

# *B-SPLINES IN VARIATIONAL ATOMIC STRUCTURE CALCULATIONS*

*CHARLOTTE FROESE FISCHER\**

*Department of Electrical Engineering and Computer Science, Vanderbilt University,  
Box 1679 B, Nashville, Tennessee, 37235, USA*

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## **Abstract**

Many of the problems associated with the use of finite differences for the solution of variational Hartree–Fock or Dirac–Hartree–Fock equations are related to the orthogonality requirement and the need for node counting to control the solution of the two-point boundary value problem. By expanding radial functions in a B-spline basis, the differential equations are replaced by non-linear systems of equations. Hartree–Fock orbitals become solutions of generalized eigenvalue problems where orthogonality requirements can be dealt with through projection operators. When

\* E-mail: Charlotte.F.Fischer@Vanderbilt.Edu.

expressed as banded systems of equations, all orbitals may be improved simultaneously using singular value decomposition or the Newton–Raphson method for faster convergence. Computational procedures are described for non-relativistic multiconfiguration Hartree–Fock variational methods and extensions to the calculation of Rydberg series. The effective completeness of spline orbitals can be used to combine variational methods with many-body perturbation theory or first-order configuration interaction. Many options are available for improving atomic structure calculations. Although spline methods are discussed only in connection with non-relativistic theory, they apply equally to Dirac–Hartree–Fock theory.

## 1. Introduction

In Hartree’s central field theory the radial wave function  $P(nl; r)$  for an  $nl$  electron is the solution of the differential equation (in atomic units),

$$\left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} [Z - Y(nl; r)] + \frac{l(l+1)}{2r^2} - \varepsilon_{nl, nl} \right) P(nl; r) = 0, \quad (1)$$

where  $Z$  is the nuclear charge and  $Y(nl; r)$  describes the screening of the nucleus by the other electrons. This differential equation can be solved numerically by finite difference methods in which the radial wave function is represented by a vector of numerical values  $P(nl, r_i)$ ,  $i = 1, \dots, N$ . The boundary conditions,  $P(nl; 0) = 0$  and  $P(nl; r) \rightarrow 0$  as  $r \rightarrow \infty$ , make this a two-point boundary value problem for which a solution exists only for selected values of  $\varepsilon_{nl, nl}$ . Inward and outward integration often are used and  $\varepsilon_{nl, nl}$  adjusted until the two solutions match (Froese Fischer, 1977). Node counting is needed to ensure that a solution has the required number of oscillations. However, when the solution is represented in terms of B-spline basis functions  $B_i(r)$ , namely

$$P(nl; r) = \sum_{i=1}^{n_s} a_i B_i(r), \quad (2)$$

and the expansion coefficients are determined by the Galerkin condition (Fletcher, 1984) for differential equations, the solution of Eq. (1) becomes a solution of the symmetric, generalized matrix-eigenvalue problem

$$(H - \varepsilon S)a = 0. \quad (3)$$

Here  $H = (H_{ij})$  and  $S = (S_{ij})$  are matrices with

$$\begin{aligned} H_{ij} &= \langle B_i(r) | -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} [Z - Y(nl; r)] + \frac{l(l+1)}{2r^2} | B_j(r) \rangle, \\ S_{ij} &= \langle B_i(r) | B_j(r) \rangle, \end{aligned} \quad (4)$$

respectively. This generalized eigenvalue problem with eigenvalues  $\varepsilon_i$ ,  $i = 1, \dots, n_s - 2$  (after boundary conditions have been applied) can be solved using routines from the LAPACK library. Node counting is not necessary. If the eigenvalues are ordered so that  $\varepsilon_i < \varepsilon_{i+1}$ , then the index  $i$  determines the principal quantum number  $n$  to be associated with the solution. Furthermore, in a B-spline basis, the matrices are banded and eigenvalues can be determined to high accuracy, even for the equivalent Dirac equation (Froese Fischer and Parpia, 1993).

As soon as exchange is introduced, extra terms appear in the radial equation which may be written as

$$\left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} [Z - Y(nl; r)] + \frac{l(l+1)}{2r^2} - \varepsilon_{nl, nl} \right) P(nl; r) = \frac{1}{r} X(nl; r), \quad (5)$$

provided no Lagrange multipliers need to be introduced to ensure orthogonality. In differential equation methods, the functions  $Y(nl; r)$  and  $X(nl; r)$  are computed from current estimates and a solution of the differential equation determined by outward and inward integration. Because now the equation is non-homogeneous, solutions exist for all values of  $\varepsilon_{nl, nl}$  and the latter often is adjusted for a normalized solution. Many problems may occur (Griffin et al., 1971). By expanding orbitals in a B-spline basis, the equation for each orbital again has the form

$$(H - \varepsilon S)a = 0, \quad (6)$$

where now the matrix  $H$  is a dense symmetric matrix. Iteration is still needed for a self-consistent solution in which case only one eigenvalue and eigenvector are physically significant. However, in a fixed core calculation for, say the  $2p$  radial function of  $1s^2 2p$ , both the potential and exchange contributions to the  $H$  matrix depend only on  $1s$  and the eigenvectors,  $i = 1, 2 \dots$  represent fixed core solutions for the Rydberg series  $2p, 3p, \dots$

The differential equation methods Hartree (1929) developed and used primarily for ground-state configurations were extended and generalized to excited states (Froese Fischer, 1987) and multiconfiguration approximations (Froese Fischer, 1991a). In some instances, approximations were made to simplify computational difficulties, as in the HFX and HFR methods of the Cowan code (Cowan, 1981). With the use of B-spline expansions, differential equations with their many special conditions are replaced by non-linear systems of equations of eigenvalue type that may be solved accurately and reliably without such assumptions.

An extensive review of the applications of B-splines in atomic and molecular physics has been reported by Bachau et al. (2001). Many methods are orbital basis set methods that use the orbitals defined by the eigenvectors of a generalized matrix-eigenvalue problem such as Eq. (3) with an appropriate Hamiltonian. This

finite set of orbitals forms a complete *orthonormal* basis for piecewise polynomial spline approximations and an “effectively” complete basis in Hilbert space for a given region. Spline orbitals computed by solving the Dirac equation for an electron in a model potential are the basis of relativistic many-body perturbation theory (RMBPT) methods. The first such study was reported by [Johnson and Saperstein \(1986\)](#). Recently, spline orbitals were used in large-scale relativistic configuration-interaction calculations for C III ([Chen et al., 2001](#)) to explore various relativistic and QED effects on some transition probabilities. Expansions in non-orthogonal B-splines have been used directly in the calculation of atomic processes such as photoionization ([Xi and Froese Fischer, 1999b](#)) and Rydberg series ([Brage and Froese Fischer, 1994a](#)) (see [Bachau et al., 2001](#), for many more examples). In the more recent B-spline R-matrix (BSR) method for collision studies, the one-electron channel functions are expanded in B-splines, a formulation that again leads to a generalized eigenvalue problem ([Zatsarinny, 2006](#)). Not fully investigated are B-spline approximations of the Hartree–Fock (HF) and multi-configuration Hartree–Fock (MCHF) methods though some initial investigations were reported in 1992 ([Froese Fischer et al., 1992](#)). Considerable progress has been made since then.

This paper begins with a review of the Hartree–Fock (HF) and multiconfiguration Hartree–Fock (MCHF) theory as well as approximation theory using B-splines, and then outlines the application of B-spline theory to the solution of the HF and MCHF equations. In differential equation theory, equations are written so that the coefficient of the highest derivative is unity. In this review we will not adhere to this practice in order to provide a view better suited for the matrix methods when spline expansions are used. In particular, equations will not be divided by the occupation number of an orbital. This change will affect the definition of the diagonal energy parameter but has the consequence that systems of equations are expressed in terms of symmetric matrices. For the latter a notation is introduced for deriving the equations for variational solutions. Advantages and disadvantages of different computational methods will be discussed. Finally, an extension to the multiconfiguration Hartree–Fock wave function will be presented including methods for Rydberg series, the use of spline orbital methods for capturing the numerous remaining effects to first order, and the use of non-orthogonal tensor products of B-spline basis functions for pair-correlation functions.

