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A Vector Perturbation Series Based upon a Representation in a Finite Banach Space

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The atomic finite-difference Hartree-Fock equations are written as an operator equation in a finite Banach space, the finite-difference variables and Lagrange multipliers forming the components of a solution vector, **U**, in this space. The Coulomb and exchange operators are treated as A-dependent perturbations, and the solution vector is expressed in the form of a vector perturbation series, $\mathbf{U}(A) = \sum_n \mathbf{U}^n A^n$. An algorithm for calculating the coefficient vectors $\mathbf{U}^n$ is given. Through a scaling of units, one set of coefficient vectors suffices for the calculation of an isoelectronic sequence of states, starting from the neutral atom. Results are presented for the $1s^2\ ^1S$ and $1s^22s\ ^2S$ isoelectronic sequences. The Richardson procedure is used to extrapolate to the differential limit.

1. INTRODUCTION

In 1973 Cayford, Fimple, and Unger [1] applied the finite-difference Newton Raphson algorithm (FDNRA) to the solution of the atomic Hartree–Fock (HF) equations. More recently the FDNRA has been extended to treat the multi-configuration problem [2, 3]. It has also been used for diatomic molecules [4]. In all of this work, however, we have not been able to bring the full power of the FDNRA to bear on the problem because of practical limitations. Including the finite-difference variables appearing in the Coulomb and exchange integrals in the generalized Newton - Raphson iteration (GNRI) causes the Jacobian matrix to become completely full (see the Appendices of [1] and [2]), and the method becomes impractical. Consequently we were forced to employ a self-consistent field (SCF) iteration in our algorithm.

In the present work a perturbation series has been developed, based upon a representation of the finite-difference variables as a vector in a finite dimensional Banach space. Although this vector perturbation series may have a wide range of applications, it is developed here in connection with a specific problem, namely the atomic finite difference Hartree Fock (FDHF) problem, treating the interelectron potential as a perturation. In this case it is the finite difference analog of the Z dependent perturbation of the HF equations [5, 6].

Our previous work [1–4] can be considered from various points of view. One is simply as approximate numerical solutions of integrodifferential equations. On the

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other hand, the algebraic finite difference systems exist in their own right, and have properties which do not change as one goes to the differential limit. In studying these algebraic equations it is conceptually fruitful to consider them as operator equations in a finite-dimensional Banach space, the algebraic variables (including Lagrange multipliers) becoming vector components in this space. It is this second point of view which is adopted in this paper.

In the following section the FDHF equations are introduced for a general atom with the Coulomb and exchange terms treated as a perturbation. Then, in Section 3, the Banach space representation of these equations is developed. In Section 4 the vector perturbation series is introduced and equations for the calculation of the coefficient vectors are determined. Some practical details concerning calculations are given in Section 5, and results for the $1s^2 2s\ ^2S$ and $1s^2\ ^1S$ isoelectronic sequences are presented in Sections 6 and 7. Some conclusions are drawn in the final section. As an aid in implimenting the algorithm, Appendix A gives equations written out in detail for the $1s^2 2s\ ^2S$ case. Appendix B gives a procedure for controlling accuracy in the calculation of the coefficient vectors.

2. The FDHF Equations

As introduced in [1], the FDHF equations are the result of a finite-difference algebraization of the HF integrodifferential equations, using first-order approximations for the derivatives and integrals. Here we consider the FDHF equations with the Coulomb and exchange terms treated as a perturbation.

In the HF approximation the total wavefunction of an N_e-electron atom or ion is approximated by an antisymmetric product of single-electron spin-orbitals of the form,

$$\phi_t = R_{n_t l_t}(r)\, Y_{l_t}^{m_t}(\omega)\, \chi_{1/2}^{m_{st}}, \qquad t = 1,..., N_e\,. \tag{1}$$

Generally, all spin-orbitals with the same values of the quantum numbers $n_t = n$ and $l_t = l$ have a common radial function $R_{nl}(r)$ and we wish to consider the FDHF equations relating to the set of $N < N_e$ independent radial functions. As in [1], we use a radial variable ρ with a finite range defined by

$$\rho = \frac{r}{1 + ar}, \qquad (a > 0), \tag{2}$$

and define a minimal set of transformed radial functions,

$$P_\alpha(\rho) = \rho R_{n_\alpha l_\alpha}(r(\rho)), \qquad \alpha = 1,..., N, \tag{3}$$

where the quantum number pair, $n_\alpha l_\alpha$, take on all of the different values, $n_t l_t$, in (1) without repetition.

Following the procedures in [1], the ρ axis between $\rho = 0$ and $\rho = 1/a$ is divided by a mesh of $M - 1$ evenly spaced internal points, giving a mesh spacing of $h = 1/Ma$, and the FDHF equations are written in terms of the algebraic variables,

$$P_\alpha^k \xrightarrow[M\to\infty]{h\to 0} P_\alpha(kh), \qquad \alpha = 1,\ldots, N; \qquad k = 1,\ldots, M-1, \tag{4}$$

which are approximations to the values of the transformed radial functions at the mesh points. For an atom or ion of central charge Z, requiring N radial functions, the FDHF equations for $M - 1$ internal mesh points can be written in atomic units (au) as follows (see [1] for details).

$$\begin{aligned} F_\alpha^k = &-\frac{\nu_\alpha}{2h^2}(1-\delta_{k,1})P_\alpha^{k-1} + \nu_\alpha\left[\frac{1}{h^2} - \frac{Z}{khz_k^3} + \frac{l_\alpha(l_\alpha+1)}{2k^2h^2z_k^2}\right]P_\alpha^k \\ &-\frac{\nu_\alpha}{2h^2}(1-\delta_{k,M-1})P_\alpha^{k+1} + \Lambda(V_\alpha^k P_\alpha^k - X_\alpha^k) \\ &-\sum_{\beta=1}^{N}\epsilon_{\alpha\beta}\frac{\delta(l_\alpha, l_\beta)}{z_k^4}P_\beta^k = 0, \qquad \alpha = 1,\ldots, N; \qquad k = 1,\ldots, M-1, \end{aligned} \tag{5a}$$

$$F_{\alpha\alpha} = h\sum_{j=1}^{M-1}\frac{P_\alpha^j P_\alpha^j}{z_j^4} - 1 = 0, \qquad \alpha = 1,\ldots, N, \tag{5b}$$

$$F_{\alpha\beta} = h\sum_{j=1}^{M-1}\frac{P_\alpha^j P_\beta^j}{z_j^4} = 0 \qquad \begin{array}{l}\text{for all values of } \alpha \text{ and } \beta \text{ such} \\ \text{that } \beta < \alpha \text{ and } \delta(l_\alpha, l_\beta) = 1,\end{array} \tag{5c}$$

where $z_k = 1 - akh$, and ν_α is the number of spin-orbitals ϕ_t containing the radial function α.

Equations (5a) are first-order finite difference equations written for each radial function α at each internal mesh point k. The Kronecker deltas in the first and third terms are due to the boundary conditions, $P_\alpha(0) = P_\alpha(1/a) = 0$. The V_α^k and X_α^k are the Coulomb and exchange terms respectively for radial function α at the kth mesh point. They are multiplied by a perturbation-strength parameter Λ. The $\epsilon_{\alpha\beta}$ are the Lagrange multipliers on normalization ($\alpha = \beta$) and orthogonality ($\beta \neq \alpha$, $\epsilon_{\alpha\beta} = \epsilon_{\beta\alpha}$), and the corresponding constraints are given by (5b) and (5c) respectively. If a representation is sought where the Lagrange multiplier matrix is diagonal or partially diagonal, the appropriate multiplier term in (5a) and orthogonality equations (5c) can be eliminated.

