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Multiple Solutions of Hartree–Fock Equations*

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ABSTRACT

In the calculation of electron-atom cross sections it is often quite useful to obtain wave functions for the scattered particles which are orthogonal to the wave functions of the electrons bound in the atom. This constraint, although it may neglect certain couplings, provides a considerable simplification in obtaining certain transition matrix elements. A straightforward technique for enforcing this orthogonality condition is to include Lagrange multipliers in the differential equation.

It has been found that depending on the values of the Lagrange multipliers there may be zero, one, or two solutions. However, the solution which yields orthogonality is unique. Non-iterative schemes for solutions are discussed and applied to electron-hydrogen atom scattering.

I. INTRODUCTION

In many applications of scattering theory to atomic ([1]–[3]) and nuclear processes the behavior of the projectile particle is described by an uncoupled, linearized version of the Hartree–Fock formalism. The wave function of the target particle is assumed to be known and a partial wave expansion of the projectile wave function leads to second order, integro-differential equations for the radial wave functions. The equations are linear and are often assumed for convenience to be uncoupled.

The radial equations may also contain terms which arise from the requirement that the projectile wave function be orthogonal to the target wave function. For some orbitals this condition is satisfied automatically by symmetry requirements (e.g. angular momentum); for others this constraint is imposed through the use of Lagrange multipliers. It is largely with these orthogonalizing terms that the present paper is concerned. It will be shown for fairly general conditions that the number of

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physically acceptable solutions to the radial equations depends on the values of the Lagrange multipliers, there being either two solutions, one solution or no solutions for each set of values of the multipliers. It will also be shown that there is precisely one solution corresponding to neglecting the requirement of orthogonalization (setting all multipliers equal to zero) and that there is precisely one solution corresponding to fully orthogonalized wave functions. It is this last solution that is usually sought for in physical applications.

More specifically, attention is restricted to cases in which the target may be assumed to be in some definite state (usually the ground state) and to be described by one particle Hartree–Fock orbitals containing single variable radial wave functions. Then the radial equations for the projectile particle take the form

$$\left[\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + k^2 - V(r)\right] y(r) - \int_0^\infty dr' K(r, r')\, y(r') = \sum_{k=1}^{n} \lambda_k N P_k(r), \tag{1}$$

where the lth radial wave function $u_l(r)$ is related to $y(r)$ by

$$u_l(r) = \frac{1}{r} y(r), \tag{2}$$

the potential term $V(r)$ describes direct interactions with the orbitals of the target particle and may include polarization (optical potential) effects, and the kernel $K(r, r')$ arises from exchange interactions with the target orbitals. The radial functions $P_k(r)$ $(k = 1,..., n)$ are the radial part of those target orbitals which are not orthogonal to the lth partial wave by virtue of the angular or spin parts of the orbitals. The Lagrange multipliers, λ_k, insure that the solutions of Eq. (1) satisfy the condition

$$\int_0^\infty dr\, y(r)\, P_k(r) = 0 \qquad \text{for} \quad k = 1, 2,..., n.$$

However, for many states the λ_k are not needed as the orthogonality is imposed by the spin or orbital angular momenta.

It is further assumed that the quantities appearing in Eq. (1) are sufficiently regular that the standard asymptotic forms of potential scattering theory [4],

$$y(r) \xrightarrow[r\to 0]{} r^{l+1} \tag{3}$$

and

$$y(r) \xrightarrow[r\to\infty]{} N \sin\left(kr - \frac{l\pi}{2} + \delta\right), \tag{4}$$

may be imposed here on $y(r)$. The normalization constant N is introduced into the orthogonalizing terms of Eq. (1) in order to simplify the analysis of this equation

by having Eq. (1) formally homogeneous in $y(r)$. In this way values of the multipliers λ_k may be considered independently of the normalization of the wave function. It is also assumed for convenience that the radial functions $P_k(r)$ are normalized to unity. Attention is restricted to kernels $K(r, r')$ which may be represented in the form