## 2. The Hartree–Fock Approximation

In theoretical quantum chemistry, the Hartree–Fock wave function is defined as being a single Slater determinant. In atomic physics, the general definition is a single configuration state function (CSF)  $\Phi(\gamma LS)$  for a configuration  $\gamma$  that is anti-symmetric and an eigenfunction of the total orbital-angular momentum and

spin-angular operators  $\mathbf{L}^2$ ,  $L_z$ ,  $\mathbf{S}^2$  and  $S_z$ . In some cases the two definitions may be equivalent but, in general, a CSF is a linear combination of determinants for the same configuration (see Froese Fischer et al., 1997; Cowan, 1981, for more details).

In both cases, the wave function for an  $N$ -electron system is constructed from one-electron spin-orbitals of the form

$$\phi(nl m_l m_s) = \frac{1}{r} P(nl \dots; r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}, \quad (7)$$

where  $P(nl \dots; r)$  is a real-valued radial function,  $Y_{lm_l}(\theta, \varphi)$  a complex-valued spherical harmonic function, and  $\chi_s$  a spin function. Theories based on determinants derive equations for complex orbitals and may differ depending on how the radial functions depend on quantum numbers  $m_l$  and  $m_s$  (Szabo and Ostlund, 1982). The orbitals themselves are determined by applying the variational principle to the energy,  $E^{\text{HF}} = \langle \Psi(\gamma) | \mathcal{H} | \Psi(\gamma) \rangle$ , subject to orthonormality constraints where  $\Psi(\gamma)$  is the Slater determinant for configuration  $\gamma$  and  $\mathcal{H}$  is the  $N$ -electron Hamiltonian for the system. Equations derived by Roothaan in 1951 (Roothaan, 1951) expressed the energy in terms of one-electron integrals and direct and exchange matrix elements of the Coulomb operator. In contrast, when the HF wave function is a configuration state function, the radial functions  $P(nl; r)$  depend only on  $nl$  quantum numbers, and angular integrations can be performed using Racah algebra producing an energy expression involving only real radial integrals. Examples of expressions can be found in Froese Fischer et al. (1997) and the associated code is available from Froese Fischer (2000).

Let us define the operator,  $\mathcal{I}$ , as

$$\mathcal{I} = -\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2}. \quad (8)$$

Then the contribution from the one-electron part of the Hamiltonian (in coordinate space) for a CSF consisting of subshells,  $a^{q_a}$ , is

$$\langle \gamma LS | \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) | \gamma LS \rangle = \sum_a q_a I(a, a), \quad (9)$$

where  $I(a, a) = \langle a | \mathcal{I} | a \rangle$  and  $a$  denotes the  $nl$  quantum numbers of an orbital. Contributions from the two-electron Coulomb-repulsion operator  $\sum_{i < j} 1/r_{ij}$  lead to Slater integrals  $R^k(a, b; c, d)$ .

The introduction of these integrals presented many computational difficulties in the 1930s (McDougall, 1932), but Hartree soon realized that a feasible solution was to first compute the function

$$Y^k(ac; r) = r \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} P(a; s) P(c; s) ds$$

$$\begin{aligned}
&= \int_0^r \left(\frac{s}{r}\right)^k P(a; s) P(c; s) ds \\
&\quad + \int_r^\infty \left(\frac{r}{s}\right)^{k+1} P(a; s) P(c; s) ds,
\end{aligned} \tag{10}$$

where  $r_< = \min(r, s)$  and  $r_> = \max(r, s)$ . Then the general Slater integral  $R^k(a, b; c, d)$  could be evaluated as

$$R^k(a, b; c, d) = \int_0^\infty P(b; r) P(d; r) \left(\frac{1}{r}\right) Y^k(ac; r) dr. \tag{11}$$

In a direct integral  $cd = ab$  whereas in an exchange integral,  $cd = ba$  and the integrals are denoted as  $F^k(a, b)$  and  $G^k(a, b)$  respectively.

Let us consider some cases that illustrate the nature of the Hartree–Fock problem. For brevity, we will refer to orbitals simply as  $a, b, \dots$  and only give the spectroscopic notation when needed for clarity. We shall also use the notation  $\mathcal{E}$  for the energy expression,  $E$  for the value of the energy in atomic units,  $\varepsilon$  for Lagrange multipliers also in atomic units,  $\mathcal{C}$  for conditions, and  $\mathcal{F}$  for the energy functional,

$$\mathcal{F} = \mathcal{E}(\gamma LS) + \sum_a \sum_b \varepsilon_{ab} \delta(l_a, l_b) \mathcal{C}_{ab}, \tag{12}$$

where  $\delta(l, l')$  is the Dirac delta function and the conditions are

$$\mathcal{C}_{ab} = \begin{cases} (1 - \langle a|a \rangle), & a = b \text{ (for normalization),} \\ -\langle a|b \rangle, & a \neq b \text{ (for orthogonality).} \end{cases} \tag{13}$$

Since  $\mathcal{C}_{ab} = \mathcal{C}_{ba}$ , it follows that  $\varepsilon_{ab} = \varepsilon_{ba}$ .

## 2.1. A CASE WITH NO ORTHOGONALITY CONSTRAINTS

For the  $1s^2 2p^2 P$  CSF, the energy expression is

$$\begin{aligned}
\mathcal{E}(1s^2 2p^2 P) &= 2I(a, a) + I(b, b) + F^0(a, a) + 2F^0(a, b) \\
&\quad - (1/3)G^1(a, b),
\end{aligned} \tag{14}$$

where  $a$  refers to  $1s$ , and  $b$  to  $2p$ . The orbitals are orthogonal through their angular factors, and no additional constraint is needed. The energy expression was derived under the assumption that all orbitals were normalized. For such a constrained variation, Lagrange multipliers  $\varepsilon_{aa}$  and  $\varepsilon_{bb}$  need to be introduced and the variational principle applied to the functional,

$$\mathcal{F}(a, b) = \mathcal{E}(1s^2 2p^2 P) + \varepsilon_{aa}(1 - \langle a|a \rangle) + \varepsilon_{bb}(1 - \langle b|b \rangle). \tag{15}$$

The stationary condition with respect to variations of  $P(a; r)$  and  $P(b; r)$  respectively, after dividing by two for Lagrange multipliers in atomic units, lead to the equations (see [Froese Fischer et al., 1997](#), for more details)

$$\begin{aligned} & \left( 2\mathcal{I} + \frac{2}{r} [Y^0(aa; r) + Y^0(bb; r)] - \varepsilon_{aa} \right) P(a; r) \\ & - \frac{1}{3r} Y^1(ab; r) P(b; r) = 0 \end{aligned} \quad (16)$$

and

$$\left( \mathcal{I} + \frac{2}{r} Y^0(aa; r) - \varepsilon_{bb} \right) P(b; r) - \frac{1}{3r} Y^1(ba; r) P(a; r) = 0. \quad (17)$$

Let us define an integral equation operator,

$$Y^k(b \bullet; r) = r \int_0^\infty \frac{r_{\leq}^k}{r_{>}^{k+1}} P(b; s) \bullet ds \quad (18)$$

so that  $Y^k(b \bullet; r) P(a; r) = Y^k(ba; r)$ . Then these equations become

$$\begin{aligned} & \left( 2\mathcal{I} + \frac{2}{r} [Y^0(aa; r) + Y^0(bb; r)] \right. \\ & \left. - \frac{1}{3r} P(b; r) Y^1(b \bullet; r) - \varepsilon_{aa} \right) P(a; r) = 0 \end{aligned} \quad (19)$$

and, since  $Y^k(ba; r) = Y^k(ab; r)$ ,

$$\left( \mathcal{I} + \frac{2}{r} Y^0(aa; r) - \frac{1}{3r} P(a; r) Y^1(a \bullet; r) - \varepsilon_{b,b} \right) P(b; r) = 0. \quad (20)$$