The Coulomb and exchange terms in (5a) are given respectively by

$$V_\alpha^k = \frac{1}{z_k^4}\sum_{t=1}^{N_e}\sum_{r}^{(\alpha)}\sum_{\lambda,\mu}\frac{4\pi}{2\lambda+1}B_{rr}^{\lambda\mu *}B_{tt}^{\lambda\mu}\sum_{j=1}^{M-1}P_{\beta_t}^j P_{\beta_t}^j g_\lambda^{jk}, \tag{6a}$$

$$X_\alpha^k = \frac{1}{z_k^4}\sum_{t=1}^{N_e}\sum_{r}^{(\alpha)}\sum_{\lambda,\mu}\delta(m_{s_t}m_{s_r})\frac{4\pi}{2\lambda+1}|B_{tr}^{\lambda\mu}|^2 P_{\beta_t}^k\sum_{j=1}^{M-1}P_\alpha^j P_{\beta_t}^j g_\lambda^{jk}, \tag{6b}$$

where

$$B_{tr}^{\lambda\mu} = \int_0^{4\pi} Y_{l_t}^{m_t}(\omega)^* \, Y_\lambda^\mu(\omega) \, Y_{l_r}^{m_r}(\omega) \, d\omega$$

and

$$g_\lambda^{jk} = \frac{p^\lambda z_q^{\lambda+1}}{z_p^\lambda q^{\lambda+1} z_j^4},$$

where $p = \min(j, k)$ and $q = \max(j, k)$. The symbol $\sum_r^{(\alpha)}$ denotes a restricted summation over the ν_α spin-orbitals, ϕ_r, which share the radial function α, while the subscript notation β_t denotes the radial function (value of β) belonging to the spin-orbital ϕ_t.

The FDHF equations (5) are a set of A-dependent nonlinear algebraic equations in the variables P_α^k and $\epsilon_{\alpha\beta}$, one equation for each variable. The problem is to determine the A-dependent roots of these equations.

3. Banach Space Representation

The variables P_α^k and $\epsilon_{\alpha\beta}$ are now considered as vector components in a real finite-dimensional vector space. To be specific, let us suppose we are dealing with N' off-diagonal multipliers, in which case our vector space is $NM + N'$ dimensional. Denote a general vector in the space by $\mathbf{U}$, with components U_i, $i = 1,..., NM + N'$. Because of computational considerations (see Section 5), the variables are associated with the components of $\mathbf{U}$ in the following order.

$$U_{N(k-1)+\alpha} = P_\alpha^k, \qquad \alpha = 1,..., N; \qquad k = 1,..., M-1, \tag{7a}$$

$$U_{N(M-1)+\alpha} = \epsilon_{\alpha\alpha}, \qquad \alpha = 1,..., N, \tag{7b}$$

$$U_{NM+\gamma_{\alpha\beta}} = \epsilon_{\alpha\beta}, \qquad \gamma_{\alpha\beta} = 1,..., N', \tag{7c}$$

where in (7c) $\gamma_{\alpha\beta}$ simply increases by 1 for each off-diagonal multiplier $\epsilon_{\alpha\beta}$. In (7a), as the component of $\mathbf{U}$ increases sequentially, the index α (radial function) goes through a complete cycle for each increase of k (mesh point) by one. Thus all of the variables P_α^k for a given mesh point k are grouped together in $\mathbf{U}$.

If the norm of $\mathbf{U}$ is given its usual definition of

$$\| \mathbf{U} \| = (\mathbf{U}^T\mathbf{U})^{1/2}, \tag{8}$$

and the distance between two vectors, $\mathbf{U}$ and $\mathbf{V}$, is taken to be the norm of the difference $\| \mathbf{U} - \mathbf{V} \|$, then our vector space satisfies all of the axioms of a normed metric space or Banach space $\mathscr{B}$. We note that $\mathscr{B}$ is the direct sum of two disjoint subspaces,

$$\mathscr{B} = \mathscr{B}_P \oplus \mathscr{B}_\epsilon, \tag{9}$$

where $\mathscr{B}_P$ is the $N(M-1)$ dimensional subspace of the radial variables, P_α^k, and $\mathscr{B}_\epsilon$ is the $N+N'$ dimensional subspace of the multipliers, $\epsilon_{\alpha\beta}$. We define Q_P and Q_ϵ to be projection operators onto $\mathscr{B}_P$ and $\mathscr{B}_\epsilon$ respectively.

We can now express the FDHF equations (5) very concisely as an operator equation in $\mathscr{B}$

$$(Q_P(H+\Lambda V-\Lambda X-E)+Q_\epsilon O)\mathbf{U}=0. \tag{10}$$

Comparison with (5), bearing in mind the ordering of (7a), shows that H is a linear operator with a block tridiagonal matrix representation (with $N\times N$ subblocks) in $\mathscr{B}_P$, and can be taken to be the identity in $\mathscr{B}_\epsilon$, although this latter is unimportant because of the following projector Q_P. V and X are nonlinear operators which map the components of $\mathbf{U}$ in $\mathscr{B}_P$ into the values, $V_\alpha^k P_\alpha^k$ and X_α^k, in (6a) and (6b) respectively, with the same ordering for the resulting vector as that established in (7a). Again, for completeness, we can take V and X to be identities in $\mathscr{B}_\epsilon$.

Unlike H, V, and X, the operators, E and O, mix the subspaces $\mathscr{B}_P$ and $\mathscr{B}_\epsilon$. E is a nonlinear operator which replaces each component P_α^k in $\mathscr{B}_P$ by the sum,

$$\sum_{\beta=1}^{N}\epsilon_{\alpha\beta}\frac{\delta(l_\alpha l_\beta)}{z_k^4}P_\beta^k,$$

the $\epsilon_{\alpha\beta}$ being mapped from $\mathscr{B}_\epsilon$. O is a nonlinear operator which replaces each component $\epsilon_{\alpha\alpha}$ in $\mathscr{B}_\epsilon$ by the sum,

$$h\sum_{j=1}^{M-1}\frac{P_\alpha^j P_\alpha^j}{z_k^4}-1,$$

and each component $\epsilon_{\alpha\beta}$ by the sum

$$h\sum_{j=1}^{M-1}\frac{P_\alpha^j P_\beta^j}{z_j^4}.$$

As E is followed by Q_P and O by Q_ϵ, the effect of E in $\mathscr{B}_\epsilon$ and of O in $\mathscr{B}_P$ are unimportant, but to have an unambiguous definition we can take them to be identities in the respective subspaces.

For a given value of the perturbation parameter Λ, there exist $N(M-1)$ solution vectors $\mathbf{U}$ which are reduced to the null vector by the operator of (10). Since this operator is Λ dependent, the solution vectors $\mathbf{U}(\Lambda)$ which satisfy (10) must also depend upon Λ.

4. The Vector Perturbation Series

Let us concentrate our attention on the solution vector corresponding to the ground state, and assume it can be expanded in a power series in Λ.

$$\mathbf{U}(\Lambda)=\sum_{m=0}^{\infty}\mathbf{U}^m\Lambda^m, \tag{11}$$

where the coefficient vectors $\mathbf{U}^m$ are independent of Λ. We now require that the vector perturbation series (11) be a solution of (10) for arbitrary values of Λ.

When we operate on the vector series (11) with the operator of (10), the resulting vector has a different power series in Λ in each of its components. Since the operator is nonlinear, the resultant vector is not simply the sum, $\sum_m (Q_P(H + \Lambda V - \Lambda X - E) + Q_\epsilon O)\,\mathbf{U}^m \Lambda^m$, but rather we must substitute the series for each and every component of the original vector $\mathbf{U}$ where it occurs in products in the resultant vector components. In order for the series (11) to be a solution for arbitrary Λ, each term in Λ^n ($n = 0, 1, 2,...$) in each component of the resultant vector must be zero independently.

