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Iterative Solution of the Hartree–Fock Equations with Improved Stability

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Standard methods for solving the Hartree–Fock equations for excited states often fail to converge or oscillate about the solution. Two new methods with improved stability properties are proposed which require only one computation of the exchange function per SCF iteration. These methods have solved satisfactorily all the cases found to be unstable by Griffin, Cowan and Andrew [1] as well as other test cases.

I. INTRODUCTION

Recently Griffin, Cowan and Andrew [1] performed extensive studies of instabilities in the iterative solution of the Hartree–Fock (HF) equations for excited configurations in atoms. They define a configuration to be *unstable* if, when using solutions of the Hartree-plus-statistical-exchange (HX) equations [2] as initial estimates, a "standard" method for solving the radial equation leads to a self-consistent field iteration which fails to converge. Some examples are K $4d$, Ca $4s4d$, Sc $4s^24d$, Ti $3d^24s4d$ and $3d^24s5d$ [3]. For the last case, even with an input 5d radial function self-consistent to 10^{-7}, the standard method slowly diverged. Griffin *et al.* analyzed the reasons for instabilities, classified solutions as being of three types and devised two new methods for finding solutions in these cases. Their methods have been successful in solving HF equations for such complex cases as Pt $6s5d^86f$ but at the expense of vast amounts of computer time. In this paper two new but simple methods are suggested which, when used as the "standard" method, would greatly reduce the class of unstable configurations. In particular, all the configurations mentioned above (with the exception of Pt $6s5d^86f$ which was not tried) converged satisfactorily using screened hydrogenic functions as initial estimates. Such estimates are not nearly as accurate as the HX solutions used by Griffin *et al.* [1].

II. The Nature of the Problem

The HF equations for atoms are a system of coupled, integrodifferential equations of the form

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r}(Z - Y_i(r)) - \frac{l_i(l_i + 1)}{r^2} - \epsilon_{ii} \right\} P_i(r)$$

$$= \frac{2}{r} X_i(r) + \sum_{j \neq i} \delta_{l_i l_j} \epsilon_{ij} P_j(r), \qquad i = 1,\ldots, n \tag{1}$$

which satisfy

(i) boundary conditions: $P_i(0) = P_i(\infty) = 0$,

(ii) normalization conditions: $\| P_i \| \equiv \{\int P_i^2(r)\, dr\}^{1/2} = 1$,

(iii) orthogonality conditions between functions with the same angular quantum number: $(P_i, P_j) \equiv \int P_i(r)\, P_j(r)\, dr = 0$ for $l_i = l_j$, $i \neq j$.

Here $\delta_{ll'}$ is the Kronecker delta function and, for a single configuration approximation,[1]

$$Y_i(r) = \sum_{j,k} a_{ijk}\, Y^k(jj; r)$$

and

$$X_i(r) = \sum_{j \neq i} b_{ijk}\, Y^k(ij; r)\, P_j(r),$$

where

$$Y^k(ab; r) = \int_0^r P_a(t) \left(\frac{t}{r}\right)^k P_b(t)\, dt + \int_r^\infty P_a(t) \left(\frac{r}{t}\right)^{k+1} P_b(t) dt.$$

Quantum numbers $n_i l_i$ are associated with each radial function $P_i(r)$. The angular quantum number l_i appears explicitly in the equations; the principal quantum number n_i, however, influences the solution only indirectly in that the number of nodes in the solution, excluding minor oscillations in the tail region as well as the node at the origin, should be $n_i - l_i - 1$. Furthermore, by convention, the functions are defined to be positive near the origin. The latter requirement can always be satisfied since, if $P_i(r)$ is a solution, then $-P_i(r)$ is also a solution with ϵ_{ij} replaced by $-\epsilon_{ij}$. Auxiliary conditions then are

(iv) Number of nodes-$n_i - l_i - 1$.

(v) The initial "slope," $a_0 = P_i(r)/r^{l_i+1} > 0$, $r \rightarrow 0$.

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[1] For simplicity, the discussion will be restricted to the single-configuration approximation but the arguments can be extended to the multiconfiguration approximation as well.