$$\begin{aligned} K(r, r') &= \sum_{i=1}^{m} \varphi_{i-}(r)\, \psi_{i-}(r') \qquad \text{for} \quad r < r' \\ &= \sum_{i=1}^{m} \varphi_{i+}(r)\, \psi_{i+}(r') \qquad \text{for} \quad r > r', \end{aligned} \tag{5}$$

where the $\varphi_{i\pm}(r)$ and $\psi_{i\pm}(r)$ can be any regular functions. The important point is that the kernels $K(r, r')$ be made up of products of functions of r and r'. This represents a genuine restriction on the class of processes to be considered, but such kernels arise very naturally in the Hartree–Fock theory of electron-atom scattering and are also often used for convenience in nuclear problems. This restriction greatly facilitates the analysis of the properties of Eq. (1). Finally, it is assumed that certain sets of linear equations which have integrals of solutions of reduced equations as coefficients are nonsingular.

It is shown in Section II that under these restrictions the totality of values of the parameters λ_j, which may be regarded as an Euclidean n-space specified by the vector $\boldsymbol{\lambda}$, is divided into four regions R_1, R_2, R_3, and R_4 such that in R_1 Eq. (1) has one physically acceptable solution, in R_2 the equation has two solutions, while in R_3 and R_4 the equation has no solutions. These regions have a simple geometric structure, being defined by hyperellipsoids and hyperplanes in the n-space. The origin of the n-space $\boldsymbol{\lambda} = 0$, which corresponds to neglecting all requirements of orthogonality, always lies in R_1, where the equation is uniquely soluble. The value of $\boldsymbol{\lambda}$ corresponding to a fully orthogonalized solution always lies in either R_1 or R_2. That is, there is always a value of $\boldsymbol{\lambda}$ for which a solution to Eq. (1) exists which is physically acceptable and which is orthogonal to all the orbitals appearing in the equation. If, however, the functions appearing in the equation are such that the value of $\boldsymbol{\lambda}$ leading to orthogonality lies in R_2, then there will be another physically acceptable but non-orthogonal solution to the equation at the same value of $\boldsymbol{\lambda}$. These results are the principal content of the paper.

The above results are concerned, of course, with the basic structure of equations used to describe scattering processes in physical systems. But they also have implications for the numerical techniques used to solve the equations. Some of these implications are explored in Section III, where electron-atom, principally electron-hydrogen, calculations are discussed. It is shown that for singlet s-wave scattering iteration techniques for solution yield precisely one of the two solutions

in R_2 and none of the solutions in R_1. It turns out that the orthogonalized solution lies in R_2 but is not on the branch of solutions which may be found by iteration. The boundary of R_2, as defined by the limits of the region in which the iteration scheme converges, agrees very well with the expressions for the boundary given in Section II and provides a numerical test of the theory.

II. Existence and Uniqueness of Solutions

The structure of Eq. (1) is conveniently analyzed in terms of certain reduced equations, which were apparently first considered by Marriott [5] to obtain a method for avoiding iteration techniques in obtaining solutions. The reduced equations occur naturally when Eq. (1) is rewritten in terms of a linear operator L which contains integrals only from 0 to r and numbers h_i which are integrals from 0 to ∞. Specifically, Eq. (1) takes the form

$$Ly(r) = \sum_{i=1}^{m} h_i \varphi_{i-}(r) + \sum_{k=1}^{n} N\lambda_k P_k(r), \tag{6}$$

where

$$h_i = \int_0^\infty dr' \psi_{i-}(r')\, y(r') \qquad \text{for} \quad i = 1, 2, \ldots, m, \tag{7}$$

and

$$Ly(r) = \left[\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + k^2 - V(r)\right] y(r) + \int_0^r dr' M(r, r')\, y(r'), \tag{8}$$

with $M(r, r')$ given by

$$M(r, r') = \sum_{i=1}^{m} \varphi_{i-}(r)\, \psi_{i-}(r') - \sum_{j=1}^{m'} \varphi_{j+}(r)\, \psi_{j+}(r').$$

