HF}}$ is the mean radius of the Hartree–Fock radial function, and $\langle r_{nl} \rangle^{\mathrm{H}}$ the one for hydrogen. Some fairly extensive changes have occurred.

Table II also shows the final degree of self-consistency of each radial function and the number of times a particular function was improved. For $n \geqslant 4$, the shells are sufficiently interpenetrating that changes in the radial function of one, result in changes

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[1] The final total energy of -14.57302316 a.u. agrees to 10 significant figures with that of Raffenetti [16] who used an analytic basis for the calculation. But clearly this accuracy depends more on the implementation itself than the method.

TABLE II

SCF Convergence for Ra $7s^2$ Starting with Screened Hydrogenic Functions

nl	Screening Initial	 Final	Number of Iterations	ΔP_{nl}
$1s$	1	0.7	8	8.1×10^{-12}
$2s$	3	4.7	8	3.2×10^{-10}
$2p$	7	5.8	8	4.7×10^{-11}
$3s$	11	12.9	10	2.9×10^{-9}
$3p$	15	14.1	11	1.5×10^{-9}
$3d$	23	17.4	12	1.5×10^{-9}
$4s$	29	25.1	14	2.1×10^{-9}
$4p$	33	28.6	14	4.0×10^{-9}
$4d$	41	33.6	14	4.0×10^{-9}
$5s$	47	42.3	14	5.5×10^{-9}
$5p$	51	45.7	16	1.0×10^{-8}
$4f$	61	40.6	14	7.0×10^{-9}
$5d$	73	53.0	14	5.3×10^{-9}
$6s$	79	59.6	13	8.6×10^{-8}
$6p$	83	63.4	17	6.9×10^{-8}
$7s$	87	74.8	17	3.7×10^{-8}

in the other, and all equations need to be solved about the same number of times. But for $n \leqslant 3$ fewer improvements suffice.

7. CONCLUDING REMARKS

The examples of the previous section illustrative the general convergence characteristics of the SCF process. They show that, when rotations are used to satisfy a stationary condition, convergence is observed in all cases with a scheme which improves a *single* function at a time. The improvement scheme M1, which does not attempt to find a normalized solution of a boundary-value problem, in general has a faster rate of convergence than M2 or $\widetilde{\mathrm{M2}}$, which may be viewed as the first stage of an iterative process for finding a normalized solution. Though it was not illustrated explicitly, M1 encounters difficulties when no exchange term is present and the diagonal energy parameter is not known accurately. In this case $\widetilde{\mathrm{M2}}$ performs well being, in effect, inverse iteration with a difference correction.

A study of the convergence characteristics of typical examples also has shown the SCF process to have an inherently *linear* rate of convergence. This is due to the coupling *between* equations and also due to the fact that the functions $g^{(k)}(r)$ (and sometimes $f(r)$) of Eq. (9) depend on the solution. For this reason, we do not advocate solving Eq. (9) itself by a subiteration process but rather, recommend improving the solution with a *single* iteration of a rapidly converging process.

Figures 1–4 also show that after about four or five cycles the SCF iterations converge in a very regular, linear fashion provided no changes are made to accelerating parameters and the SCF cycle is not appended with additional improvements. Such linear convergence suggests that extrapolation techniques would be effective. However, the overhead in space would be high since all functions would have to be saved over three cycles before the SCF extrapolation process could be applied. This might be feasible if a very high degree of self-consistency is required, or convergence is very slow. For most applications, high accuracy is not required. It should be remembered too, that self-consistency does not guarantee accuracy. The latter also depends on the discretization error introduced by replacing the differential equation of Eq. (9), for example, by the linear system of Eq. (10).

Earlier conventional methods for the numerical solution of the HF equations [3, 4] relied on the matching of solutions from outward an inward integration for the adjustment of certain parameters. Both M1 and M2 are direct methods with the boundary conditions incorporated into the discretized problem. More recently, Cayford *et al.* [17] have proposed a similar direct approach, but one where the radial functions are improved by a generalized Newton–Raphson iteration (GNRI). Suppose Eq. (9) is to be solved for a solution vector $\mathbf{y}^{(k+1)}$ and an energy parameter, ϵ, such that $\| \mathbf{y}^{(k+1)} \| = 1$. Then the discretized problem,