Because of the nonlinear nature of these equations, they are solved iteratively by a procedure called the self-consistent field (SCF) method. In this procedure, estimates of the radial functions are used to compute estimates of ϵ_{ij}, $j \neq i$ [4], and the functions

$$f(r) = (2/r)(Z - Y_i(r)) - l_i(l_i + 1)/r^2,$$

and

$$g(r) = \frac{2}{r} X_i(r) + \sum_{j \neq i} \delta_{l_i l_j} \epsilon_{ij} P_j(r).$$

Then the solution of the differential equation

$$\{(d^2/dr^2) + f(r) - \epsilon\} y(r) = g(r) \tag{2}$$

satisfying conditions (i), (ii), (iv) and (v) (all except orthogonality) is used to form a new estimate. Let $P_i^{(k)}$ be the k-th estimate of $P_i(r)$ and $y^{(k)}$ the solution of the above boundary-value problem associated with that estimate. In the simplest SCF iteration

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

but this often causes oscillations which slow the rate of convergence or even result in divergence. A common technique for minimizing this problem is the introduction of accelerating parameters c and the use of

$$P_i^{(k+1)} = cP_i^{(k)} + (1 - c)\, y^{(k)},$$

(normalized) as the next estimate. This procedure has the effect of damping out oscillations when $0 \leqslant c < 1$.

The boundary-value problem as given by Eq. (2) is solved repetitively for all i, in some order, until all solutions are consistent with the current estimate of the corresponding radial function. The nature of this boundary value problem plays a key role in the convergence of the SCF iteration.

For a homogeneous equation where $g(r) \equiv 0$, the diagonal energy parameter ϵ, is an eigenvalue of the differential equation and a normalized solution satisfying the boundary values exists only for certain discrete values, say ϵ^H. When $g(r) \not\equiv 0$ a solution can be found for any $\epsilon \neq \epsilon^H$. Only for certain values, however, will constraints (i), (ii), (iv) and (v) be satisfied. A solution of the differential equation satisfying the boundary conditions (i) and the auxiliary constraints (iv) and (v) will be called on "acceptable solution"; when (ii) is also satisfied it will be referred to as a "normalized acceptable solution."

Hartree [5] described two methods for finding normalized acceptable solutions. Both involve iterative adjustment of the energy parameter ϵ and an adjustment of the initial slope a_0, but they differ in the way in which the iteration is performed. His methods in somewhat modified form are the basis of nearly all commonly used computer programs [6–9].

Inherent in both his methods is the assumption that the normalized acceptable solution is unique. It is well known that the solutions to the HF equations are not unique for certain states. Configurations with complete groups only or some excited states such as $1s2s\,^3S$ are examples. In these cases a unitary transformation of radial functions with the same angular quantum numbers will also be a solution of the HF equations but with diagonal and off-diagonal energy parameters transformed. Koopmans [10] showed that in such cases, solutions for which the off-diagonal energy parameters are zero have the property that their diagonal energy parameter is related to the ionization potential. With this convention, the solutions of the HF equations satisfying all the constraints are unique [11].

The situation with respect to the intermediate boundary-value problem is quite different. The orthogonality condition is not part of the problem and, as shown by Mjolness and Ruppel [11], zero, one or two acceptable solutions may exist. This situation is clearly presented in the work of Griffin et al., but they did not consider the role of off-diagonal energy parameters (or orthogonality).

Griffin et al. propose two new methods for solving the boundary-value problem both of which use a self-consistency criterion. In this way, their procedure can choose between two normalized acceptable solutions. They noted that instabilities tended to occur when there was a single electron in an orbital. In such cases, the function $f(r)$ is not directly dependent on the orbital in question, only $g(r)$. Their methods can be described briefly as follows. For a particular value of ϵ, a solution of the boundary-value problem is obtained which, in general, is not normalized and is called a first-generation integral. This function is normalized and used in the recomputation of $g(r)$. The differential equation with the same $f(r)$ but the new $g(r)$ is solved again, this time for a second-generation integral. The two methods differ in their requirements on the second-generation integral. This process is repeated for a series of ϵ values always using the same exchange function $g(r)$, for the first-generation integral but different ones for the second-generation integrals. Finally that solution is accepted for which the first- and second-generation solutions are most nearly self-consistent. As is evident, such an algorithm, which requires that the exchange function be recomputed many times, can consume vast amounts of computer time. For large atoms, the computation of the exchange term is far more time consuming than the integration of the differential equation. The exchange term for Ti $3d^24s4d$ has eleven $Y^{(k)}$ integrals, each of which is about as time consuming as the integration of a differential equation, and this is still a relatively small atom.