Attention is then restricted to those kernels $M(r, r')$ for which the homogeneous equation

$$Ly(r) = 0 \tag{9}$$

has precisely one solution $y_{00}(r)$ satisfying the boundary conditions of Eqs. (3) and (4). The $n + m + 1$ reduced equations

$$Ly_{i0}(r) = \varphi_{i-}(r) \qquad \text{for} \quad i = 0, 1, \ldots, m \tag{10}$$

and

$$Ly_{0k}(r) = P_k(r) \qquad \text{for} \quad k = 0, 1,..., n, \tag{11}$$

where

$$\varphi_{0-}(r) \equiv P_0(r) \equiv 0, \tag{12}$$

will then have $n + m + 1$ unique solutions, y_{ik}, where $i = 0, 1,..., m$, $k = 0, 1,..., n$ and at least one of the indices i and k are zero. Eq. (9) is then the special case of Eq. (10) or (11) in which $i = k = 0$. In the above it is assumed that Eqs. (3) and (4) are the boundary conditions for each y_{ik}.

These equations occur very naturally in the context of numerical solutions of Eq. (1), since $Ly(r)$ depends explicitly only on values of $y(r')$ for $r' \leqslant r$. If the equations are solved by integrating outward from $r = 0$, then at each step the equations are determinate, depending only on previously computed values of $y(r)$ and $y'(r)$. The problem of solving Eq. (6) then reduces, when λ is assumed to be known, to the algebraic problem of solving for the unknown numbers h_i and N in terms of the y_{ik}. With these numbers known, Eq. (6) is then a determinate equation. It turns out that the algebraic process of solving for h_i and N is also the key step in examining the existence and uniqueness of the solutions.

If the functions $y_{ik}(r)$ are assumed to be known, then the unique solution of Eq. (6) which satisfies Eq. (3) may be specified in terms of the (as yet unknown) h_i and N as

$$y(r) = y_{00}(r) + \sum_{i=1}^{m} h_i[y_{i0}(r) - y_{00}(r)] + \sum_{k=1}^{n} \lambda_k N[y_{0k}(r) - y_{00}(r)]. \tag{13}$$

Through use of the auxiliary quantities

$$h_{ijk} = \int_0^\infty dr' \psi_{i-}(r')\, y_{jk}(r'), \tag{14}$$

where

$$i = 0, 1,..., m$$

$$j = 0, 1,..., m$$

$$k = 0, 1,..., n$$

and at least one of the indices j and k is zero, and use of Eq. (13) it is possible to obtain from the defining Eq. (7) for the h_i a set of linear equations for the h_i

$$\sum_{j=1}^{m} [\delta_{ij} - (h_{ij0} - h_{i00})]\, h_j = h_{i00} + \sum_{k=1}^{n} (h_{i0k} - h_{i00})\, \lambda_k N \qquad \text{for} \quad i = 1, 2,..., m. \tag{15}$$

This set is assumed to be nonsingular and the discussion is restricted to coefficients for which this is true. Then the h_i are uniquely determined when λ_k and N are specified.

The existence and uniqueness of solutions may thus be determined by displaying the conditions under which one or more positive values of N will exist for a set of values λ_k. The quantities h_{ijk} are all real, so the solutions h_j of Eq. (15) have the form

$$h_j = f_j + g_j N \qquad \text{for} \quad j = 1, 2, \ldots, \mathrm{m}, \tag{16}$$

where the g_j are linear forms in λ_k,

$$g_j = \sum_{k=1}^{n} G_{jk}\lambda_k \qquad \text{for} \quad j = 1, 2, \ldots, m, \tag{17}$$

and the quantities f_j, G_{jk} and λ_k are all real and all specified. For each $y_{ik}(r)$, Eq. (4) imposes a unique N_{ij} and δ_{ij}. Thus the boundary condition at ∞

$$N \sin(\beta + \delta) = N_{00} \sin(\beta + \delta_{00}) + \sum_{j=1}^{m} h_j[N_{j0} \sin(\beta + \delta_{j0}) - N_{00} \sin(\beta + \delta_{00})]$$

$$+ \sum_{k=1}^{n} \lambda_k N[N_{0k} \sin(\beta + \delta_{0k}) - N_{00} \sin(\beta + \delta_{00})], \tag{18}$$