This procedure results in the following equations which serve to calculate the coefficient vectors sequentially.

$$(Q_P(H - E) + Q_\epsilon O)\,\mathbf{U}^0 = 0, \tag{12}$$

$$J\mathbf{U}^n = \mathbf{G}^{n-1}, \qquad n = 1, 2,..., \tag{13}$$

where the components of $\mathbf{G}^{n-1}$ are given by

$$\begin{aligned} G^{n-1}_{N(k-1)+\alpha} = &- \frac{1}{z_k^4} \sum_{l=0}^{n-1} U^{n-l-1}_{N(k-1)+\alpha} \sum_{t=1}^{N_e} \sum_{r}^{(\alpha)} \sum_{\lambda,\mu} \frac{4\pi}{2\lambda+1} B^{\lambda\mu *}_{rr} B^{\lambda\mu}_{tt} \\ &\times \sum_{j=1}^{M-1} g^{jk}_\lambda \sum_{m=0}^{l} U^{l-m}_{N(j-1)+\beta_t} U^m_{N(j-1)+\beta_t} \\ &+ \frac{1}{z_k^4} \sum_{l=0}^{n-1} \sum_{t=1}^{N_e} \sum_{r}^{(\alpha)} \delta(m_{s_t} m_{s_r}) \sum_{\lambda,\mu} \frac{4\pi}{2\lambda+1} |\, B^{\lambda\mu}_{tr} \,|^2\, U^{n-l-1}_{N(k-1)+\beta_t} \\ &\times \sum_{j=1}^{M-1} g^{jk}_\lambda \sum_{m=0}^{l} U^{l-m}_{N(j-1)+\alpha} U^m_{N(j-1)+\beta_t} \\ &+ \sum_{\beta=1}^{N} \frac{\delta(l_\alpha l_\beta)}{z_k^4} \sum_{m=1}^{n-1} U^{n-m}_{NM+\gamma_{\alpha\beta}} U^m_{N(k-1)+\beta}, \quad k = 1,..., M-1; \quad \alpha = 1,..., N, \end{aligned} \tag{14a}$$

$$G^{n-1}_{N(M-1)+\alpha} = -h \sum_{j=1}^{M-1} \frac{1}{z_j^4} \sum_{m=1}^{n-1} U^{n-m}_{N(j-1)+\alpha} U^m_{N(j-1)+\alpha}, \qquad \alpha = 1,..., N, \tag{14b}$$

$$G^{n-1}_{NM+\gamma_{\alpha\beta}} = -h \sum_{j=1}^{M-1} \frac{1}{z_j^4} \sum_{m=1}^{n-1} U^{n-m}_{N(j-1)+\alpha} U^m_{N(j-1)+\beta}, \quad \gamma_{\alpha\beta} = 1,..., N', \tag{14c}$$

and J is a partly block tridiagonal Jacobian matrix of the same form as that given in the Appendix of [2]. A complete definition of the J matrix is best postponed until the next section, and given as part of a discussion of the solution of (12).

Before going into the details of the solution of (12) and (13), it would be well to establish the important point that the calculation of a single set of coefficient vectors

$\mathbf{U}^n$ suffices for a whole isoelectronic series. Equations (5) with $\Lambda = 1$ are the FDHF equations for a central charge Z written in au. The same equations with $\Lambda \neq 1$ can be viewed in two ways: (1) written in au for a central charge Z and the Coulomb and exchange terms at strength Λ, or (2) written in scaled units (su) for a central charge of $Z_{\text{eff}} = Z/\Lambda$ and the Coulomb and exchange terms at full strength. In the scaled system of units we still have $\hbar = m_e = 1$, but $e = \Lambda^{1/2}$. To justify the second viewpoint, we note that the Coulomb and exchange terms, $V_\alpha{}^k$ and $X_\alpha{}^k$, physically contain the square of the electronic charge, e^2. Then, in su where $e^2 = \Lambda$, the terms $\Lambda V_\alpha{}^k$ and $\Lambda X_\alpha{}^k$, are at full strength. Next, the central potential term $Z/khz_k{}^3$, physically contains a factor e^2 which does not appear when written in au since $e = 1$. It should appear in su, however, as a Λ, and therefore we can set $Z \equiv Z_{\text{eff}}\Lambda$, where Z_{eff} is the effective central charge. In su the unit of length is $1/\Lambda$ Bohr radii, and the unit of energy is $1/\Lambda^2$ au (i.e., 1 su $= 1/\Lambda^2$ au).

Since the coefficient vectors $\mathbf{U}^m$ in (11) and the equations used to calculate them, (12) and (13), are independent of Λ, only one calculation with a given value of Z can generate solutions for a range of values of $Z_{\text{eff}} = Z/\Lambda$.

5. Calculation of The Coefficient Vectors

The equations (12) and (13) can be used sequentially to calculate the coefficient vectors $\mathbf{U}^n$ up to any desired order. Equation (12) is just the Banach space representation of the FDHF equations (5) with $\Lambda = 0$, the correspondence between the variables, $P_\alpha{}^k$ and $\epsilon_{\alpha\beta}$, and the components of $\mathbf{U}^0$ being given by (7), (n.b. $\mathbf{U}(\Lambda = 0) \equiv \mathbf{U}^0$). A solution of this base problem is readily obtained by means of the generalized Newton Raphson iteration (GNRI) [2],

$$\mathbf{U}^{0(m+1)} = \mathbf{U}^{0(m)} - (J^{(m)})^{-1}\,\mathbf{F}^{(m)} \tag{15}$$

where (m) denotes the iteration, and the function vector $\mathbf{F}$ has components given by (5) with $\Lambda = 0$,

$$F_{N(k-1)+\alpha} = F_\alpha{}^k, \qquad \alpha = 1,\ldots, N; \qquad k = 1,\ldots, M-1, \tag{16a}$$

$$F_{N(M-1)+\alpha} = F_{\alpha\alpha}, \qquad \alpha = 1,\ldots, N, \tag{16b}$$

$$F_{NM+\gamma_{\alpha\beta}} = F_{\alpha\beta}, \qquad \gamma_{\alpha\beta} = 1,\ldots, N', \tag{16c}$$

and the Jacobian matrix at the (m)th iteration has elements given by

$$J_{ii'}^{(m)} = \left(\frac{\partial F_i}{\partial U_{i'}}\right)_{\Lambda=0}^{(m)}, \qquad i, i' = 1,\ldots, NM + N'. \tag{17}$$

A detailed inspection of the partial derivatives (17) reveals that J is a partly block tridiagonal matrix (with $N \times N$ subblocks), and can be effectively inverted by means

of a partitioning (see Appendix of [2]). It is this computational consideration that dictates the particular ordering given by (7) and (16).

For the complete solution of (12) it remains only to specify a starting vector for the GNRI (15). With $\Lambda = 0$ in (5), the Coulomb and exchange terms are removed, and in the differential limit the solution would consist of hydrogenic radial functions (with central charge Z), hydrogenic energies for the diagonal multipliers, and off-diagonal multipliers zero. Therefore, a good starting vector $\mathbf{U}^{0(0)}$ would have components consisting of the values of the appropriate hydrogenic functions at the various mesh points and corresponding hydrogenic values of the multipliers, with the proper ordering (7).

It is important to note that the hydrogenic functions and multipliers themselves do not provide sufficiently accurate values for the $\mathbf{U}^0$ coefficient vector in the series (11), because the components of the latter are the roots of the finite-difference system, not the differential system.

The GNRI (15) is terminated when

$$\max(|F_i|, i = 1,..., NM + N') < \text{tolerance}. \tag{18}$$

Since the higher-order coefficient vectors depend upon $\mathbf{U}^0$, it is well to solve the base problem (12) to a small tolerance. Since the Coulomb and exchange terms are missing in (12), no SCF iteration is necessary for the solution of the base problem.

Having determined the zeroth-order coefficient vector $\mathbf{U}^0$ to a low tolerance, we turn our attention to the sequential solution of (13) for the higher-order coefficient vectors $\mathbf{U}^n$, $n = 1, 2,...$, and we must now fully define the J matrix appearing in (13). It is simply the same J matrix used in the GNRI (15) for the base problem at the final iteration when the tolerance (18) is satisfied.

Inspection of (14) will show that $\mathbf{G}^{n-1}$ depends upon all coefficient vectors $\mathbf{U}^m$ of order $n - 1$ and lower. By using the algorithm of [2] in the same manner as for the GNRI, we can effectively invert J and sequentially solve (13) for the coefficient vectors $\mathbf{U}^n$, using the ones previously determined to calculate the next $\mathbf{G}$ vector. In this sequence only the $\mathbf{U}^n$ and $\mathbf{G}^{n-1}$ vectors change with n, while the J matrix remains constant. Its effective inversion must be carried out for each order, however, since the inverse matrix J^{-1} is never computed. It would be impractical to do so.

In solving (13), the computation of $\mathbf{G}^{n-1}$ takes a major share of the time because of the multiple summations. It is therefore wise to program (14) with finesse, taking advantage of relationships between $G^{n-1}_{N(k-1)+\alpha}$ and $G^{n-1}_{Nk+\alpha}$.