III. NEW METHODS OF SOLUTION

One difficulty with the standard methods is their reliance upon normalized solutions of the boundary-value problem. If no normalized acceptable solution exists, an iterative procedure will obviously fail to converge; if two solutions exist the iterations may oscillate between them.

At this stage it is enlightening to consider the HF equations in terms of unnormalized function. Let

$$Y_i(r) = \sum_{j,k} a_{ijk}\, Y^k(jj;\, r)/\|\, P_j \,\|^2,$$

$$X_i(r) = \sum_{j,k} b_{ijk}\, Y^k(ij;\, r)\, P_j(r))/\|\, P_j \,\|^2.$$

Also replace $\epsilon_{ij} P_j(r)$ by $\epsilon_{ij} P_j(r)/\|\, P_j \,\|^2$ and note that

$$\epsilon_{ij} = \int_0^\infty P_j(r) \left[\left\{ \frac{d^2}{dr^2} + \frac{2}{r}(Z - Y_i(r)) - \frac{l_i(l_i + 1)}{r^2} \right\} P_i(r) - \frac{2}{r} X_i(r) \right] dr.$$

In this form it is evident that the HF equation is homogeneous of degree one and so normalization is an arbitrary process. It is, therefore, not necessary to insist that the approximate solutions should be normalized, only that they converge to normalized solutions as the iterations converge. Another fact not used in the standard Hartree–Fock methods, is that the Rayleigh quotient is an accurate means of estimating ϵ_{ii} since it may be stationary with respect to variations δP_i (but not with respect to variations δP_j, $j \neq i$.) Furthermore, numerical differentiation may be avoided by working entirely with the discretized problems.

Let y_m, $m = 1, \ldots, N$ be the computed approximation to the solution of the differential equation $y(r_m)$. Define a column vector $Y = (y_1, y_2, \ldots, y_N)^t$. A numerical method such as Numerov's method would define Y as a solution of a system of algebraic equations

$$(A - \epsilon I) Y = b, \tag{3}$$

where I is the identity matrix and the elements of A and b depend on the functions $f(r)$ and $g(r)$, respectively.[2] Multiplication of Eq. (3) by Y^t results in the following expression for an energy estimate,

$$\epsilon = (Y^t A Y - Y^t b)/Y^t Y. \tag{4}$$

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[2] Transformed HF equations are often solved numerically [6, 7] with $\rho = \ln r$ as independent variable and $P(r)/r^{1/2}$ as dependent variable. In this case the system of algebraic equations has the form $(A - \epsilon B) Y = b$ and appropriate changes must be made to the equations derived later.

Once the functions $f(r)$ and $g(r)$ have been computed, an estimate of ϵ can be determined with very little extra work provided the current estimate of the radial function is used in Eq. (4) instead of Y. This method of estimating ϵ has been found most satisfactory when the radial functions are reasonably accurate. With screened hydrogenic functions as initial estimates, the Rayleigh quotient as given by Eq. (4) tends to be too small and a node-adjustment procedure is required. In fact as long as the radial functions are orthogonal, the Rayleigh quotient has always resulted in a lower bound (i.e., a one-electron energy that is too small.) This is not too surprising, however, one should remember that different radial functions generally are associated with different functionals and so the usual mathematical theory concerning bounds for excited states does not apply directly. Once a solution with the correct number of nodes has been obtained, an energy-adjustment procedure based on Cooley's formula [9, 12] is most effective.[3] When $b = 0$, the formula adjusts ϵ to be an eigenvalue of A, but when $b \neq 0$, it adjusts ϵ so that the solution has a given initial slope a_0 and thus assists in the search for an acceptable solution. For core electrons the exchange effect is relatively small or $b \approx 0$ and it was found that, even though a_0 may not be known accurately, convergence is improved if an attempt is made to find an acceptable solution for which $|\Delta\epsilon/\epsilon| < 0.1/(Z - s_i)$, where s_i is Hartree's screening parameter [5].