where

$$\beta = kr - l\frac{\pi}{2}, \tag{19}$$

is obtained by requiring that the y of Eq. (13) should satisfy Eq. (4) as well as Eqs. (3) and (6) and may be regarded as a nonlinear defining equation for N. Specifically, by eliminating β and δ from Eq. (18), the resulting equation

$$N^2 = \Big[N_{00} \cos \delta_{00} + \sum_{j=1}^{m} h_j(N_{j0} \cos \delta_{j0} - N_{00} \cos \delta_{00})$$

$$+ \sum_{k=1}^{n} \lambda_k N(N_{0k} \cos \delta_{0k} - N_{00} \cos \delta_{00})\Big]^2$$

$$+ \Big[N_{00} \sin \delta_{00} + \sum_{j=1}^{m} h_j(N_{j0} \sin \delta_{j0} - N_{00} \sin \delta_{00})$$

$$+ \sum_{k=1}^{n} \lambda_k N(N_{0k} \sin \delta_{0k} - N_{00} \sin \delta_{00})\Big]^2, \tag{20}$$

when supplemented by Eqs. (16) and (17), becomes a simple quadratic equation for N

$$aN^2 + 2bN + c = 0 \tag{21}$$

whose real coefficients are expressed in terms of the known quantities of the theory.

The dependence of the coefficients on λ is most simply expressed by means of the quantities

$$\begin{aligned} R &= \sum_{j=1}^{m} g_j N_{j0} \cos(\delta_{j0} - \delta_{00}) + \sum_{k=1}^{n} \lambda_k N_{0k} \cos(\delta_{0k} - \delta_{00}) \\ S &= \sum_{j=1}^{m} g_j N_{j0} \sin(\delta_{j0} - \delta_{00}) + \sum_{k=1}^{n} \lambda_k N_{0k} \sin(\delta_{0k} - \delta_{00}) \\ T &= N_{00} \Big(\sum_{j=1}^{m} g_j + \sum_{k=1}^{n} \lambda_k \Big), \end{aligned} \tag{22}$$

which are linear in λ_k, and the quantities

$$\begin{aligned} U &= N_{00} \Big(1 - \sum_{j=1}^{m} f_j\Big) + \sum_{j=1}^{m} f_j N_{j0} \cos(\delta_{j0} - \delta_{00}) \\ V &= \sum_{j=1}^{m} f_j N_{j0} \sin(\delta_{j0} - \delta_{00}) \end{aligned} \tag{23}$$

which are independent of λ_k. The coefficients are then given by

$$c = U^2 + V^2 > 0 \tag{24}$$

$$b = U(R - T) + VS \tag{25}$$

and

$$a = \hat{a} - 1, \tag{26}$$

where

$$\hat{a} = (R - T)^2 + S^2 > 0. \tag{27}$$

Thus c is independent of λ_k, b is linear and homogeneous in λ_k and $\hat{a}$ is homogeneous and quadratic in λ_k.

The discriminant of Eq. (21)

$$D \equiv b^2 - ac = U^2(1 - S^2) + 2UVS(R - T) + V^2[1 - (R - T)^2] \tag{28}$$

provides one condition for the existence of solutions, since if $D < 0$ the two roots for N are complex. Thus the condition

$$D \geqslant 0, \tag{29}$$

or

$$[US - V(R - T)]^2 \leqslant U^2 + V^2, \tag{30}$$

is a necessary condition that Eq. (1) have physically acceptable solutions. The region defined by Eq. (30) is the region between the two parallel hyperplanes in λ space

$$US - V(R - T) = \pm(U^2 + V^2)^{1/2} \tag{31}$$

which are equidistant from and symmetric with respect to the origin. The origin is, of course, in the center of this region. The region, R_4, where the equations have no solution consists of the two half spaces outside the two hyperplanes defined by Eq. (31).