There are some complications concerning the accuracy of the effective inversion of J with the algorithm of [2] which are discussed in Appendix B.

As with all perturbation theories, the radius of convergence of the vector perturbation series (11) depends upon the specific application. For any given isoelectronic sequence there is a minimum value of $Z_{\text{eff}} = Z/\Lambda$ below which the series diverges.

For closed-shell configurations with no off-diagonal multipliers $\epsilon_{\alpha\beta}$, the particular ordering of $\mathbf{U}$ given by (7a), leading to a partially block-tridiagonal J matrix, is not necessary. In this case it would be more efficient to group all of the variables $P_\alpha{}^k$ with

the same value of α together in $\mathbf{U}$ (i.e. $U_{(M-1)(\alpha-1)+k} = P_\alpha^k$). This ordering leads to a partially tridiagonal J matrix. With nonzero off-diagonal multipliers, however, it would have nonzero elements far off the diagonal; hence the need for the ordering (7a) in the general case.

6. Isoelectronic Sequence of The $1s^2 2s\ ^2S$ State

Using the procedure outlined in the preceeding sections, the vector equations (12) and (13), for the case of the Li $1s^2 2s\ ^2S$ ($Z = 3$) isoelectronic sequence, were sequentially solved for $\mathbf{U}^n$, $n = 0, 1,..., 15$. Appendix A gives (12) and (13) written for this specific case. With the intent of using Richardson extrapolation [7] to obtain values of HF energy and multipliers in the $h \to 0$ limit, the calculation was carried out four times for $M = 50$, 70, 90, and 110. Double precision was used throughout and the GNRI was always terminated when the condition (18) with a tolerance of 10^{-18} was satisfied (see Appendix B regarding the accuracy of the solution (13)).

The coefficient vectors $\mathbf{U}^n$, corresponding to each mesh spacing, were then used to sum the vector perturbation series (11), for integer values of Z_{eff} from 3 to 10. Due to the scaling property, one set of coefficient vectors generates a set of self consistent solution vectors of the FDHF equations (5) for the whole isoelectronic sequence, $Z_{\text{eff}} = 3, 4,...$. One simply sums the perturbation series (11) with different values of the perturbation parameter $\Lambda = Z/Z_{\text{eff}}$, Z being the value used to calculate the $\mathbf{U}^n$ in (12) and (13). The particular value of Z used in the calculation does not effect the convergence of the series for a given value of Z_{eff}, the larger or smaller values of Λ^m in each term being compensated by smaller or larger components of $\mathbf{U}^m$.

We begin by investigating the convergence of the series for different values of Z_{eff}. As all components in the vector series converge at approximately the same rate, independent of mesh spacing, we can examine conveniently just one component, U_{2M-1} say, for $M = 90$. U_{2M-1} is the Lagrange multiplier on normalization of the $1s$ function. In Table I a list of partial sums,

$$U_{2M-1}(Z_{\text{eff}}, n) \equiv \sum_{m=0}^{n} U_{2M-1}^m (3/Z_{\text{eff}})^m, \quad n = 0, 1,..., 15; \quad Z_{\text{eff}} = 3, 4, 6, 8, 10, \quad (19)$$

are presented for $M = 90$. The values in Table I are in su. One must multiply them by $Z_{\text{eff}}^2/9$ to convert to au.

Examination of the consistent figures in the final partial sums for each value of Z_{eff} in Table I shows that the number of significant figures achieved by the sixteen term series as a function of Z_{eff} is that given in Table II. For the neutral atom ($Z_{\text{eff}} = 3$) we are close to the radius of convergence of the series. To substantially increase the accuracy would require a very long series indeed. In fact, a 31 term series was calculated, but it provided only a one figure improvement for $Z_{\text{eff}} = 3$. On the other hand, the series is strongly convergent for all positive ions, the 16 term series ranging from 6 figure accuracy for $Z_{\text{eff}} = 4$, to 12 figures for $Z_{\text{eff}} = 10$.

TABLE I

Partial Sums $U_{2M-1}(Z_{\text{eff}}, n)^a$
$1s^2 2s\ ^2S$ State

n	$Z_{\text{eff}} \to 3$	4	6	8	10
0	−8.99995343545	−8.99995343545	−8.99995343545	−8.99995343545	−8.99995343545
1	−4.05446785918	−5.29083925325	−6.52721064732	−7.14539634435	−7.51630776257
2	−4.87513034341	−5.75246190063	−6.73237626837	−7.26080200619	−7.59016738615
3	−4.91747021822	−5.77032403531	−6.73766875272	−7.26303477303	−7.59131056277
4	−4.93603960371	−5.77619950494	−6.73882933932	−7.26340198988	−7.59146097479
5	−4.94467020107	−5.77824758615	−6.73909904549	−7.26346599242	−7.59148194714
6	−4.94897862959	−5.77901439386	−6.73916636468	−7.26347797379	−7.59148508799
7	−4.95126490744	−5.77931957512	−6.73918422623	−7.26348035802	−7.59148558800
8	−4.95252974030	−5.77944620122	−6.73918916698	−7.26348085265	−7.59148567098
9	−4.95324602013	−5.77949998287	−6.73919056596	−7.26348095769	−7.59148568508
10	−4.95365640366	−5.77952309301	−6.73919096673	−7.26348098026	−7.59148568750
11	−4.95389306544	−5.77953308845	−6.73919108229	−7.26348098514	−7.59148568792
12	−4.95403030489	−5.77953743569	−6.73919111579	−7.26348098620	−7.59148568800
13	−4.95411038605	−5.77953933820	−6.73919112557	−7.26348098644	−7.59148568801
14	−4.95415743496	−5.77954017652	−6.73919112844	−7.26348098649	−7.59148568801
15	−4.95418526401	−5.77954054841	−6.73919112929	−7.26348098650	−7.59148568801

[a] See Eq. (19); $U_{2M-1} = \epsilon_{1s,1s}$ is the Lagrange multiplier on $1s$ normalisation and the values are in scaled units (su); $M = 90$.

TABLE II

Summary of Significant Figures

Z_{eff}	16–Term series	Double series
3	4	14
4	6	
6	8	
8	10	
10	12	

The self consistency of the solution vector $\mathbf{U}(\Lambda)$, obtained by summing the 16 term series (11) for the various values of $\Lambda = 3/Z_{\text{eff}}$, has been checked by using it to calculate the Coulomb and exchange terms (6), inserting these in (5) (with $Z = 3$ and $\Lambda = 3/Z_{\text{eff}}$), and solving (5) by the GNRI. It has been determined that in each case

TABLE III

Self-Consistency Check
$1s^2 2s\ ^2S$ State, $Z_{\text{eff}} = 6$

i^a	U_i from perturbation series	U_i after one *SCF* iteration
1	0.1846 0720 6277	0.1846 0720 6125
2	0.0497 3876 5378	0.0497 3876 6842
9	0.7047 2243 9014	0.7047 2243 8442
10	0.1877 8439 7991	0.1877 8440 3510
17	0.9227 5881 4417	0.9227 5881 3704
18	0.2363 6847 1802	0.2363 6847 8715
25	0.9103 4677 6379	0.9103 4677 5763
26	0.2094 2937 0104	0.2094 2937 6188
33	0.7466 0121 2287	0.7466 0121 1941
34	0.1252 8939 5191	0.1252 8939 8878
41	0.5128 3345 8555	0.5128 3345 8568
42	0.0074 7285 6005	0.0074 7285 6618
49	0.2840 7631 1595	0.2840 7631 1953
50	−0.1141 3946 3848	−0.1141 3946 5878
57	0.1159 3234 1467	0.1159 3234 2042
58	−0.2030 9607 0870	−0.2030 9607 3972
65	0.0289 5171 1778	0.0289 5171 2358
66	−0.2216 3332 9099	−0.2216 3333 1067
73	0.0030 0601 5919	0.0030 0601 6288
74	−0.1522 3861 6434	−0.1522 3861 5972
81	0.0000 8583 2870	0.0000 8583 2968
82	−0.0436 6943 6818	−0.0436 6943 5515
89	0.0000 0083 6654	0.0000 0083 6656
90	−0.0007 3769 2688	−0.0007 3769 2193
97	0.0000 0000 0000	0.0000 0000 0000
98	−0.0000 0000 0005	−0.0000 0000 0005
99	−6.7372 8750 1630	−6.7372 8750 1263
100	−0.5921 9848 2568	−0.5921 9848 5516
101	−0.0062 8193 5987	−0.0062 8194 7538

[a] U_i corresponds to the $1s(2s)$ radial function for i odd (even); U_{99}, U_{100}, and U_{101} are Lagrange multipliers whose values are in scaled units (su); $M = 50$.