The new method M1 for improving the estimated radial function can then be summarized as follows:

1. Compute $f(r)$ and $g(r)$ for the radial function under consideration.
2. Determine ϵ from current estimates and the Rayleigh quotient. [Eq. (4)].
3. Solve the boundary-value problem for that ϵ.
4. Determine whether the solution is acceptable, if not, adjust ϵ and repeat 3; if an acceptable solution cannot be found, orthogonalize all estimates and go back to 1.
5. Form a new estimate of the radial function,

$$P^{(k+1)} = cP^{(k)} + (1 - c)\, y/\|y\| \qquad \text{(normalized)},$$

where $c = \max(1 - \|y\|, 1 - \|y\|^{-1})$.

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[3] For the nonhomogeneous Eq. (3) the correct energy adjustment is

$$\epsilon^{m+1} = \epsilon^m + y_{NJ}^H\{(A - \epsilon I)Y - b\}_{NJ}/(h^2 \textstyle\sum y_i^H y_i) + O(h^2),$$

where y^H is a solution of the homogeneous equation with the same initial slope as y, r_{NJ} is the point at which inward and outward integration are matched and $\{V\}_{NJ}$ denotes the NJ-th component of the vector V. When $\rho = \ln r$ is the independent variable, the sum is replaced by $\sum r_i^2 y_i^H y_i$.

It was found that this method has greater stability than Hartree's methods and that the simple algorithm for determining the acceleration factor given above was adequate in all the cases tried.

Method M1 was used successfully to solve the HF equations for K $4d$, Ca $4s4d$, and Sc $4s^2 4d$, all of which are unstable by the Griffin *et al.* definition. It also performed excellently for stable configurations such as He $1s2s\,{}^3S$, the mutli-configuration approximation for $C^{+2}\ 2s^2 + 2p^2\,{}^1S$, and a relatively large atom Fr $7s\,{}^2S$ $(Z = 87)$. However, the results for Na $3p\,{}^2P$ and He ${}^1S$ were not nearly as satisfactory.

Both of these cases have significant orthogonality constraints, and in the case of He $1s2s\,{}^1S$, the orthogonality constraint precludes a Z^{-1} perturbation expansion [13]. The relationship of this fact with SCF iterations is not clear but it does suggest that the problem is special in some way. Indeed, the He $1s2s\,{}^1S$ case has been one of the most difficult to solve accurately.

The work of Mjolness and Ruppel [11] shows that the solution of the HF equation which yields orthogonality is unique (except for sign). This suggests that M1 may not give enough attention to orthogonality and so another method was tested.

Method M2 adjusts pairs of radial functions simultaneously so that each is normalized to first order, and the pair is orthogonal to first order. Let the pair of functions be $P_1(r)$ and $P_2(r)$ and let the discretized pair of equations be represented in matrix notation as

$$\begin{aligned} A_1 Y_1 - b_1 &= \epsilon_{11} Y_1 + \epsilon_{12} P_2 , \\ A_2 Y_2 - b_2 &= \epsilon_{21} P_1 + \epsilon_{22} Y_2 . \end{aligned} \tag{5}$$

This form implies that $\epsilon_{12} P_2$, for example, is omitted from the definition of $g(r)$ for the radial function $P_1(r)$. Multiplying the first of these equations by $Y_1{}^t$, then $Y_2{}^t$ we get two equations,

$$\begin{aligned} Y_1{}^t A_1 Y_1 - Y_1{}^t b &= \epsilon_{11} Y_1{}^t Y_1 + \epsilon_{12} Y_1{}^t P_2 , \\ Y_2{}^t A_1 Y_1 - Y_2{}^t b &= \epsilon_{11} Y_2{}^t Y_1 + \epsilon_{12} Y_2{}^t P_2 , \end{aligned} \tag{6}$$

which can be solved for ϵ_{11} and ϵ_{12} using *estimates* of Y_1 and Y_2, namely, $P_1^{(k)}$ and $P_2^{(k)}$. Similar equations hold for ϵ_{21} and ϵ_{22}. Note that the inner product will not be zero for orthogonal functions since orthogonality is defined in terms of an integral, but it will be small. As a result the systems are well conditioned.