These can be expressed as the system of equations,

$$\begin{aligned} & (\mathcal{H}^a - \varepsilon_{aa}) P(a; r) = 0, \\ & (\mathcal{H}^b - \varepsilon_{bb}) P(b; r) = 0, \end{aligned} \quad (21)$$

where we have introduced the notion of a Hartree–Fock operator that is different for each radial function. Let  $\mathcal{E}(\gamma; a)$  be the contribution from the subshell  $a^{q_a}$  to  $\mathcal{E}(\gamma LS)$  and  $\mathcal{E}(\gamma; \underline{a})$  the remaining contribution which, in the single configuration Hartree–Fock approximation, is the energy expression for the configuration that remains after  $a^{q_a}$  has been removed. Then,

$$E(\gamma LS) = E(\gamma; a) + E(\gamma; \underline{a}). \quad (22)$$

(Here we distinguish between the expression  $\mathcal{E}(\gamma LS)$  for which orbitals need not be known and the value of the expression  $E(\gamma LS)$ .) The diagonal Lagrange

multiplier is derived from  $\mathcal{E}(\gamma; a)$  and it can readily be confirmed that

$$\varepsilon_{aa} = E(\gamma; a) + \sum_k c_k F^k(a, a) \quad (23)$$

where the sum represents the Coulomb “self-energy” correction

$$\langle a^{q_a} | \sum_{ij} 1/r_{ij} | a^{q_a} \rangle$$

due to the fact that the  $F^k(a, a)$  terms in the energy expression are multiplied by a factor two larger than integrals  $F^k(a, b)$  where  $a \neq b$ . From Eq. (22), Koopmans’ theorem follows, namely

$$\varepsilon_{aa} = E(\gamma LS) - E(\gamma; \underline{a}) + \langle a^{q_a} | \sum_{ij} 1/r_{ij} | a^{q_a} \rangle. \quad (24)$$

For a singly occupied shell the self-energy correction is zero and  $\varepsilon_{aa}$  becomes the binding energy of orbital  $a$ . In the case of a multiply occupied shell,  $\varepsilon_{aa}$  is the binding energy of the shell plus the self-energy correction. Because of this relationship to the binding energy the Lagrange multipliers are also referred to as diagonal and off-diagonal energy parameters. In earlier publications (Froese Fischer et al., 1997; Dylla et al., 1989) energy parameters  $\varepsilon_{ab}$  were related to Lagrange multipliers  $\lambda_{ab}$  in that  $\varepsilon_{ab} = \lambda_{ab}/q_a$ . Consequently the  $\varepsilon$ -matrix was not symmetric, in general. In this present paper, their definition is the same. We will refer to Lagrange multipliers when discussing their role in the derivation of the variational equations, and energy parameters when referring to the numerical values of these quantities. In order for the latter to be in atomic units, it is necessary to divide the stationary condition by a factor of two. This step often has not been taken leading to energy parameters in Rydbergs (Froese Fischer et al., 1997; Cowan, 1981).

Notice that the two equations are not explicitly coupled, only implicitly through the fact that  $\mathcal{H}^a$ , for example, depends on  $P(b; r)$ . The solutions of these equations satisfy Brillouin’s theorem in that the single excitation  $1s \rightarrow ns$  (without a change in coupling) or  $2p \rightarrow np$  lead to configuration states for which  $\langle 1s^2 2p^2 P | \mathcal{H} | 1s ns ({}^1S) 2p^3 P \rangle = 0$  and  $\langle 1s^2 2p^3 P | \mathcal{H} | 1s^2 np^3 P \rangle = 0$ , respectively. In a more complex general case, this is an excitation of a radial function that does not affect the spin-angular factor of the configuration state, only the radial functions. Another way of viewing this result is that the HF approximation has already included these single excitations to unoccupied orbitals to first order.

## 2.2. CASES WITH ORTHOGONALITY CONSTRAINTS

Discussions about the Hartree–Fock equations for the  $1s2s^{1,3}S$  CSFs have a long history. Whereas the triplet state was straight forward the singlet state was



problematic. Trefftz et al. (1957) had shown in 1957 that good results could be obtained for  $1s2s^1S$  using non-orthogonal orbitals. Sharma and Coulson (1962) claimed that a non-orthogonal approach was in fact needed, that orthogonality lead to some serious inconsistencies. Sharma (1967) went on to prove that the requirement of orthogonality was inconsistent with the zero-order orbitals being hydrogenic when  $1/Z$  was treated as a perturbation parameter in the expansion of the orbitals. But by 1972, the idea that the orbitals were each a linear superposition of the two hydrogenic orbitals was investigated by Rebelo and Sharma (1967) and the existence of *two* solutions was reported. In the meantime, it was also shown that results improved by requiring the excited state to be orthogonal to the ground state (Froese, 1967). These papers, along with others, were very specific to  $1s2s^1,^3S$ . Here we will present a discussion that can be generalized to other cases.

The  $1s2s^3S$  and  $^1S$  cases differ in that the former is the lowest  $nsn's^3S$  CSF whereas the latter is the second  $nsn's^1S$  CSF so that its energy is not a minimum but rather a stationary point. Also, the wave function for the former is a single Slater determinant whereas the latter is not. The energy expressions are

$$\mathcal{E}(1s2s^1,^3S) = I(a, a) + I(b, b) + F^0(a, b) \pm G^0(a, b), \quad (25)$$

and the radial parts of the configuration state functions are

$$\frac{1}{\sqrt{2}}[P(a; r_1)P(b; r_2) \pm P(b; r_1)P(a; r_2)], \quad (26)$$

where the  $+$  sign applies to the  $^1S$  state, and the  $-$  to the  $^3S$ . These expressions are based on the assumption that radial functions are orthonormal, and so the energy functional now becomes

$$\begin{aligned} \mathcal{F}(a, b) = & \mathcal{E}(1s2s^3,^1S) + \varepsilon_{aa}(1 - \langle a|a \rangle) \\ & + \varepsilon_{bb}(1 - \langle b|b \rangle) - 2\varepsilon_{ab}\langle a|b \rangle. \end{aligned} \quad (27)$$

The stationary condition with respect to variations of  $P(a; r)$  and  $P(b; r)$  leads to the equations:

$$\begin{aligned} & \left( \mathcal{I} + \frac{1}{r} [Y^0(bb; r) \pm P(b; r)Y^1(b \bullet; r)] - \varepsilon_{aa} \right) P(a; r) \\ & - \varepsilon_{ab} P(b; r) = 0, \end{aligned} \quad (28)$$

and a similar equation with  $a$  and  $b$  interchanged. These are coupled equations of the form

$$\left( \begin{bmatrix} \mathcal{H}^a & 0 \\ 0 & \mathcal{H}^b \end{bmatrix} - \begin{bmatrix} \varepsilon_{aa} & \varepsilon_{ab} \\ \varepsilon_{ba} & \varepsilon_{bb} \end{bmatrix} \right) \begin{bmatrix} P(a; r) \\ P(b; r) \end{bmatrix} = 0, \quad (29)$$

where the Lagrange multipliers form a symmetric  $\varepsilon$ -matrix. The solution of these equations is greatly simplified when the  $\varepsilon$ -matrix is diagonal.

From the orthonormality of the radial functions, it readily can be shown that the elements of  $\varepsilon$  are matrix elements of the one electron Hartree–Fock Hamiltonians:

$$\begin{aligned}\varepsilon_{aa} &= \langle a | \mathcal{H}^a | a \rangle, & \varepsilon_{ab} &= \langle b | \mathcal{H}^a | a \rangle, \\ \varepsilon_{bb} &= \langle b | \mathcal{H}^b | b \rangle, & \varepsilon_{ba} &= \langle a | \mathcal{H}^b | b \rangle.\end{aligned}\quad (30)$$

The condition that  $\varepsilon_{ab} = \varepsilon_{ba}$  then becomes the condition,

$$\langle b | \mathcal{H}^a | a \rangle = \langle a | \mathcal{H}^b | b \rangle, \quad (31)$$

and affects the  $^3S$  and  $^1S$  states quite differently. When several radial functions with the same angular symmetry are present, the solutions of the HF equations not only are stationary with respect to single excitations to unoccupied radial functions, they also are stationary with respect to orthogonal transformations.

Let us rewrite Eq. (29) in matrix vector form as

$$(\mathcal{H} - \varepsilon)\mathbf{P} = 0, \quad (32)$$

where  $\mathcal{H}$  and  $\varepsilon$  are  $2 \times 2$  matrices and  $\mathbf{P}$  is the column vector  $[P(a; r), P(b; r)]^t$ . Let  $\mathbf{O}$  be an orthogonal matrix. Multiplying Eq. (32) on the left by  $\mathbf{O}^t$  and using the property that  $\mathbf{O}\mathbf{O}^t = \mathbf{I}$  (the identity matrix), we get

$$(\mathbf{O}^t \mathcal{H} \mathbf{O} - \mathbf{O}^t \varepsilon \mathbf{O}) \mathbf{O}^t \mathbf{P} = 0 \quad (33)$$

or, in terms of the transformed quantities,

$$(\mathcal{H}^* - \varepsilon^*) \mathbf{P}^* = 0, \quad (34)$$

where  $\mathbf{P}^* = \mathbf{O}^t \mathbf{P}$  are the transformed radial functions and, equivalently, since  $\mathbf{O}^t = \mathbf{O}^{-1}$ ,  $\mathbf{P} = \mathbf{O} \mathbf{P}^*$ .