$U(\lambda)$ is nearly self consistent in all its components to the number of significant figures indicated in Table II. Table III gives an example of this check for $Z_{\text{eff}} = 6$ and $M = 50$, and we see that the solution vector is nearly self consistent to 8 figures, with a few components differing by 1 in the 8th place.

Before proceeding to the extrapolation of the FDHF energies and multipliers, we have employed the vector perturbation series a second time to improve the results

potential for the new base problem also includes Coulomb and exchange terms calculated from the solution generated by the first series. New Coulomb and exchange terms are multiplied by λ and treated as perturbations, while the old terms, multiplied by $(1 - \lambda)$, are turned off as the new ones are turned on. So, effectively, the new perturbation is the difference between the new and the old terms. Since the first series is converging only slowly for the $Z_{\text{eff}} = 3$ case, this procedure is certainly preferable to calculating more terms in the original series. Some details of the calculation of the second series are given in Appendix A.

The convergence of the second series for $Z_{\text{eff}} = 3$ is checked by once again considering the partial sums (19) for $M = 90$. These are shown in Table IV. Although the second series was also calculated up to 15th order, the partial sums in Table IV show that the first order is sufficient for 8 figure accuracy, while the fourth order gives

TABLE IV

Partial Sums $U_{2M-1}(3, n)^a$
$1s^2 2s\ ^2S$ State, $Z_{\text{eff}} = 3$

n	$U_{2M-1}(3, n)$
0	−4.95414796964
1	−4.95422684278
2	−4.95422682026
3	−4.95422681938
4	−4.95422681944
5	−4.95422681948
6	−4.95422681950
7	−4.95422681951
8	−4.95422681951
9	−4.95422681951
10	−4.95422681952
11	−4.95422681952
12	−4.95422681952

[a] See Eq. (19); second series following on from first series shown in Table I for $Z_{\text{eff}} = 3$; $M = 90$; atomic units (au).

TABLE V

Neville Tables for Hartree–Fock Energy and Lagrange Multipliers
$1s^2 2s\ ^2S$ State, $Z_{eff} = 3$

	HF Energy[a]			
h = mesh[b] spacing = 1/(aM)	0th-order extrapolant	1st-order extrapolant	2nd-order extrapolant	3rd-order extrapolant
1/50	−7.43118818668			
		−7.43272874277		
1/70	−7.43194274477		−7.43272692990	
		−7.43272748943		−7.43272693121
1/90	−7.43225276735		−7.43272693094	
		−7.43272715711		
1/110	−7.43240959041			
	$U_{2M-1} = \epsilon_{1s,1s}{}^a$			
1/50	−4.95140990147			
		−4.95548530173		
1/70	−4.95340601588		−4.95548294890	
		−4.95548367508		−4.95548298359
1/90	−4.95422681952		−4.95548297642	
		−4.95548325935		
1/110	−4.95464217153			
	$U_{2M} = \epsilon_{2s,2s}{}^a$			
1/50	−0.196720803886			
		−0.196322705834		
1/70	−0.196525817085		−0.196322828803	
		−0.196322790850		−0.196322830075
1/90	−0.196445609190		−0.196322829812	
		−0.196322814034		
1/110	−0.196405015750			
	$U_{2M+1} = \epsilon_{1s,2s}{}^a$			
1/50	−0.002865470414			
		−0.002863576058		
1/70	−0.002864542566		−0.002863567730	
		−0.002863570300		−0.002863567335
1/90	−0.002864158461		−0.002863567417	
		−0.002863568585		
1/110	−0.002863963461			

[a] Atomic units (au).
[b] $a = 1$ (see Eq. (2)).

TABLE VI

Neville Tables for Hartree–Fock Energy and Lagrange Multipliers
$1s^2 2s\ ^2S$ State, $Z_{\text{eff}} = 4$

	HF Energy[a]			
h = mesh[b] spacing = 1/(aM)	0th-order extrapolant	1st-order extrapolant	2nd-order extrapolant	3rd-order extrapolant
1/50	−14.2757143426			
		−14.2773976073		
1/70	−14.2765387988		−14.2773946226	
		−14.2773955438		−14.2773946194
1/90	−14.2768772659		−14.2773946200	
		−14.2773949941		
1/110	−14.2770484157			
	$U_{2M-1} = \epsilon_{1s,1s}$[a]			
1/50	−10.2703740842			
		−10.2766889576		
1/70	−10.2734670834		−10.2766846743	
		−10.2766859963		−10.2766846259
1/90	−10.2747387527		−10.2766846359	
		−10.2766851868		
1/110	−10.2753822020			
	$U_{2M} = \epsilon_{2s,2s}$[a]			
1/50	−0.667280787783			
		−0.666145712675		
1/70	−0.666724832628		−0.666146177486	
		−0.666146034026		−0.666146173401
1/90	−0.666496171452		−0.666146174245	
		−0.666146117462		
1/110	−0.666380451125			
	$U_{2M+1} = \epsilon_{1s,2s}$[a]			
1/50	−0.009396537633			
		−0.009379985505		
1/70	−0.009388430468		−0.009379974099	
		−0.009379977619		−0.009379975986
1/90	−0.009385091071		−0.009379975596	
		−0.009379976416		
1/110	−0.009383400276			

[a] Atomic units (au).
[b] $a = 1$ (see Eq. (2)).

TABLE VII

Neville Tables for Hartree–Fock Energy and Lagrange Multipliers
$1s^2 2s\ ^2S$ State, $Z_{eff} = 6$

	HF Energy[a]			
h = mesh[b] spacing = 1/(aM)	0th-order extrapolant	1st-order extrapolant	2nd-order extrapolant	3rd-order extrapolant
1/50	−34.7251676776			
		−34.7260666477		
1/70	−34.7256079894		−34.7260609197	
		−34.7260626876		−34.7260609172
1/90	−34.7257876233		−34.7260609177	
		−34.7260616344		
1/110	−34.7258782055			
	$U_{2M-1} = \epsilon_{1s,1s}$[a]			
1/50	−26.9491500065			
		−26.9601678466		
1/70	−26.9545464996		−26.9601577359	
		−26.9601608565		−26.9601577366
1/90	−26.9567645172		−26.9601577365	
		−26.9601590000		
1/110	−26.9578866602			
	$U_{2M} = \epsilon_{2s,2s}$[a]			
1/50	−2.36879393027			
		−2.36500133336		
1/70	−2.36693633179		−2.36500308547	
		−2.36500254470		−2.36500308187
1/90	−2.36617236652		−2.36500308261	
		−2.36500286478		
1/110	−2.36578575437			
	$U_{2M+1} = \epsilon_{1s,2s}$[a]			
1/50	−0.025127743948			
		−0.025064645130		
1/70	−0.025096838404		−0.025064679408	
		−0.025064668829		−0.025064679624
1/90	−0.025084129436		−0.025064679579	
		−0.025064675226		
1/110	−0.025077698292			

[a] Atomic units (au).
[b] $a = 1$ (see Eq. (2)).