Let

$$U_1 = \partial Y_1 / \partial \epsilon_{11} , \qquad V_1 = \partial Y_1 / \partial \epsilon_{12} , \qquad U_2 = \partial Y_2 / \partial \epsilon_{22} \quad \text{and} \quad V_2 = \partial Y_2 / \partial \epsilon_{21} .$$

Then these vectors are solutions of the equations

$$\begin{aligned} A_1 U_1 &= \epsilon_{11} U_1 + Y_1, & A_1 V_1 &= \epsilon_{11} V_1 + P_2, \\ A_2 U_2 &= \epsilon_{22} U_2 + V_2, & A_2 V_2 &= \epsilon_{22} V_2 + P_1. \end{aligned} \tag{7}$$

Estimates of orthogonal functions are then formed as

$$\begin{aligned} \bar{P}_1 &= Y_1 + \Delta\epsilon_{11} U_1 + \Delta\epsilon_{12} V_1, \\ \bar{P}_2 &= Y_2 + \Delta\epsilon_{22} U_2 + \Delta\epsilon_{21} V_2, \end{aligned} \tag{8}$$

where the changes in the energy parameters are such that

(i) each function is normalized to first order;

(ii) the pair is orthogonal to first order;

(iii) $q_1(\epsilon_{12} + \Delta\epsilon_{12}) = q_2(\epsilon_{21} + \Delta\epsilon_{21})$.

Here q_1, q_2 are the occupation numbers for orbitals 1 and 2. This conditions is required since the pair of off-diagonal energy parameters is related to the same Lagrange multiplier, $\lambda_{ij} = \lambda_{ji}$ and $\epsilon_{ij} = \lambda_{ij}/q_i$. These conditions result in the following system of equations:

$$\begin{pmatrix} (Y_1, U_1)/\| Y_1 \| & 0 & (Y_1, V_1)/\| Y_1 \| & 0 \\ 0 & (Y_2, U_2)/\| Y_2 \| & 0 & (Y_2, V_2)/\| Y_2 \| \\ (U_1, Y_2) & (U_2, Y_1) & (V_1, Y_2) & (V_2, Y_1) \\ 0 & 0 & q_1 & -q_2 \end{pmatrix} \begin{pmatrix} \Delta\epsilon_{11} \\ \Delta\epsilon_{22} \\ \Delta\epsilon_{12} \\ \Delta\epsilon_{21} \end{pmatrix} = \begin{pmatrix} 1 - \| Y_1 \| \\ 1 - \| Y_2 \| \\ -(Y_1, Y_2) \\ q_2\epsilon_{21} - q_1\epsilon_{12} \end{pmatrix}, \tag{9}$$

where $(Y, U) = \int_0^\infty y(r)\,u(r)\,dr$, i.e., integration over the grid points at which the vectors Y and U are defined, and $\| Y \| = (Y, Y)^{1/2}$. When q_1 and q_2 are nearly complete groups, this system of equations is ill conditioned and method M2 should not be used. An example is the multiconfiguration problem

$$C^{+2} 1s^2 2s^2 + 1s^2 2p^2 \; {}^1S.$$

Since the $1s^2 2p^2$ component is small, the expected occupation of the $2s$ orbital is very nearly 2 and the $1s$ and $2s$ radial equations are like those for complete groups. As already mentioned, such equations do not have unique solutions when the off-diagonal energy parameters are allowed to vary.

In order to faciliate a convenient search strategy for an acceptable solution for P_1, say, an intermediate function

$$P_1{}^* = Y_1 + \Delta\epsilon_{11}^* U_1 + \Delta\epsilon_{12}^* V_1$$

is determined such that $P_1{}^*$ is normalized to first order and orthogonal to first order to the current estimate of P_2. The diagonal energy parameter is adjusted until an accpetable solution is found. If $\bar{P}_1$ (or $\bar{P}_2$) as determined by Eqs. (8) and (9) is not an acceptable solution, it is replaced by $P_1{}^*$ (or $P_2{}^*$).

Method M2 may then be summarized as follows:

1. For each pair of orbitals, compute energy parameters and vectors, Y, U, V and hence P^*; if P^* is not acceptable adjust the diagonal energy parameter and repeat the calculation of Y, U, V and P^*.
2. Solve the system of equations (9) and form $\bar{P}_1$ and $\bar{P}_2$; check if acceptable; if not, replace by $P_1{}^*$ or $P_2{}^*$, repsectively.
3. Form new estimates of $P_i^{(k+1)}$ using accelerating factors defined as

$$c = \max(\alpha, 1 - \| \bar{P} \|, 1 - \| \bar{P} \|^{-1}),$$

where α is an input parameter. It was found in this algorithm that more control over the accelerating factor was occasionally desirable.