Orthogonal transformations represent the rotation of orbitals in orbital space that in 2-dimensional space can be defined in terms of a single parameter  $\eta \in [-1, 1]$ . Larger values of  $\eta$  correspond to an interchange of the orbitals. Let

$$\mathbf{O} = \begin{bmatrix} 1 & -\eta \\ \eta & 1 \end{bmatrix} / \sqrt{1 + \eta^2}, \quad (35)$$

where  $1/\sqrt{1 + \eta^2} = \cos(\theta)$  and  $\theta$  represents the angle of rotation  $\theta \in [-45, 45]$  degrees. Then the transformation

$$\begin{bmatrix} P^*(a; r) \\ P^*(b; r) \end{bmatrix} = \begin{bmatrix} 1 & \eta \\ -\eta & 1 \end{bmatrix} \begin{bmatrix} P(a; r) \\ P(b; r) \end{bmatrix} / \sqrt{1 + \eta^2} \quad (36)$$

allows us to study the effect of a rotation as a function of  $\eta$ .

### 2.2.1. The $1s2s^3S$ Case

In this case the wave function is a single determinant which is invariant under orthogonal transformations (Szabo and Ostlund, 1982) and consequently the total energy will not change. Using Eq. (36), it is easy to confirm the invariance of the radial factor of the wave function, namely

$$\begin{aligned} P^*(a; r_1)P^*(b; r_2) - P^*(b; r_1)P^*(a; r_2) \\ = P(a; r_1)P(b; r_2) - P(b; r_1)P(a; r_2), \end{aligned} \quad (37)$$

from which it follows that the energy expression

$$\mathcal{E}(1s^*2s^*{}^3S) = \mathcal{E}(1s2s^3S) \quad (38)$$

and the operator  $\mathcal{H}^* = \mathcal{H}$ .<sup>1,2</sup> Thus, for a given energy, the radial functions are not unique.

Transformations do not leave the scalar  $\varepsilon$ -matrix of Eq. (33) invariant. For all orthonormal orbitals ( $a, b$ ), it can be shown by direct substitution that  $\langle b|\mathcal{H}^a|a\rangle = \langle a|\mathcal{H}^b|b\rangle$ . Consequently the  $\varepsilon$ -matrix is symmetric for all transformations. The trace of this matrix (sum of diagonal elements) is invariant under orthogonal transformations and for the particular transformation that diagonalizes the matrix, the diagonal elements assume their extreme values and  $\varepsilon_{ab} = \varepsilon_{ba} = 0$ . This solution ensures that the  $1s$  is the most bound and  $2s$  the least bound solution. This choice was suggested by Koopmans (1933) and is part of his theorem that relates diagonal energy parameters to binding energies. What characterizes the  ${}^3S$  case is the fact that the wave function and energy are unchanged by an orthogonal transformation of the radial functions of a given symmetry and that the  $\varepsilon$ -matrix is symmetric for all orthonormal orbitals.

### 2.2.2. The $1s2s^1S$ Case

Now the rotation of the orbital basis changes the energy expression as well as the wave function. In the present case, it can be shown by direct substitution into

<sup>1</sup> The  $\mathcal{H}$ -matrix also appears to be transformed but it can be shown that  $\mathbf{O}^t\mathcal{H}(P)\mathbf{O} = \mathcal{H}(P^*) = \mathcal{H}(P)$ . This is most readily shown by introducing the Fock operator used in determinantal Hartree-Fock theory of quantum chemistry (Szabo and Ostlund, 1982), namely

$$f = \mathcal{L} + \frac{2}{r} [Y^0(aa; r) + Y^0(bb; r) - P(a; r)Y^0(a\bullet; r) - P(b; r)Y^0(b\bullet; r)]. \quad (39)$$

In this form, one direct and one exchange contribution cancel in the application of the operator to an operand depending on whether the operand is  $a$  or  $b$ . Notice that the operator itself depends on both  $a$  and  $b$  but a simple substitution shows that  $f(\mathbf{P}^*) = f(\mathbf{P})$  and finally, also that  $\mathcal{H}^* = \mathcal{H}$ .

<sup>2</sup> To better represent the diagonal energy parameters as energies in atomic units, the  $\mathcal{L} = -(1/2)\mathcal{I}$  operator has been abandoned and variational equations divided by a factor of two from those appearing in Froese Fischer et al. (1997).

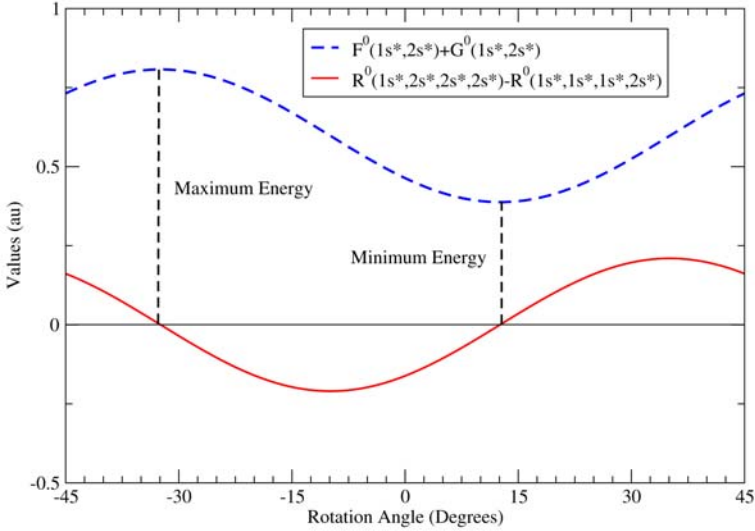


FIG. 1. The values of  $F^0(1s^*, 2s^*) + G^0(1s^*, 2s^*)$  and the condition  $R^0(1s^*, 2s^*; 2s^*, 2s^*) - R^0(1s^*, 1s^*; 1s^*, 2s^*)$  for rotated orbitals  $\{1s^*, 2s^*\}$  as a function of the degree of rotation of hydrogenic orbitals  $\{1s, 2s\}$  for  $Z = 2$ .

Eq. (26) that, in terms of CSFs,

$$|1s^* 2s^{*1} S\rangle = c_1 |1s 2s^1 S\rangle + c_2 (|2s^2^1 S\rangle - |1s^2^1 S\rangle) / \sqrt{2}, \quad (40)$$

where  $c_1 = (1 - \eta^2)/(1 + \eta^2)$  and  $c_2 = 2\eta/(1 + \eta^2)$ . Stationary solutions can be determined by diagonalizing the  $2 \times 2$  interaction matrix with the result that there will be *two* eigenstates, one where the rotation lowers the energy and another where the energy is raised.

The requirement that the  $\varepsilon$ -matrix be symmetric reduces to the condition

$$R^0(a, b; b, b) - R^0(a, a; a, b) = 0. \quad (41)$$

Figure 1 shows how  $F^0(a^*, b^*) + G^0(a^*, b^*)$  and  $R^0(a^*, b^*; b^*, b^*) - R^0(a^*, a^*; a^*, b^*)$  vary as a function of the degree of rotation as  $\{1s, 2s\}$  hydrogenic orbitals for helium ( $Z = 2$ ) are rotated. Notice that there are exactly two stationary values of the former and that the orbitals associated with these stationary points satisfy the required condition. The stationary condition of the former is related directly to a stationary point of the total energy since  $I(a, a) + I(b, b)$  is invariant under these rotations.

It is important to note that, starting with a CSF, the rotation of the radial functions (which does not affect the spin-angular factor) produced a “perturbation” as shown in Eq. (40) that is a linear combination of two CSFs that may be thought

of as a “pseudo-state” (not an approximation to an observed state). A Hartree–Fock solution requires that the energy be stationary with respect to the rotation of orbitals, or equivalently, that the effect of this interaction already be included in the solution, at least to first order. It can readily be verified that in  $Z$ -dependent perturbation theory, this pseudo-state is degenerate with the  $1s2s^1S$  CSF, and that the zero-order radial functions should then be the rotated hydrogenic orbitals for the smallest rotation.