The region, R_1, where Eq. (1) has a unique solution is defined by the condition

$$a \leqslant 0 \tag{32}$$

or

$$S^2 + (R - T)^2 \leqslant 1. \tag{33}$$

Since in this region

$$D = b^2 + |a| c \geqslant 0, \tag{34}$$

R_1 lies entirely between the two hyperplanes of Eq. (31). In this region N is given by

$$N = \frac{b \pm (b^2 + |a| c)^{1/2}}{|a|}. \tag{35}$$

Thus, when λ is specified, the coefficients a, b and c are uniquely determined and there is precisely one root of Eq. (35) which leads to positive N and hence to physically acceptable solutions. This, then, is the region where the equation is uniquely soluble. The boundary of this region

$$S^2 + (R - T)^2 = 1 \tag{36}$$

defines a hyperellipsoid E, centered at the origin of λ space, since R, S, and T are linear and homogeneous in λ_k and the LHS of Eq. (36) is positive definite. In particular, the origin of λ space (corresponding to neglect of all orthogonality requirements) belongs to R_1 and thus yields a unique solution for Eq. (1).

In the region outside E, but inside the hyperplanes of Eq. (31)

$$a > 0, \tag{37}$$

$$b^2 - ac > 0, \tag{38}$$

and N is given by

$$N = \frac{-b \pm (b^2 - ac)^{1/2}}{a}. \tag{39}$$

Thus N is real and both roots are positive (negative) when b is negative (positive). Thus the region R_2, in which Eq. (1) has two physically acceptable solutions, is given by Eq. (37), Eq. (38) and

$$b \leqslant 0. \tag{40}$$

More explicitly, these conditions become

$$S^2 + (R - T)^2 \geqslant 1, \tag{41}$$

Eq. (30), and

$$U(R - T) + VS \leqslant 0. \tag{42}$$

Finally, the other region, R_3, where Eq. (1) has no physically acceptable solutions, is given by Eq. (30), Eq. (41) and

$$U(R - T) + VS \geqslant 0. \tag{43}$$

The boundary between R_2 and R_3

$$U(R - T) + VS = 0 \tag{44}$$

is, in view of the linearity and homogeneity of R, S and T in the λ_k, a hyperplane not parallel to the hyperplanes defined by Eq. (31). This completes the classification of $\boldsymbol{\lambda}$ space into four regions R_1, R_2, R_3, R_4 according to the number of physically acceptable solutions possessed by Eq. (1) at each $\boldsymbol{\lambda}$ value. The classification is algebraic in the sense that when the reduced quantities N_{ij} and δ_{ij} have been determined, a finite number of elementary operations suffices to construct the boundaries of the regions.

It is also of interest to know how many fully orthogonalized solutions will exist among the infinitely many solutions filling regions R_1 and R_2. It will be shown here that there is precisely one such solution which, however, may lie in either R_1 or R_2. Of course, when the functions appearing in Eq. (1) are such that this

solution lies in R_2, then there will be a second, non-orthogonalized solution at the same value of λ. Any orthogonalized solution will satisfy the conditions

$$\int_0^\infty dr' P_l(r')\, y(r') = 0 \qquad \text{for} \quad l = 1, 2, \ldots, n. \tag{45}$$

Since the y_{jk} are considered to be known, the auxiliary quantities

$$P_{ljk} = \int_0^\infty dr' P_l(r')\, y_{jk}(r'), \tag{46}$$

where

$$l = 1, 2, \ldots, n$$
$$j = 0, 1, \ldots, m$$

and

$$k = 0, 1, \ldots, n,$$

and at least one of the indices j and k are zero, are uniquely determined. Thus, when Eq. (13) for $y(r)$ is substituted into the defining Eq. (44) for the orthogonalized solution, n additional linear equations

$$\sum_{j=1}^{m} h_j(p_{lj0} - p_{l00}) + \sum_{k=1}^{n} \lambda_k N(p_{l0k} - p_{l00}) = -p_{l00} \qquad \text{for} \quad l = 1, 2, \ldots, n \tag{47}$$