Method M2 was used successfully for a variety of cases including Na $3p\ {}^2P$, He $1s2s\ {}^1S$, Ti $3d^24s4d$ and $3d^24s5d$, and also Pr^{+2} $4f^25f$. No instabilities appeared in connection with Ti $3d^24s5d$. Much time had been spent previously, without success, in an attempt to obtain solutions for Pr^{+2} $4f^25f$ by standard methods. With method M2 the iterations converged surprisingly rapidly.

IV. Comparison of Methods

Obviously our method M2 involves more integrations of differential equations than M1. However, both these methods require only one computation of the potential and exchange functions per improvement cycle. As already mentioned earlier, this may be the most time-consuming operation of all. In Table I some comparisons are made of these two methods both on the basis of efficiency and accuracy of results.[4] In C^{+2} ${}^1S$ and He ${}^3S$, orthogonality is not a significant factor and both methods achieve good accuracy, but M1 requires fewer calculations. For He ${}^1S$ and Na ${}^2P$, orthogonality is significant and though M1 is converging the accuracy is not as good as for M2, particularly for He ^{1}S.

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[4] The MCHF program described in [9] modified to include deferred corrections [14] was used.

TABLE I

Comparison of Methods M1 and M2

XCH — Number of times the potential and exchange functions are computed.
NMRVS — Number of times a differential equation is integrated.
GRANGE — Number of times off-diagonal energy parameters were computed.
DPM — Maximum errors in a radial function due to lack of self-consistency.
ORTHO — Maximum orthogonality integral
RATIO — ratio of potential to kinetic energy (should be −2.0 exactly)
E — total energy

1. $C^{+2}\, 2s^2 + 2p\, {}^1S$

	M1	M2
XCH	34	33
NMRVS	70	99
GRANGE	9	9
DPM	0.0000005	0.0000002
ORTHO	0.00000001	0.00000001
RATIO	−2.0000001	−2.0000001
E	−36.4809561	−36.4809562

2. He $1s2s\, {}^3S$

	M1	M2
XCH	20	22
NMRVS	42	69
DPM	0.0000002	0.0000004
ORTHO	−0.00000014	−0.00000013
RATIO	−2.0000001	−2.0000001
E	−2.1742508	−2.1742508

3. He $1s2s\, {}^1S$

	M1	M2
XCH	94	38
NMRVS	200	160
GRANGE	21	5
DPM	0.0000992	0.0000003
ORTHO	−0.00005887	0.00000005
RATIO	−1.9997487	−2.0000002
E	−2.1698718[a]	−2.1698544

4. Na $3p\, {}^2P$

	M1	M2
XCH	57	56
NMRVS	120	220
GRANGE	9	7
DPM	0.0000064	0.0000008
ORTHO	0.00000507	0.00000000
RATIO	−2.0000005	−2.0000000
E	−161.7864055	−161.7864085

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[a] This value ignores the contribution to the total energy arising from a lack of orthogonality.

TABLE II

Convergence of $\epsilon_{4d,4d}$ for Ti $3d^2 4d$ in the Fixed-Core Approximation[a]

Iteration number	Method M1		Method M2	
	RQ	ACC	RQ	ACC
1	0.06086	0.11119	0.06086	−0.02146
2	0.10865	0.10865	0.08436	0.30904
3	0.10661	0.10661	0.09445	0.13355
4	0.10821	0.10821	0.10584	0.10965
5	0.10860[b]	0.10860[b]	0.10839	0.10878
6	0.10860	0.10860	0.10865[b]	0.10872[b]
7	0.10867[b]	0.10867[b]	0.10867	0.10870
8	0.10867	0.10867	0.10868	0.10869
9	0.10868[b]	0.10868[b]	⋮	⋮
10	0.10868	0.10868		0.10868
	⋮			

[a] RQ — Rayleigh quotient; ACC — accepted energy, adjusted for normalization in M2.

[b] At this stage the estimates were orthogonalized and off-diagonal energy parameters recomputed.