TABLE VIII

Neville Tables for Hartree–Fock Energy and Lagrange Multipliers
$1s^2 2s\ ^2S$ State, $Z_{\text{eff}} = 10$

	HF Energy[a]			
h = mesh[b] spacing = 1/(aM)	0th-order extrapolant	1st-order extrapolant	2nd-order extrapolant	3rd-order extrapolant
1/50	−102.636170110			
		−102.631121196		
1/70	−102.633697172		−102.631108885	
		−102.631112685		−102.631108878
1/90	−102.632676140		−102.631108880	
		−102.631110421		
1/110	−102.632158547			
	$U_{2M-1} = \epsilon_{1s,1s}$[a]			
1/50	−84.3353462369			
		−84.3563220920		
1/70	−84.3456201251		−84.3562961529	
		−84.3563041588		−84.3562961579
1/90	−84.3498409779		−84.3562961569	
		−84.3562993973		
1/110	−84.3519759926			
	$U_{2M} = \epsilon_{2s,2s}$[a]			
1/50	−8.78413726228			
		−8.77022588106		
1/70	−8.77732352454		−8.77023301301	
		−8.77023081179		−8.77023300232
1/90	−8.77452146518		−8.77023300452	
		−8.77023211656		
1/110	−8.77310349869			
	$U_{2M+1} = \epsilon_{1s,2s}$[a]			
1/50	−0.058735007017			
		−0.058560085473		
1/70	−0.058649331159		−0.058560254992	
		−0.058560202671		−0.058560255253
1/90	−0.058614119904		−0.058560255200	
		−0.058560233928		
1/110	−0.058596306358			

[a] Atomic units (au).
[b] $a = 1$ (see Eq. (2)).

10 figures. The whole 16 term series gives 14 figures accuracy. This compares with only 5 figures for the original series up to 30th order.

We are now in a position to extrapolate the FDHF values of total energy and Lagrange multipliers to the $h \to 0$ limit using Richardson's procedure [7]. Neville tables [8] of these extrapolations are given in Tables V through VIII for $Z_{\text{eff}} = 3, 4, 6,$ and 10, where all values have been converted to au. Perhaps ideally, the series for the various values of Z_{eff} should be truncated differently to give a standard SCF tolerance. However, the SCF tolerance desired for the smallest value of Z_{eff} of interest sets the number of terms required in the series, and then for higher values of Z_{eff} the series may as well be summed completely since the coefficient vectors are available. Here the 16 term series was summed throughout the range of Z_{eff} considered (except that for $Z_{\text{eff}} = 3$ the double series was used), and therefore the extrapolated values in the Neville tables are self consistent to the number of figures shown in Table II.

In the Neville tables the four 0th order extrapolants are the FDHF values corresponding to the values of mesh point spacing ($h = 1/Ma$; $a = 1$; $M = 50$, 70, 90 and 110) in the first column. The three 1st order extrapolants are each obtained by order h^2 extrapolations of the two adjacent FDHF values. The two 2nd order extrapolants are the results of order h^4 extrapolations of the upper and lower three FDHF values respectively, while the 3rd order extrapolant is the result of an order h^6 extrapolation of all four FDHF values. The 3rd order extrapolant is the most accurate, and the retention of significant figures moving from left to right in the table gives an indication of its accuracy.

All of the FDHF values of Tables V through VIII extrapolate very well, giving at least 7 figure accuracy. In particular, the extrapolated value of HF energy for the neutral Li atom (−7.43272693 au) agrees to six figures with a calculation by Clementi [9] using an analytic basis set (−7.4327257 au). It can be argued that the current value is the more accurate: (1) it is based upon a set of solution vectors which are self consistent to 1 part in 10^{14}; (2) the Neville table (Table V) indicates the extrapolation is good to at least 9 figures; and (3) since Clementi was using a finite basis set, by the variational theorem, his value of HF energy should be higher than a more accurate solution of the HF equations, and it is.

The current value of the HF energy for neutral Li does not agree with a previous FDNRA calculation [1] because the former was for the spin unrestricted case (the two $1s$ functions not constrained to be equal).

7. Isoelectronic Sequence of The $1s^2\,{}^1S$ State

A vector perturbation series was also calculated with $Z = 2$ for the isoelectronic sequence of the helium ground state. Here the solution vector $\mathbf{U}(\Lambda)$ contains the finite-difference variables corresponding to the $1s$ radial function for the first $M - 1$ components, and $U_M(\Lambda)$ is the Lagrange multiplier on normalization.

Again a 16 term perturbation series was calculated for $Z_{\text{eff}} = 2$, 6, and 10, and we

check on the convergence of the series for each of these values of Z_{eff} by considering the partial sums of the Mth component,

$$U_M(Z_{\text{eff}}, n) = \sum_{m=0}^{n} U_M{}^m (2/Z_{\text{eff}})^m, \quad n = 0, 1, \ldots, 15; \quad Z_{\text{eff}} = 2, 6, 10, \tag{20}$$

which corresponds to the Lagrange multiplier. These partial sums are shown in Table IX, in su for $M = 90$. Here we see that even for the neutral atom ($Z_{\text{eff}} = 2$) the 16 term series is good to 8 figures, and of course the accuracy improves from there as Z_{eff} is increased.

TABLE IX

Partial Sums $U_{2M-1}(Z_{\text{eff}}, n)^a$
$1s^2\ {}^1S$ State

n	$Z_{\text{eff}} \to 2$	6	10
0	−2.00020833441	−2.00020833441	−2.00020833441
1	−0.74976945188	−1.58339537356	−1.75012055790
2	−0.91644106657	−1.60191444186	−1.75678742249
3	−0.91747472428	−1.60195272548	−1.75679569175
4	−0.91776355238	−1.60195629126	−1.75679615387
5	−0.91784161846	−1.60195661252	−1.75679617886
6	−0.91786308137	−1.60195664196	−1.75679618023
7	−0.91786912507	−1.60195664472	−1.75679618031
8	−0.91787087663	−1.60195664499	−1.75679618031
9	−0.91787139953	−1.60195664502	−1.75679618031
10	−0.91787156006	−1.60195664502	−1.75679618031
11	−0.91787161060	−1.60195664502	−1.75679618031
12	−0.91787162686	−1.60195664502	−1.75679618031
13	−0.91787163219	−1.60195664502	−1.75679618031
14	−0.91787163397	−1.60195664502	−1.75679618031
15	−0.91787163457	−1.60195664502	−1.75679618031

[a] See Eq. (20); $U_{2M-1} = \epsilon_{1s,1s}$ is the Lagrange multiplier on $1s$ normalization and the values are in scaled units (su); $M = 90$.

An extrapolation of the HF energy and the Lagrange multiplier is shown in Table X for $Z_{\text{eff}} = 2$. The extrapolated value of HF energy agrees with the accepted value to 9 figures, about the limit of accuracy of the present calculation.

It is interesting to compare the convergence of the series for the $1s^2\ {}^1S$ case with that of the previous section for $1s^2 2s\ {}^2S$. While the present series is strongly convergent for neutral He, the corresponding series for neutral Li is only marginally so. The

TABLE X

Neville Tables for Hartree–Fock Energy and Lagrange Multiplier
$1s^2\ ^1S$ State, $Z_{\text{eff}} = 2$

	HF Energy[a]			
h = mesh[b] spacing = 1/(aM)	0th-order extrapolant	1st-order extrapolant	2nd-order extrapolant	3rd-order extrapolant
1/50	−2.86193462178			
		−2.86168040729		
1/70	−2.86181010856		−2.86167999508	
		−2.86168012230		−2.86167999516
1/90	−2.86175875596		−2.86167999514	
		−2.86168004664		
1/110	−2.86173273635			
		$U_M = \epsilon_{1s,1s}$[a]		
1/50	−0.917683273358			
		−0.917955830101		
1/70	−0.917816770538		−0.917955562522	
		−0.917955645108		−0.917955562543
1/90	−0.917871634566		−0.917955562538	
		−0.917955595976		
1/110	−0.917899390404			

[a] atomic units (au).
[b] $a = 1$ (see Eq. (2))

question of whether or not the convergence of the series for the neutral atom continues to get worse with increasing atomic number, can only be answered by further calculations. The different behavior for He and Li may be due to the fact that one is a closed-shell atom and the other open shell.

8. Conclusions

A vector perturbation-series solution of the FDHF equations, based upon a representation in a finite Banach space has been developed. One set of coefficient vectors can be used to generate the FDHF solution vectors for an isoelectronic sequence (neglecting relativistic corrections). Through Richardson extrapolation, matrix elements or expectation values of any operator of physical interest can be determined in the differential limit.

Considering the fact that each order in the vector perturbation series higher than the first requires more computation and storage than the SCF iteration, the latter

is preferable, assuming it converges easily, particularly if one is only interested in a single atom or ion. On the other hand, the set of coefficient vectors represents the solution for an isoelectronic sequence. Consequently, the vector perturbation approach might be very useful for calculations of electronic states of ionized impurity species in plasmas.