occur as constraints among the $m + n$ quantities h_j and $\lambda_k N$. Of course, Eq. (15) may also be viewed as m linear constraints among the same $m + n$ quantities. Both sets of equations together suffice to determine these quantities uniquely, provided that the equations are nonsingular. The discussion of this section is therefore restricted to those cases for which this condition is met. Then the (uniquely determined) quantities h_j and $\lambda_k N$ will be algebraic functions of the numbers h_{ijk} and p_{ljk}, but will not depend explicitly on the normalization constant N. When these expressions are substituted into the defining Eq. (20) for N, the result is a defining equation of the form

$$N^2 = H^2, \tag{48}$$

where H^2 is independent of N. This yields, of course, precisely one positive value for N,

$$N = |H|, \tag{49}$$

and one unique set of values for the λ_k. It is a matter of examining the numerical magnitudes of all the quantities entering the theory to determine whether this value of λ lies in R_1 or R_2. Both cases can occur. An example of this is discussed in the next section.

III. *S*-Wave Scattering of Electrons on Hydrogen

The *s*-wave scattering of electrons on hydrogen is often discussed ([6], [7]) as a scientific problem of importance for its own sake. Its theory and some numerical results are treated here as a specific application of the theory developed in Section II. The radial equation for the *s*-wave of the scattered electron may be written as

$$\left[\frac{d^2}{dr^2} + k^2 - V(r)\right] y(r) - 2Q\left[\int_0^r dr' \frac{P(r)}{r} P(r')\, y(r') + \int_r^\infty dr' P(r) \frac{P(r')}{r'} y(r')\right] + \lambda N P(r) = 0, \tag{50}$$

where $P(r)$ is the radial orbital of the ground state ($1s$) orbital of hydrogen and Q is $+1(-1)$ for scattering in the singlet (triplet) state. Thus in the notation of Section II the equation becomes

$$Ly(r) = h_1 \varphi_{1-}(r) + \lambda_1 N P_1(r), \tag{51}$$

where

$$\begin{aligned} \lambda_1 &= \lambda, & P_1(r) &= P(r), \\ \varphi_{1-}(r) &= P(r), & \varphi_{1+}(r) &= \frac{P(r)}{r}, \\ \psi_{1-}(r) &= 2Q \frac{P(r)}{r}, & \psi_{1+}(r) &= 2QP(r), \end{aligned} \tag{52}$$

and, of course,

$$h_1 = \int_0^\infty dr' 2Q \frac{P(r')}{r'} y(r').$$

Similarly, the reduced equations take the form

$$Ly_{00} = 0, \qquad Ly_{10} = P(r) \qquad \text{and} \qquad Ly_{01} = P(r), \tag{53}$$

yielding, in particular,

$$y_{10}(r) = y_{01}(r). \tag{54}$$

For this case the hyperellipsoid E, the hyperplanes of Eq. (31) and the hyperplane of Eq. (44) degenerate to the points $\lambda = \pm\lambda_1$, $\lambda = \pm\lambda_2$ and $\lambda = 0$ respectively, where

$$\lambda_1^2 = \frac{[1 - h_{110} + h_{100}]^2}{[N_{00}^2 + N_{10}^2 - 2N_{00}N_{10}\cos(\delta_{10} - \delta_{00})]}, \tag{55}$$

and

$$\lambda_2{}^2 = \frac{[h_{100}^2 N_{10}^2 + (1 - h_{110})^2 N_{00}^2 + 2h_{100}(1 - h_{110}) N_{00} N_{10} \cos(\delta_{10} - \delta_{00})]}{N_{00}^2 N_{10}^2 [1 - \cos^2(\delta_{10} - \delta_{00})]}. \quad (56)$$

The region R_1 is the line segment

$$\lambda^2 < \lambda_1{}^2, \quad (57)$$

where

$$b = B\lambda, \quad (58)$$

and

$$B = \frac{[h_{100} N_{10}^2 - (1 - h_{110}) N_{00}^2 + (1 - h_{110} - h_{100}) N_{00} N_{10} \cos(\delta_{10} - \delta_{00})]}{(1 - h_{110} + h_{100})^2} \quad (59)$$

is positive for the singlet and negative for triplet scattering. The region R_2 is given by the line segment

$$-\lambda_2 < \lambda < -\lambda_1$$

for singlet scattering and by the line segment

$$\lambda_2 > \lambda > \lambda_1$$

for triplet scattering. Finally, the value of $N\lambda_0$ corresponding to the orthogonalized solution may be expressed analytically as

$$N\lambda_0 = \frac{[p_{100} h_{110} - p_{110} h_{100} - p_{100}]}{[p_{110} - p_{100}]}. \quad (60)$$