A numerical multiconfiguration Hartree–Fock (MCHF) program (Froese Fischer, 1986) treats the energy  $E$  as a function of  $\eta$ , namely

$$E(\eta) = E(0) + \eta \Delta E + \eta^2 \Delta^2 E + \dots \quad (42)$$

Then the stationary condition, neglecting higher order terms, becomes

$$\Delta E + 2\eta \Delta^2 E = 0, \quad (43)$$

from which it follows that  $\eta = -\Delta E/(2\Delta^2 E)$  (Froese Fischer, 1986). This process selects the smaller rotation that satisfies the stationary condition.

From expressions for  $I(a, a)$  and Slater integrals of rotated orbitals in terms of the original orbitals, rules can be derived correct to order  $O(\eta^2)$  such as

$$\begin{aligned} I(a^*, a^*) &= I(a, a) + 2\eta I(a, b) + \eta^2 [I(b, b) - I(a, a)] \\ &\quad + \text{higher order terms,} \\ I(b^*, b^*) &= I(b, b) - 2\eta I(a, b) + \eta^2 [I(a, a) - I(b, b)] \\ &\quad + \text{higher order terms.} \end{aligned} \quad (44)$$

Thus  $q_a I(a, a) + q_b I(b, b)$  is invariant under rotation for equally occupied, orthogonal subshells ( $q_a = q_b$ ), but not when the subshells are unequally occupied as in  $2p^2 3p$ .

A direct Slater integral  $F^k(a, b)$  has the same transformation properties as  $(aa)_1(bb)_2$  where the subscripts indicate the radial coordinates and the symmetry rules are those of Slater integrals: symmetry with regard to interchange of orbitals with a given coordinate, or the interchange of the coordinates themselves. Then

$$(a^*a^*)_1(b^*b^*)_2 = [(a + \eta b)_1^2(b - \eta a)_2^2] / (1 + \eta^2)^2 \quad (45)$$

$$= [(aa + 2\eta ab + \eta^2 bb)_1(bb - 2\eta ab + \eta^2 aa)_2] / (1 + \eta^2)^2. \quad (46)$$

Collecting terms by order in  $\eta$  and converting to the notation of Slater integrals we get

$$F^0(a^*, b^*) = F^0(a, b) + 2\eta [R^0(a, b; b, b) - R^0(a, a; a, b)] \quad (47)$$

$$+ \eta^2 [F^0(a, a) + F^0(b, b) - 4G^0(a, b) - 2F^0(a, b)] + \dots \quad (48)$$

The Slater exchange integrals have the same transformational properties as  $(a^*b^*)_1(a^*b^*)_2$  and, expanding in powers of  $\eta$ , the first and second order terms

are exactly the same as those for the direct integral. Thus

$$\mathcal{E}(a^*b^*{}^1S) = \mathcal{E}(ab^1S) + 4\eta[R^0(a, b; b, b) - R^0(a, a; a, b)] \quad (49)$$

$$+ 2\eta^2[F^0(a, a) + F^0(b, b) - 4G^0(a, b) - 2F^0(a, b)] + \dots \quad (50)$$

and this equation defines the rotation parameter needed for a stationary solution with respect to the current orbital pair  $(a, b)$ . When this parameter is zero, the  $\varepsilon$ -matrix will satisfy the symmetry requirement of Eq. (31) and the off-diagonal energy parameter can be eliminated, becoming a projection operator for the orbital Hartree–Fock operator. (We shall prove this for spline-matrix methods.) The solution then is the solution of a pair of eigenvalue problems where the operators are integro–differential operators.

An important consequence of orbital rotations for finite difference methods is that rotations introduce extra nodes into the radial functions, making node-counting an art. See [Froese Fischer \(1986\)](#) for a description of numerical algorithms for solving the HF and MCHF radial equations.

### 2.2.3. The General Case

When  $m$  orbitals of the same angular symmetry are present in the Hartree–Fock configuration state,  $m \times m$  orthogonal transformations need to be considered. [Vilkas et al. \(1998\)](#) have reported a quadratically convergent method for finding a unitary transformation for variational solutions of the Dirac–Coulomb Hamiltonian, that transforms an initial set of orthonormal one-electron orbitals to stationary solutions. A similar procedure could be used for finding the needed orthogonal transformations. However in the MCHF program ([Froese Fischer, 1986](#)) it was found sufficient to consider each constrained orbital pair separately, and express the  $m$ -dimensional orthogonal transformation as  $m(m - 1)/2$  pairs of rotations.

It should be mentioned that rotation analysis is computationally intensive. In our  $1s2s^1S$  example, the first-order variation of  $\eta$  required the evaluation of two Slater integrals, whereas the second order variation required four additional integrals. For the multiple shell case, the energy expressions are not as simple. What is essential is that the stationary condition be satisfied, at least approximately at each iteration, and that the process be convergent. Thus there are trade-offs between iterative procedures with a minimum number of self-consistent field (SCF) iterations and extensive computation per iteration and simpler calculations requiring more iterations. In the final analysis, an accurate, stable and robust process is of prime importance. In the early 1950s, Hartree spent a lot of effort on trying to get good initial estimates ([Hartree, 1955](#)). A decade or two later, computers were sufficiently powerful that simpler, general procedures were sufficient and preferred.

### 3. Multiconfiguration Hartree–Fock Approximation

In a multiconfiguration Hartree–Fock approximation, the wave function  $\Psi(\gamma LS)$  for a state labelled  $\gamma LS$  is a linear combination of orthonormal configuration state functions (CSF)  $\Phi(\gamma LS)$  so that

$$\Psi(\gamma LS) = \sum_{i=1}^M c_i \Phi(\gamma_i LS), \quad \text{where } \sum_{i=1}^M c_i^2 = 1, \quad (51)$$

and the energy is required to be stationary both with respect to the variation of the radial functions and the expansion coefficients. When all the radial functions are known, this becomes a configuration-interaction (CI) problem. where the expansion coefficients are an eigenvector of an interaction matrix  $H = (H_{ij})$  where  $H_{ij} = \langle \gamma_i LS | \mathcal{H} | \gamma_j LS \rangle$  and  $\mathcal{H}$  is an  $N$ -electron Hamiltonian.

Many of the difficulties caused by the orthogonality condition in the HF approximation may not be present in the multiconfiguration approximation. Orthogonality conditions are avoided in the more complex non-orthogonal theory but wave functions expressed in terms of non-orthogonal orbitals can be shown to be equivalent to an orthogonal MCHF theory. Consider the  $1s2s\ ^1S$  case. In a non-orthogonal  $1s2s'\ ^1S$  approximation the  $2s'$  orbital need not be orthogonal to  $1s$ , so no off-diagonal Lagrange multiplier is needed for the derivation of the orbital equations though the expression for the energy now includes overlap integrals. Solutions can readily be obtained (Froese Fischer, 1966). However, projecting out the  $1s$  orbital from a non-orthogonal  $2s'$ , so that  $2s' = a_1 2s + a_2 1s$ , and  $\langle 1s | 2s \rangle = 0$ , we get a multiconfiguration expansion,

$$|1s2s'\ ^1S\rangle = a_1 |1s2s\ ^1S\rangle + \sqrt{2}a_2 |1s^2\ ^1S\rangle. \quad (52)$$

In general, by expressing a non-orthogonal set of orbitals in terms of an orthonormal set, expansions in terms of the former can be shown to be equivalent to larger multiconfiguration expansions in terms of the latter. Thus the MCHF calculation for the second eigenstate of

$$\Psi(1s2s\ ^1S) = c_1 |1s^2\ ^1S\rangle + c_2 |1s2s\ ^1S\rangle \quad (53)$$

is computationally simpler than the HF calculation for  $1s2s\ ^1S$ . Furthermore, the energy is now an upperbound to the exact energy. Though non-orthogonal computations are robust, the multiconfiguration calculations generally do not present a problem as long as node-counting can be avoided.

Many different models may be used for generating an expansion. An important concept is that of an active space method, where all configuration states that can be generated from a given set of orbitals are included. In such cases, rotations again will leave the wave function invariant, giving the calculation some degrees of freedom. They could be used to set off-diagonal energy parameters to zero but

now there also is the possibility of setting certain coefficients in the expansion to zero or, equivalently, removing a CSF and reducing the size of the problem.