$$(\mathbf{T} = \epsilon \mathbf{S})\, \mathbf{y}^{(k+1)} = \mathbf{c}^{(k)},$$

$$(\mathbf{y}^{(k+1)}, \mathbf{y}^{(k+1)}) = 1,$$

is a system of M equations in the M unknowns $y_1^{(k+1)},\ldots, y_{M-1}^{(k+1)}$, and ϵ. (Their discretization is somewhat different from ours but that does not affect the main idea.) Orthogonality conditions involving $\mathbf{y}^{(k+1)}$ can be added to the system of equations, and off-diagonal energy parameters, one for each condition, to the set of unknowns. In this way, orthogonality can be treated in a natural way and no arbitrary orthogonalization process need be introduced. The resulting system is now a non-linear system of equations, but special properties make possible the efficient solution of the problem by a generalized Newton–Raphson iteration, with the well-known quadratic rate of convergence. Typically four iterations are required for a convergence tolerance of 10^{-10}. This improvement scheme is then imbedded in the usual SCF process for obtaining solutions of the HF equations. Our experience, though, leads us to believe that difficulties may occur when orthogonality with inaccurate functions is required, particularly when many orthogonality constraints are present. Also, the GNRI method assumes the existence of a normalized solution for a given estimated potential and exchange function. Griffin *et al.* [5] show that zero, one, or two acceptable, normalized solutions may exist. In the case of the former, GNRI would clearly fail, and the latter tends to produce instabilities in the SCF iteration of certain configurations with 4d or 5f electrons. In the SCF–GNRI process, these problems are controlled by "tracking," that is, the functions $Y_{nl}(r)$ and $X_{nl}(r)$ appearing in Eq. (11) are multiplied by a factor θ. Then, for $\theta = 0$, the solutions are all unscreened hydrogenic functions. With these as initial estimates, θ is increased in stages until $\theta = 1$. Each time the results from one stage form the initial estimates for the next. Consequently, several intermediate stages must be solved, though convergence tolerances for these stages may be set correspondingly high.

The essential difference between our methods is the way in which the sequence $\{\epsilon^{(k)}, k = 0, 1,...\}$ is selected so as to converge to an eigenvalue of the integro-differential equation, Eq. (8). The methods of this paper use the Rayleigh quotient, whereas GNRI selects a value for which the solution of Eq. (9) is normalized. Method $\widetilde{\text{M}}2$ also relies on a normalization criterion for the improvement of the function, but is used only when the exchange effect is small. Earlier methods too, solved for normalized solutions, though not by the GNRI method, and SCF instabilities were observed. M1, in particular, has been shown to have greater stability [2]. In fact, the calculation for Ra 7s^2, included in Table 1, converged without the necessity of resorting to tracking.

In their paper, Cayford *et al.* include some data for an unrestricted Hartree–Fock calculation for Li 1$s^2$2s. In order to compare our methods more reliably, the MCHF program was modified for this case. (Actually, only the orthogonality constraint between radial functions for orbitals of different spin had to be removed.) Starting with unscreened hydrogenic functions, using no acceleration, and with each SCF iteration simply improving the radial functions in turn, and then orthogonalizing the orbitals with the same spin, we obtained convergence to within numerical accuracy in *eight* SCF iterations. The final self-consistency parameter was $\Delta P = 4 \times 10^{-8}$, and the total energy, -7.432750920 a.u. The ratio of the potential and kinetic energy differed from the exact value of -2.0 by 2.0×10^{-9}. By contrast, the SCF–GNRI method for a given mesh spacing, achieved convergence with an SCF tolerance of 10^{-10} in *seventeen* iterations, and the total energy was -7.432614303 a.u. When energies for *four* different mesh spacings were extrapolated, a value of -7.432750918 a.u. was obtained which differs from our value by only two units in the last place, or 2×10^{-9} a.u. We conclude that our eight SCF iterations have converged satisfactorily. To test the effect of relying on normalization as a criterion for improvement we also solved the system of equations using $\widetilde{\text{M}}2$ for all functions. This slowed convergence of the 2s radial function to such an extent that thirteen SCF iterations were required where eight had sufficed before. This rate of convergence is similar to the one reported for SCF–GNRI, but it is not clear from the data provided, just how tracking affected convergence. These results for Li 1$s^2$2s as well as the earlier ones for He 1s2p ^3P, plotted in Fig. 1, both indicate that the SCF convergence rate may be slower when normalization is used as a criterion for the improvement of radial functions, at least when exchange effects are significant.

The program MCHF72 [15], used here for the study of convergence, was designed to take advantage of properties of the Hartree–Fock equations. The discretized approximation may not satisfy these exactly, thereby limiting the convergence of the

[redacted]

Fifty years have passed since Hartree published his first paper on the numerical solution of the radial equation [18]. Since then, many ideas have been proposed for the efficient solution of the Hartree–Fock equations [1]. The present methods are generally simpler, involving fewer iterative processes, and unlike earlier procedures, rarely rely upon accelerating parameters for achieving convergence. Experience seems to indicate that Hartree–Fock calculations now can be performed on a routine basis.

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