Numerical solutions of Eq. (50) have been obtained for both triplet and singlet scattering by a method which closely parallels the theoretical development of Section II. Solutions to the reduced equations are obtained. Then all relevant parameters are computed and used to render Eq. (51) determinate. Eq. (51) is solved directly and the parameters are recomputed to check for consistency. When possible, the equations are also solved by iteration methods similar to those described in [2]. The results will be discussed below for scattering at 6 ev incident energy.

In triplet scattering it turns out that evaluation of the preceding expressions yields

$$\lambda_0 = 0.03$$

and

$$\lambda_1 = 1.17. \tag{61}$$

Thus the orthogonalized solution lies well within R_1 and Eq. (50) has only one solution when λ is near to λ_0 (i.e., near the orthogonalized solution). Iteration solutions are readily obtained for λ near λ_0, and are quite similar in convergence to the oxygen and nitrogen calculations, where $\lambda = 0$, reported in [2]. The advantage of the non-iterative method is, in this case, that less machine time is required.

The situation is somewhat different for singlet scattering. Evaluation of the preceding expressions yields

$$\lambda_1 = 0.0879, \qquad \lambda_2 = 0.8948, \qquad \lambda_0 = -0.5606 \tag{62}$$

and

$$b = 93.62\,\lambda.$$

Clearly λ_0 lies in R_2 and for λ near λ_0 there will be two solutions, one of which will be near to the desired orthogonalized wave function. However, iterative solutions were obtainable only in the region R_2 and not in R_1, R_3 or R_4 and yielded only one of the two existing solutions in R_2. The iterative solutions were continuous with λ and hence formed one branch of solutions, with the other branch of solutions being unreachable by the iteration techniques employed. When the orthogonalized solution was used as input to the iteration scheme, successive iterations would diverge from this solution and then converge on the second (non-orthogonalized) solution.

The iteration scheme converged very slowly for λ in R_2 but near λ_1 or λ_2, requiring hundreds of iterations in a few cases. Thus, a numerical test of the theoretical values for λ_1 and λ_2 is obtained by recording the largest and smallest (negative) values of λ for which convergence of the iteration procedure was possible. This yields

$$\lambda_1 = 0.088 \qquad \text{and} \qquad \lambda_2 = 0.8944, \tag{63}$$

and clearly agrees with Eq. (62). Further tests were provided by the agreement between numerical computation of and the analytic expressions for N_{ij}, h_i and p_l. These were tested in both the singlet and triplet scattering and yielded at least five figure agreement in all cases.

IV. Conclusions

The phenomena discussed here—non-existence of solutions and double solutions—as well as unique solvability of equations are of general occurrence in linearized Hartree–Fock calculations and each possibility will occur under well

defined circumstances. The same situation would hold true for the full non-linear Hartree–Fock theory if iterative numerical methods were employed in which the nonlinearity were treated as already determined, and the phenomena could be of more general occurrence. These phenomena could explain some of the somewhat puzzling instabilities that have been observed in calculational procedures and could lead to incorrect wave functions being obtained if, for example, solutions were calculated numerically in R_2 on a branch not containing the orthogonalized solution and the Gram–Schmidt process were used to produce an orthogonalized solution.

In particular, the utility of the Marriott [5] calculational procedure, in which the orthogonalized solution is calculated essentially algebraically from certain stable reduced equations, is seen very clearly. In this fashion it is possible to avoid certain instabilities of iterative calculations.

The discussion has, through use of Eq. (4), implicitly excluded potentials which are Coulomb-like at large r. However, changing this asymptotic boundary condition to allow for a logarithmic contribution to the phase should not affect the form of the results of Section II. Thus, this restriction is not essential.

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