Consider an expansion for the  $1s^2$  ground state over the set of 55 CSFs  $|nsm s^1 S\rangle$ , for orbitals  $ns, ms \in \{1s, \dots, 10s\}$ . There are 45 orthogonality conditions and so 45 coefficients can be set to zero, leading to the natural orbital expansion,

$$\Psi(1s^2 {}^1S) = \sum_{n=1}^{10} c_n \Phi(ns^2 {}^1S), \quad (54)$$

first proposed by Löwdin (1955) where all CSFs differ by two electrons. In the case of  $1s2s {}^1S$ , the expansion is similar, but with  $2s^2$  replaced by  $1s2s$ . Such optimizations are very state selective (Froese Fischer, 1977; Froese Fischer et al., 1997).

In the Hartree–Fock approximation, the advantage of a variational method lay in the fact that Brillouin’s theorem was satisfied for perturbations in the form of an excitation of an occupied orbital to an unoccupied orbital and sometimes also for rotations. Often, as in  $1s2s {}^1S$ , the perturbation produced a pseudo-state that is a constrained linear combination of CSFs (Froese Fischer, 1973). To get the correct combination of each CSF, they must be included explicitly in the expansion. Furthermore, in MCHF a given occupied orbital may appear in many CSFs, so any radial perturbation of an occupied orbital to a virtual orbital will also be in terms of combinations of CSFs. So the advantage of Brillouin’s theorem is reduced and the CSFs included in the expansion become a more important factor in the accuracy of a calculation.

In the discussion so far, it has always been assumed that optimization is for a single HF or MCHF eigenstate, but an energy expression can also be a weighted linear combination of energy expressions for different LS terms and/or different eigenstates for a given LS term. Such procedures are referred to as “simultaneous optimization” in MCHF (Tachiev and Froese Fischer, 1999), “extended optimal level” in the general relativistic atomic structure package (GRASP) (Parpia et al., 1996) or “state-averaged” in multi-reference Möller–Plesset (MR-MP) methods (Vilkas and Ishikawa, 2004b). In the calculation of energy levels associated with a spectrum (where energy differences are more important than the total energies themselves) independently optimized calculations introduce an imbalance in correlation and prevent an accurate prediction of level separation, an imbalance that would disappear only for “exact” calculations (Vilkas and Ishikawa, 2004b).

Variational methods are adept at determining radial functions for the larger components of a wave function, those that contribute significantly to the energy. Such wave functions may be considered the zero-order approximation and the CSFs in this set are referred to as the “multi-reference set”. This set needs to account for near-degeneracy effects and strong interactions within the complex of



CSFs with the same principal quantum numbers. Additional CSFs (and orbitals) may then be introduced to represent the first-order approximation through single- (S) and double- (D) excitations from the reference set. Since the Coulomb operator is a 2-electron operator, this set will include all CSFs obtained through SD excitations that interact with one or more members of the multi-reference set and defines the contributions to the first-order correction to the wave function for the orbital set. Normally these orbitals too are determined variationally, but the effective completeness of spline orbitals may be used to combine variational methods with many-body perturbation theory as done by [Vilkas et al. \(1998\)](#) using an analytic basis.

#### 4. B-Spline Theory

Let us now consider a method in which continuous functions are approximated locally by polynomials to arbitrary accuracy.

Consider an interval  $[a, b]$ , partitioned into subintervals  $[t_i, t_{i+1}]$  defined by the knot sequence,  $t_i$ ,  $i = 1, \dots$ , also called “break-points”. A B-spline, say  $B_i(r)$ , of order  $k_s$  is a positive function over  $k_s$  adjacent intervals beginning at  $t_i$ . In the first interval it increases from zero as  $(r - t_i)^{k_s-1}$  as  $r$  increases and in the last, it decreases to zero as  $(t_{i+k_s} - r)^{k_s-1}$ . In each intervening subinterval the B-spline is a polynomial of degree  $k_s - 1$ , and in going from one subinterval to the next the B-spline function and all derivatives up to order  $k_s - 2$  are continuous. The only discontinuity is in the derivative of order  $k_s - 1$ . With sufficiently large values of  $k_s$ , a spline has a high degree of smoothness. For each subinterval, there are  $k_s$  non-zero B-splines defined in the interval and define the basis for any polynomial approximation in the interval. The leftmost spline requires  $k_s - 1$  extra knots at points  $t \leq a$  and similarly the rightmost spline requires  $k_s - 1$  extra knots at points  $t \geq b$ . Thus with  $n_v$  intervals, there are  $n_t = n_v + 2k_s - 1$  knots and  $n_s = n_v + k_s - 1$  basis functions,  $B_i(r)$ ,  $i = 1, \dots, n_s$ . When the additional knots are selected to be  $t = a$  or  $t = b$ , the end-points become knots of multiplicity  $k_s$  and the B-spline basis acquires some useful properties. At  $t = a$ , only  $B_1(a)$ ,  $B'_2(a)$ ,  $B''_3(a)$ ,  $\dots$  are non-zero for derivatives up to  $k_s - 1$ . Similarly, at  $t = b$ , only  $B_{n_s}(b)$ ,  $B'_{n_s-1}(b)$ ,  $B''_{n_s-2}(b)$ ,  $\dots$  are non-zero. Thus applying a zero boundary condition (either to the function or a derivative) can be interpreted as setting the coefficient of a basis function to zero.

Given the set of knots, the B-splines and their derivatives can be generated from a recurrence relation. Let  $B_{i,k_s}(r)$  be the spline of order  $k_s$  usually denoted simply as  $B_i(r)$ . Then

$$B_{i,1} = \begin{cases} 1, & t_i \leq r \leq t_{i+1}, \\ 0, & \text{otherwise} \end{cases} \quad (55)$$

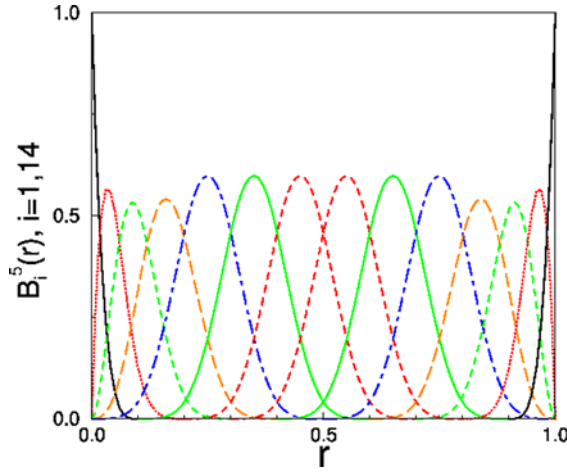


FIG. 2. B-splines of order 5 on the interval  $[0, 1]$  with 10 subintervals of equal length and knots of multiplicity 5 at each end point (from Qiu and Froese Fischer, 1999).

with

$$B_{i,k_s}(r) = \frac{r - t_i}{t_{i+k_s-1} - t_i} B_{i,k_s-1}(r) + \frac{t_{i+k_s} - r}{t_{i+k_s} - t_{i+1}} B_{i+1,k_s-1}(r) \quad (56)$$

and

$$B'_{i,k_s}(r) = \frac{k_s - 1}{t_{i+k_s-1} - t_i} B_{i,k_s-1}(r) - \frac{k_s - 1}{t_{i+k_s} - t_{i+1}} B_{i+1,k_s-1}(r) \quad (57)$$

The splines of a given order are normalized so that  $\sum_i B_i(r) = 1$ . Algorithms for generating splines and their derivatives were developed by de Boor (1985) and published in his book. Figure 2 shows some splines of order 5 on the interval  $[0, 1]$  with 10 subintervals of equal length. Note the boundary effect on the shape of the B-splines.

A function that can be expanded exactly in a the B-spline basis, say  $F(r) = \sum_j a_j B_j(r)$ , is a spline function of order  $k_s$ . It is a polynomial of degree  $k_s - 1$  in each subinterval with continuous derivatives up to order  $k_s - 2$  inside  $[a, b]$ .