In cases where the SCF convergence is difficult, the monotonic convergence of the vector perturbation series may be particularly attractive. Although not reported here, the double (or in general multiple) series solution is very useful for negative ions.

The computation of the vector perturbation series requires a large amount of storage, but not necessarily in core. The vector coefficients $\mathbf{U}^n$ can all be stored externally and each transferred into core as required, for example when performing the summations of (14) and when summing the series (11) itself.

APPENDIX A

For the $1s^22s\ ^2S$ isoelectronic sequence there are $N = 2$ radial functions and $N' = 1$ off-diagonal multiplier. The **U** and **F** vectors are ordered following (7) and (16).

$$U_{2k-1} = P_1{}^k = P_{1s}^k, \qquad k = 1,..., M-1, \tag{A1}$$

$$U_{2k} = P_2{}^k = P_{2s}^k, \qquad k = 1,..., M-1. \tag{A2}$$

Written explicitly in terms of the vector components, the FDHF equations (5) for this case become

$$\begin{aligned} F_{2k-1} = &-\frac{1}{h^2}(1-\delta_{k,1})\,U_{2k-3} + 2\left[\frac{1}{h^2} - \frac{Z}{khz_k{}^3}\right]U_{2k-1} \\ &-\frac{1}{h^2}(1-\delta_{k,M-1})\,U_{2k+1} + \Lambda V_1{}^k U_{2k-1} - \Lambda X_1{}^k \\ &-\frac{U_{2M-1}U_{2k-1}}{z_k{}^4} - \frac{U_{2M+1}U_{2k}}{z_k{}^4} = 0, \qquad k = 1,..., M-1, \end{aligned} \tag{A3a}$$

$$\begin{aligned} F_{2k} = &-\frac{1}{2h^2}(1-\delta_{k,1})\,U_{2k-2} + \left[\frac{1}{h^2} - \frac{Z}{khz_k{}^3}\right]U_{2k} \\ &-\frac{1}{2h^2}(1-\delta_{k,M-1})\,U_{2k+2} + \Lambda V_2{}^k U_{2k} - \Lambda X_2{}^k \\ &-\frac{U_{2M}U_{2k}}{z_k{}^4} - \frac{U_{2M+1}U_{2k-1}}{z_k{}^4} = 0, \qquad k = 1,..., M-1, \end{aligned} \tag{A3b}$$

$$F_{2M-1} = h\sum_{j=1}^{M-1}\frac{U_{2j-1}U_{2j-1}}{z_j{}^4} - 1 = 0, \tag{A3c}$$

$$F_{2M} = h \sum_{j=1}^{M-1} \frac{U_{2j}U_{2j}}{z_j^4} - 1 = 0, \tag{A3d}$$

$$F_{2M+1} = h \sum_{j=1}^{M-1} \frac{U_{2j-1}U_{2j}}{z_j^4} = 0. \tag{A3e}$$

where the Coulomb and exchange terms (6) are, respectively,

$$V_1^k = \frac{2}{z_k^4} \sum_{j=1}^{M-1} \frac{z_q}{qz_j^4} (U_{2j-1}U_{2j-1} + U_{2j}U_{2j}), \tag{A4a}$$

$$V_2^k = \frac{2}{z_k^4} \sum_{j=1}^{M-1} \frac{z_q}{qz_j^4} U_{2j-1}U_{2j-1}, \tag{A4b}$$

and

$$X_1^k = \frac{U_{2k}}{z_k^4} \sum_{j=1}^{M-1} \frac{z_q}{qz_j^4} U_{2j-1}U_{2j}, \tag{A4c}$$

$$X_2^k = \frac{U_{2k-1}}{z_k^4} \sum_{j=1}^{M-1} \frac{z_q}{qz_j^4} U_{2j}U_{2j-1}, \tag{A4d}$$

where $q = \max(j, k)$, and $z_k = 1 - akh$.

Substitution of the vector perturbation series (11) for each component of **U** in (A3) and (A4) and setting each term in Λ^n equal to zero, results in the vector equations (12) and (13), which for the present case become

$$-\frac{(1-\delta_{k,1})}{h^2} U_{2k-3}^n + \left[\frac{2}{h^2} - \frac{2Z}{khz_k^3} - \frac{U_{2M-1}^0}{z_k^4}\right] U_{2k-1}^n - \frac{(1-\delta_{k,M-1})}{h^2} U_{2k+1}^n$$

$$- \frac{U_{2M+1}^0}{z_k^4} U_{2k}^n - \frac{U_{2k-1}^0}{z_k^4} U_{2M-1}^n - \frac{U_{2k}^0}{z_k^4} U_{2M+1}^n = G_{2k-1}^{n-1}$$

$$k = 1,..., M-1; \qquad n = 0, 1, 2,..., \tag{A5a}$$

$$-\frac{(1-\delta_{k,1})}{2h^2} U_{2k-2}^n + \left[\frac{1}{h^2} - \frac{Z}{khz_k^3} - \frac{U_{2M}^0}{z_k^4}\right] U_{2k}^n - \frac{(1-\delta_{k,M-1})}{2h^2} U_{2k+2}^n$$

$$- \frac{U_{2M+1}^0}{z_k^4} U_{2k-1}^n - \frac{U_{2k}^0}{z_k^4} U_{2M}^n - \frac{U_{2k-1}^0}{z_k^4} U_{2M+1}^n = G_{2k}^{n-1}$$

$$k = 1,..., M-1; \qquad n = 0, 1, 2,..., \tag{A5b}$$

$$2h \sum_{j=1}^{M-1} \frac{U_{2j-1}^0}{z_j^4} U_{2j-1}^n = G_{2M-1}^{n-1}, \qquad n = 0, 1, 2,... \tag{A5c}$$

$$2h \sum_{j=1}^{M-1} \frac{U_{2j}^0}{z_j^4} U_{2j}^n = G_{2M}^{n-1}, \qquad n = 0, 1, 2,... \tag{A5d}$$

$$h \sum_{j=1}^{M-1} \frac{1}{z_j^4} (U_{2j-1}^0 U_{2j}^n + U_{2j}^0 U_{2j-1}^n) = G_{2M+1}^{n-1}, \qquad n = 0, 1, 2,..., \tag{A5e}$$

where

$$\begin{aligned} G_{2k-1}^{n-1} = &- \frac{2}{z_k^4} \sum_{l=0}^{n-1} U_{2k-1}^{n-l-1} \sum_{j=1}^{M-1} \frac{z_q}{q z_j^4} \sum_{m=0}^{l} (U_{2j-1}^{l-m} U_{2j-1}^m + U_{2j}^{l-m} U_{2j}^m) \\ &+ \frac{1}{z_k^4} \sum_{l=0}^{n-1} U_{2k}^{n-l-1} \sum_{j=1}^{M-1} \frac{z_q}{q z_j^4} \sum_{m=0}^{l} U_{2j-1}^{l-m} U_{2j}^m \\ &+ \frac{1}{z_k^4} \sum_{m=1}^{n-1} (U_{2M-1}^{n-m} U_{2k-1}^m + U_{2M+1}^{n-m} U_{2k}^m), \end{aligned} \tag{A6a}$$

$$\begin{aligned} G_{2k}^{n-1} = &- \frac{2}{z_k^4} \sum_{l=0}^{n-1} U_{2k}^{n-l-1} \sum_{j=1}^{M-1} \frac{z_q}{q z_j^4} \sum_{m=0}^{l} U_{2j-1}^{l-m} U_{2j-1}^m \\ &+ \frac{1}{z_k^4} \sum_{l=0}^{n-1} U_{2k-1}^{n-l-1} \sum_{j=1}^{M-1} \frac{z_q}{q z_j^4} \sum_{m=0}^{l} U_{2j}^{l-m} U_{2j-1}^m \\ &+ \frac{1}{z_k^4} \sum_{m=1}^{n-1} (U_{2M}^{n-m} U_{2k}^m + U_{2M+1}^{n-m} U_{2k-1}^m), \end{aligned} \tag{A6b}$$

$$G_{2M-1}^{n-1} = -h \sum_{j=1}^{M-1} \frac{1}{z_j^4} \sum_{m=1}^{n-1} U_{2j-1}^{n-m} U_{2j-1}^m, \tag{A6c}$$

$$G_{2M}^{n-1} = -h \sum_{j=1}^{M-1} \frac{1}{z_j^4} \sum_{m=1}^{n-1} U_{2j}^{n-m} U_{2j}^m, \tag{A6d}$$

$$G_{2M+1}^{n-1} = -h \sum_{j=1}^{M-1} \frac{1}{z_j^4} \sum_{m=1}^{n-1} U_{2j-1}^{n-m} U_{2j}^m. \tag{A6e}$$

The summations in (A6) should be interpreted as giving zero whenever the upper limit is less than the lower limit.