TABLE III

Convergence of $\epsilon_{3p,3p}$ for Na $3p\ ^2P$

Iteration number	Method M1	Method M2 ($\alpha = 0.0$)	Standard ($c = 0.7$)
1	0.14901	0.17062	0.20370
2	0.21740	0.20553	0.21750
3	0.20972	0.21474	0.20817
4	0.21699	0.21836	0.21851
5	0.20421[a]	0.21959[a]	0.21139
6	0.21561	0.21878	0.19879[a]
7	0.21789	0.21908	0.22821
8	0.21868[a]	0.21885[a]	0.20756
9	0.21880	0.21896	0.22460
10	0.21886[a]	0.21888	0.21196
	⋮	⋮	⋮
	0.21891	0.21891	0.21891

[a] At this stage the estimates were orthogonalized and the off-diagonal energy parameters recomputed.

The stability of these iterations is shown in Table II, by some results for Ti $3d^2 4s4d$ with the $4d$ orbital in a fixed Ti$^+$ core. In M1 the Rayleigh quotient is also the accepted energy after the first solution. In M2 the accepted energy, adjusted to first order for orthonormality, may differ radically from the Rayleigh-quotient value. Table II shows clearly that the adjusted energy from one iteration should *not* be used as an estimate in the next.

Finally, in Table III the present methods are compared with the earlier standard method [9]. Na $3p\ {}^2P$ was selected as an example since it is a case where the standard method requires a relatively large accelerating parameter ($c = 0.7$) to damp out oscillations. These are observed most readily in the diagonal energy parameters which are tabulated in Table III. Oscillations such as those of iterations 6–10 of the standard method are typical and result in many SCF iterations being required for self-consistency. Also, if a smaller value of c is used, the iterations may diverge. Table III shows M1 to converge almost monotonically; M2 exhibits some oscillation but the amplitude is rapidly decreasing.

V. CONCLUSIONS

The results to date indicate that method M1 has remarkable stability properties and that, when orthogonality of intermediate results is crucial M2 may be adequate. Possibly these two methods should replace the "standard" methods referred to by Griffin *et al.* More experience will be required before the suggestion is adopted but the methods are most promising.

One fact which method M1 made apparent was that orthonormalized screened hydrogenic functions yielded extremely poor Rayleigh-quotient estimates of acceptable energy parameters for large atomic systems such as Francium ($Z = 87$). The screening parameters used were Hartree [5] screening parameters based on the mean radius. It may be that Layzer's [15] screening parameters which minimize the total energy are more appropriate. However, his theory does not produce orthogonal functions and requires the solution of a system of nonlinear algebraic equations. For large atomic systems it may be more efficient to first determine the HX solutions, orthogonalize and use these as estimates for the HF equations.

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REFERENCES

1. D. C. GRIFFIN, R. D. COWAN AND K. L. ANDREW, *Phys. Rev. A* **3** (1971), 1233.
2. R. D. COWAN, *Phys. Rev.* **163** (1967), 54.
3. D. C. GRIFFIN, "Self-Consistent Field Calculation of Excited Electronic Configurations," Thesis, Purdue University, 1970.
4. C. FROESE, *Can. J. Phys.* **45** (1967), 7.
5. D. R. HARTREE, "The Calculation of Atomic Structures," Chapters 5 and 7, Wiley & Sons, New York, 1957.
6. C. FROESE, *Can. J. Phys.* **41** (1963), 1895.
7. D. F. MAYERS AND F. O'BRIEN, *J. Phys. B (Proc. Phys. Soc.) Ser. 2* **1** (1968), 145.
8. J. B. MANN, JR., Los Alamos Scientific Laboratory Reports LA-3690, 1967, and LA-3691, 1968.
9. C. FROESE FISCHER, *Computer Phys. Comm.* **1** (1969), 151.
10. T. A. KOOPMANS, *Physica* **1** (1933), 104.
11. R. C. MJOLNESS AND H. M. RUPPEL, *J. Comput. Phys.* **3** (1968), 259.
12. J. W. COOLEY, *Math. Comp.* **15** (1961), 363.
13. C. S. SHARMA AND C. A. COULSON, *Proc. Phys. Soc. (London)* **80** (1962), 81.
14. C. FROESE FISCHER, *Computer Phys. Comm.* **2** (1971), 124.
15. D. LAYZER, *Ann. Phys.* **8** (1959), 271.