Spline functions may accurately approximate continuous functions such as radial functions. Let  $P(r)$  be an arbitrary radial function for which  $P(0) = 0$  and  $P(R) = 0$ , where  $R$  is sufficiently large for the boundary condition to apply to the accuracy required. Given a knot sequence and the order of the spline, say  $k_s$ , the “best” spline is the one for which the error is a minimum with respect to some

norm of the error,  $\|P(r) - F(r)\|$ . Let us define

$$\|P(r) - F(r)\|^2 = \int_0^R (P(r) - F(r))^2 dr. \quad (58)$$

Then the “best” spline in the least squares norm is one for which (in the Dirac notation)

$$\langle B_i(r) | P(r) - F(r) \rangle = 0, \quad i = 1, \dots, n_s. \quad (59)$$

Expressed another way, the error  $P(r) - F(r)$  is orthogonal to each of the spline basis functions. This requirement leads to a system of equations

$$\sum_j a_j \langle B_i(r) | B_j(r) \rangle = \langle B_i(r) | P(r) \rangle, \quad i = 1, \dots, n_s \quad (60)$$

or, in matrix–vector form, as

$$Sa = b, \quad (61)$$

where the matrix  $S = (S_{ij})$ ,  $S_{ij} = \langle B_i(r) | B_j(r) \rangle$  is a symmetric, positive-definite, banded overlap matrix for the B-spline basis of bandwidth  $2k_s - 1$ ,  $b$  is the overlap of the radial function with each basis function, and  $a$  is the vector of expansion coefficients.

#### 4.1. SPLINE METHODS FOR THE SOLUTION OF DIFFERENTIAL EQUATIONS

B-spline methods can also be used to solve differential equations. Consider the central field equation (1) and assume  $P(nl; r) = \sum_j a_j B_j(r)$ . The boundary conditions require  $a_1 = 0$  and we also assume  $a_{n_s} = 0$ . Substituting the expansion into Eq. (1) we get

$$\left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} [Z - Y(nl; r)] + \frac{l(l+1)}{2r^2} - \varepsilon_{nl, nl} \right) \sum_j a_j B_j(r) = \text{res}(r), \quad (62)$$

where  $\text{res}(r)$  is the residual or amount by which the equation is not satisfied. In the Galerkin method (Fletcher, 1984), the solution minimizes  $\|\text{res}(r)\|$  and satisfies the equations

$$\langle B_i(r) | \text{res}(r) \rangle = 0, \quad i = 2, \dots, n_s - 1 \quad (63)$$

which can be written in the matrix–vector form of Eq. (1). Both matrices are symmetric, banded matrices of bandwidth  $2k_s - 1$ .

#### 4.2. SPLINE GRID FOR RADIAL FUNCTIONS

From the fact that in each interval the linear combination of  $k_s$  B-splines non-zero over this interval defines a local polynomial approximation to the radial function, it is apparent from the polynomial behavior of radial functions near the origin that small intervals are not required in spite of the singularity at the origin, and that an exponential grid can be used for large  $r$ . In atomic structure applications, it is convenient to define the grid in terms of the variable  $t = Zr$  (the hydrogenic case) and then transform to the current value of  $Z$ . Let  $h = 1/2^m$ . This is not strictly necessary, but it ensures that the arithmetic is exact in binary arithmetic. Then

$$\begin{aligned}
 t_i &= 0 \quad \text{for } i = 1, \dots, k_s, \\
 t_i &= t_{i-1} + h \quad \text{for } i = k_s + 1, \dots, k_s + m, \\
 t_i &= t_{i-1}(1 + h) \quad \text{for } i = k_s + m + 1, \dots, n_v + k_s, \\
 t_i &= t_{i-1} \quad \text{for } i = n_v + k_s + 1, \dots, n_t, \\
 t_i &= t_i / Z \quad \text{for } i = 1, n_t.
 \end{aligned} \tag{64}$$

Thus the grid is linear near the origin and linear in  $\log(r)$  thereafter. The knots of multiplicity  $k_s$  at  $t = 0$  are followed by  $m$  intervals of length  $h$ . The rightmost knot of this last interval is at  $t = 1$  which is where the  $1s$  radial function for hydrogen achieves its maximum value and begins an exponential decay. The grid reflects this behavior with intervals that increase in length for a total of  $n_v$  intervals. The rightmost knot is then repeated to have multiplicity  $k_s$  and a scaling for the nuclear charge is taken into account. This is the grid used in the examples reported here. It is not an optimal grid but, as we will see later, it has some computational advantages. We will refer to it as a logarithmic grid in order to differentiate it from a commonly used exponential grid (see [Bachau et al., 2001](#), for a summary of commonly used grids).

For a given  $Z$ , the grid has a parameter  $h$  that can be made arbitrarily small. In the absence of round-off, numerical experiments show that

$$\max_{r \in (0, R)} |P(r) - F(r)| = \mathcal{O}(h^{k_s}) \tag{65}$$

for  $1s$  and  $2s$  radial functions. Thus larger intervals (smaller number of basis functions) can be used with higher-order spline approximations.

#### 4.3. INTEGRATION METHODS

The evaluation of B-spline matrix elements of differential operators or functions in the least squares norm of Eq. (58), requires integration. Since B-splines are polynomials these integrations can be performed symbolically. However numerical integration is faster and can be almost as accurate.

Instead of representing a polynomial of order  $k_s - 1$  by  $k_s$  coefficients, we represent the polynomial by  $k_s$  values at the Gaussian points for Gauss–Legendre integration formula,

$$\int_0^1 f(x) dx = \sum_{i=1}^{k_s} g_w(x_i) f(x_i), \quad (66)$$

where  $g_w(x_i)$  are the Gaussian weights at the Gaussian points  $x_i$ . This formula is exact for integrands  $f(x)$  that are polynomials of degree  $2k_s - 1$  and, when applied to integration over an interval of length  $h$ , the error is  $\mathcal{O}(f^{2k_s}(x)h^{2k_s+1})$ , where  $x$  is some point in the interval. Thus the overlap matrix, for example, is computed exactly, except for round-off and without any cancellation. The matrix elements of  $1/r$  and  $1/r^2$  are evaluated exactly in the first interval because of the boundary conditions, but integration in the second interval is no longer exact. The polynomial form of the product of the B-splines will now have a constant, say  $c$ . Because the derivatives of  $f(r) = 1/r$  increase rapidly with order, this region may be the limiting factor for accuracy. Solutions to the Dirac equation are not polynomial near the origin. Errors can only be controlled through the use of small subintervals (Froese Fischer and Parpia, 1993) and possibly lower-order splines that reduce the size of the derivative in the expression for the error.

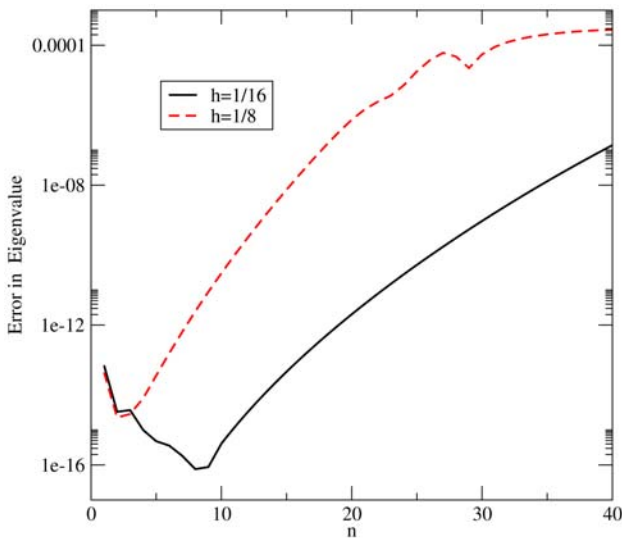


FIG. 3. The error in the eigenvalues as a function of  $n$  for two spline calculations for hydrogen with  $l = 0$  and  $k_s = 8$ . (i) dashed curve:  $h = 1/8$ ,  $R = 1000a_0$ ; (ii) solid curve:  $h = 1/16$ ,  $R = 10,000a_0$ .

Figure 3 shows the accuracy to which the eigenvalues of the radial equation for hydrogen can be computed as a function of  $n$  for  $s$ -orbital calculations with  $k_s = 8$ . Two sets of results are presented, one for  $h = 1/8$ ,  $R = 1000a_0$ , and another for  $h = 1/16$  and  $R = 10,000a_0$ . Some limitations in accuracy are noticed for  $n = 1-3$ , but for higher  $n$  the improvement in accuracy is better by 4 or more orders of magnitude primarily due to the much larger maximum radius. The size of the spline basis was  $n_s = 75$  and 175, respectively. Thus, for sufficiently large  $R$ , solutions can be obtained for highly excited states. In the smaller calculation with the dashed curve, the eigenvalues started to represent continuum states at  $n = 27$  where the irregularity in the curve appears.