Equations (A5) with $n = 0$ are the base problem for this case and correspond to (12). For $n > 0$ (A5) correspond to (13), and the elements of the J matrix can be determined by inspection.

For a double-series solution of (A3) one simply adds a term $(1 - \Lambda)(\hat{V}_1^k U_{2k-1} - \hat{X}_1^k)$ to (A3a) and a term $(1 - \Lambda)(\hat{V}_2^k U_{2k} - \hat{X}_2^k)$ to (A3b), where the $\hat{V}_1^k$, $\hat{V}_2^k$, $\hat{X}_1^k$, and $\hat{X}_2^k$ are to be calculated from (A4) with the **U** vector obtained from summing the first (truncated) series. After substitution of the vector perturbation series for the com-

ponents of $\mathbf{U}$, the above terms cause the following modifications to (A5). A term $\hat{V}_1{}^k U_{2k-1}^n$ must be added to the left of (A5a) and a term, $\hat{V}_1{}^k U_{2k-1}^{n-1} + (\delta_{n_0} - \delta_{n_1})\,\hat{X}_1{}^k$, to the right. A term $\hat{V}_2{}^k U_{2k}^n$ must be added to the left of (A5b) and a term, $\hat{V}_2{}^k U_{2k-1}^{n-1} + (\delta_{n_0} - \delta_{n_1})\,\hat{X}_2{}^k$, to the right.

Appendix B

Since each coefficient vector $\mathbf{U}^n$ in the vector perturbation series (11) depends on all lower orders $\mathbf{U}^{m<n}$ (see (12), (13), and (14)), it is important that (13) be solved very accurately so as to avoid an error buildup. Unfortunately the algorithm of [2] does not provide sufficient accuracy for the effective inversion of J in (13). One way to insure and control accuracy is to use the GNRI to solve (13).

In order to understand this difficulty and its resolution in detail, it is best to refer to the $1s^2 2s\ ^2S$ case treated in Appendix A. In the algorithm of [2] the J matrix, determined from (A5) by inspection for this case, is partitioned into four submatrices.

$$J = \begin{pmatrix} A & B \\ C & 0 \end{pmatrix}, \tag{B1}$$

where A is a $2(M-1) \times 2(M-1)$ block tridiagonal matrix with 2×2 subblocks, B is a $2(M-1) \times 3$ matrix, C is a $3 \times 2(M-1)$ matrix, and 0 is a 3×3 null matrix. The inaccuracy stems from the fact that the A matrix is singular within the tolerance (18) used in the GNRI solution of the base problem, and the algorithm requires the effective inversion of A.

The singularity of A is easily seen by referring to (A3) with $\Lambda = 0$, where the matrix elements of J are given by

$$J_{ii'} = \left(\frac{\partial F_i}{\partial U_{i'}}\right)_{\Lambda=0}, \qquad i, i' = 1,\ldots, 2M+1, \tag{B2}$$

and

$$A_{ii'} \equiv J_{ii'}, \qquad i, i' = 1,\ldots, 2M-2. \tag{B3}$$

These are the same matrix elements as given directly by (A5). The A matrix operates in the subspace $\mathscr{B}_P$. For a given mesh spacing, h, the A matrix depends only on the values of the Lagrange multipliers, U_{2M-1}, U_{2M}, and U_{2M+1}. When these three multipliers take on values which correspond to a solution of (A3) with $\Lambda = 0$ (U_{2M-1}^0, U_{2M}^0, and U_{2M+1}^0), then the A matrix becomes singular, since there exists a vector in $\mathscr{B}_P$ which is reduced to the null vector upon operation with A, namely $Q_P\mathbf{U}^0$ (where Q_P is the projector onto $\mathscr{B}_P$).

Let us note in passing that the whole J matrix is certainly not singular, since $J\mathbf{U}^0$ gives a 1 in the $2M-1$ and $2M$ components of the resulting vector, as can be seen from (A3c) and (A3d). Therefore, this difficulty does not constitute a fundamental problem with the vector perturbation series. It is the partitioning of J as in (B1) that

has run into trouble. On the other hand, J is a large $(2M + 1) \times (2M + 1)$ matrix, and it is prohibitive to invert it as a general matrix.

The solution of this problem lies in giving (A5) (and in general (13)) additional freedom and using the GNRI. Define new variables, U^n_{2M+2}, U^n_{2M+3} and U^n_{2M+4}, and constrain them to be respectively equal to U^0_{2M-1}, U^0_{2M}, and U^0_{2M+1}. Rewrite (A5), putting the G^{n-1}_{2k-1} and G^{n-1}_{2k} on the left with the other terms, and substitute the new variables respectively in place of the constants U^0_{2M-1}, U^0_{2M}, and U^0_{2M+1}. Set the resulting equations, which now all equal zero on the right, equal on the left to the first $2M + 1$ components of a $2M + 4$ dimensional function vector $\mathbf{F}^n$. Add to this set the three constraining equations,

$$F^n_{2M+2} = U^n_{2M+2} - U^0_{2M-1} = 0, \tag{B4a}$$

$$F^n_{2M+3} = U^n_{2M+3} - U^0_{2M} = 0, \tag{B4b}$$

$$F^n_{2M+4} = U^n_{2M+4} - U^0_{2M+1} = 0. \tag{B4c}$$

This extended system of equations in the variables $U_i{}^n$ $(i = 1,..., 2M + 4)$ is now nonlinear, and the solution is not simply an effective matrix inversion. Put these variables in a $2M + 4$ dimensional vector $\mathbf{U}^n$, and set up a GNRI to solve this system.

$$\mathbf{U}^{n(m+1)} = U^{n(m)} - (J^{(m)})^{-1}\,\mathbf{F}^{n(m)}, \tag{B7}$$

where (m) denotes the iteration and

$$J^{(m)}_{ii'} = \left(\frac{\partial F_i{}^n}{\partial U^n_{i'}}\right)^{(m)}, \qquad i, i' = 1,..., 2M + 4. \tag{B8}$$

The Jacobian matrix given by (B8) can be partitioned as follows.

$$J = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \tag{B9}$$

where A is the same as before, but B is a $2(M - 1) \times 6$ matrix and C is a $6 \times 2(M - 1)$ matrix with all zeros in the lower three rows. D is a 6×6 matrix whose only nonzero elements are given by $D_{44} = D_{55} = D_{66} = 1$. To accommodate the J matrix (B9), the algorithm of [2] must be modified by substituting

$$(CA^{-1}B - D)\,\Delta_2 = CA^{-1}\mathbf{F}_1 - \mathbf{F}_2 \tag{B10}$$

for (A8) of [2].

In practice this scheme works very well indeed. To obtain a good starting approximation for the GNRI, solve (A5) with the values U^0_{2M-1}, U^0_{2M}, and U^0_{2M+1} in J displaced from their accurate solution values by a small number, say 10^{-10}, so that the A matrix is nonsingular. Then solve the extended system with the GNRI with U^0_{2M-1}, U^0_{2M},

and U^0_{2M+1} in (B4) set to their accurate solution values. Typically the system is solved to a low tolerance in one iteration, going from a value of $F^n_{\max} = \max(|F_i^n|, i = 1,..., 2M + 4)$ of 10^{-10} for the starting approximation to a value less than 10^{-18} after the first iteration. Also the system is stable. If more than one iteration is taken $F^n_{\max}$ will stay below 10^{-18}.

The same scheme is applicable to the general problem. One extends the system (13) by the total number of multipliers $(N + N')$, defining a new variable for each and adding on $(N + N')$ constraining equations of the type (B4). This scheme gives one a control on the accuracy, since the precision is set for each order term in the vector perturbation series by the GNRI tolerance (18).

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