#### 4.4. SLATER INTEGRALS

The computational process Hartree suggested for determining Slater integrals involved a two-step process: first the  $Y^k$  functions of Eq. (10) were determined and then the Slater integral through direct integration. With splines, it is possible to compute  $Y^k$  functions at all the Gaussian points from the integral definition, but it is not straight-forward. On the other hand, with the Galerkin method, they can readily be determined from the differential equation,

$$\frac{d^2}{dr^2}Y^k(r) = \frac{k(k+1)}{r^2}Y^k(r) - \frac{2k+1}{r}P_{nl}(r)P_{n'l'}(r), \quad (67)$$

and the boundary conditions,

$$\begin{aligned} Y^k(0) &= 0, \\ \frac{d}{dr}Y^k(r) &= \frac{-k}{r}Y^k(r) \quad \text{as } r \rightarrow \infty. \end{aligned} \quad (68)$$

Similar equations have been derived for all the Breit–Pauli operators (Brage and Froese Fischer, 1994a; Zatsarinny, 2006). Extensive studies of accuracy have been performed by Zatsarinny (2006) using the B-spline R-matrix (BSR) code.

In variational methods, the derivation of differential equations can be avoided by starting with the assumption that the radial function of an orbital will be expanded in a B-spline basis. Let  $a, b, c, d$  denote a set of  $nl$  quantum numbers with

$$P(a; r) = \sum_i a_i B_i(r) \quad (69)$$

and similar expansions for  $b, c$ , and  $d$ . Then

$$R^k(a, b; c, d) = \sum_i \sum_j \sum_{i'} \sum_{j'} a_i b_j c_{i'} d_{j'} R^k(i, j; i', j') \quad (70)$$

where

$$R^k(i, j; i', j') = \int_0^R \int_0^R \frac{r_{\leq}^k}{r_{>}^{k+1}} B_i(r_1) B_j(r_2) B_{i'}(r_1) B_{j'+1}(r_2) dr_1 dr_2 \quad (71)$$

and will be referred to as B-spline Slater integrals or as Slater matrix elements. Many symmetries exist which can reduce the range of summations. From the definition, it follows that the elements are symmetric with respect to the exchange of indices  $i$  and  $i'$ ,  $j$  and  $j'$ , and  $\{i, i'\}$  and  $\{j, j'\}$ , i.e.

$$\begin{aligned} R^k(i, j; i', j') &= R^k(i', j; i, j') \\ &= R^k(i, j'; i', j) \\ &= R^k(j, i; j', i') \\ &= R^k(j', i; j, i') \\ &= R^k(j, i'; j', i) \\ &= R^k(j', i'; j, i) \\ &= R^k(i', j'; i, j). \end{aligned} \quad (72)$$

In addition,

$$R^k(i, j; i', j') = \begin{cases} 0 & \text{if } |i - i'| > k_s, \\ 0 & \text{if } |j - j'| > k_s. \end{cases} \quad (73)$$

This symmetry can be used to reduce the number of elements that need to be computed and stored in memory. Equation (70) can be written as

$$R^k(a, b; c, d) = \sum_i \sum_{i'} a_i c_{i'} \left( \sum_j \sum_{j'} b_j d_{j'} R^k(i, j; i', j') \right). \quad (74)$$

Using symmetry relations these sums can be rearranged to use only the values  $i \leq i'$  and  $j \leq j'$ , namely

$$\begin{aligned} \sum_j \sum_{j'} b_j d_{j'} R^k(i, j, i', j') &= \sum_j b_j d_j R^k(i, j, i', j) \\ &+ \sum_j \sum_{j' > j} (b_j d_{j'} + b_{j'} d_j) R^k(i, j, i', j') \end{aligned} \quad (75)$$

with similar rearrangements for summations over  $(i, i')$ . Combining this with the finite support of B-splines of Eq. (73), only the values  $i \leq i' \leq i + k_s - 1$  and  $j \leq j' \leq j + k_s - 1$  need to be stored. Defining “direct density” matrices,

$$A(i, i') = \begin{cases} a_i c_i & \text{if } i' = i, \\ a_i c_{i'} + a_{i'} c_i & \text{if } i' > i \text{ and } i' \leq n_s, \end{cases}$$

$$B(j, j') = \begin{cases} b_j d_j & \text{if } j' = j, \\ b_j d_{j'} + b_{j'} d_j & \text{if } j' > j \text{ and } j' \leq n_s, \end{cases} \quad (76)$$

we get

$$R^k(a, b; c, d) = \sum_{i=1}^{n_s} \sum_{i'=i}^{i+k_s-1} A(i, i') \sum_{j=1}^{n_s} \sum_{j'=j}^{j+k_s-1} B(j, j') R^k(i, j; i', j'). \quad (77)$$

The above analysis has taken into account the  $(i, i')$  and  $(j, j')$  symmetry but not the symmetry from the interchange of the  $(i, i')$  pair with the  $(j, j')$  pair.

An accurate and efficient evaluation of Slater integrals in the B-spline basis is essential in a Hartree–Fock calculation, consuming most of the computational time. [Altenberger-Siczek and Gilbert \(1976\)](#) investigated the use of a spline basis for the two-electron helium problem. Though initially optimistic about the use of splines in earlier publications, they concluded that splines were not suitable for atomic structure calculations when Slater integrals needed to be evaluated. An important factor in this decision was their reliance on splines of order 4 for which a large number of basis functions are needed to achieve high accuracy. With the publication by [de Boor \(1985\)](#) of general purpose codes for B-splines, this limitation has been removed.

At first sight, one might expect the computation of the  $R^k(i, j; i', j')$  array to be a task of order  $\mathcal{O}(n_s^2 k_s^2)$  but special properties can be exploited. In one dimension, a spline approximation subdivides an interval into subintervals. In two dimensions, the region is divided into patches or “cells”. Thus the fundamental process is one of integration over a cell,  $r_{i_v} \leq r_1 \leq r_{i_v+1}$  and  $r_{j_v} \leq r_2 \leq r_{j_v+1}$ , namely

$$\int_{r_{i_v}}^{r_{i_v+1}} \int_{r_{j_v}}^{r_{j_v+1}} \frac{r_{\leq}^k}{r_{>}^{k+1}} B_i(r_1) B_j(r_2) B_{i'}(r_1) B_{j'+1}(r_2) dr_1 dr_2. \quad (78)$$

But for an off-diagonal cell, the above two-dimensional integral is separable and equal to (for  $i_v < j_v$ )

$$\begin{aligned} & \int_{r_{i_v}}^{r_{i_v+1}} B_i(r_1) r_1^k B_{i'}(r_1) dr_1 \int_{r_{j_v}}^{r_{j_v+1}} B_j(r_2) (1/r_2^{k+1}) B_{j'}(r_2) dr_2 \\ & \equiv r^k(i, i', i_v) \times r^{-(k+1)}(j, j'; j_v) \end{aligned} \quad (79)$$

where  $r^k(i, i', i_v)$  and  $r^{-(k+1)}(j, j'; j_v)$  are referred to as moments.

The diagonal cells reduce to integrations over upper and lower triangles or, through an interchange of arguments, as

$$R^k(i, j; i', j'; i_v) = R_{\Delta}^k(i, j; i', j'; i_v) + R_{\Delta}^k(j, i; j', i'; i_v) \quad (80)$$



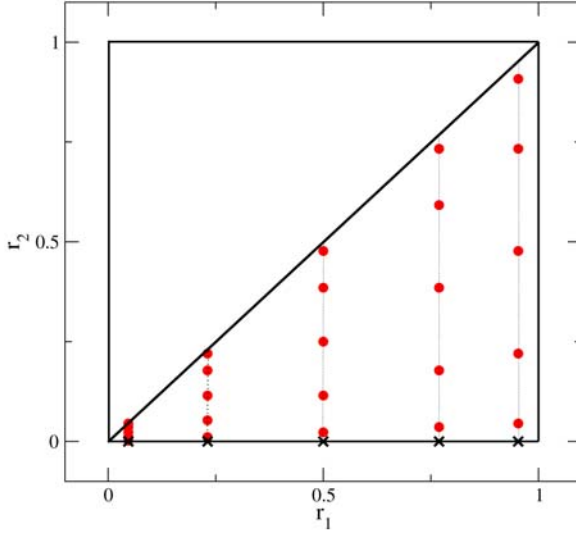


FIG. 4. Gaussian integration points for integration over the lower portion of a diagonal cell of unit dimensions for splines of order  $k_s = 5$ .

and

$$R_{\Delta}^k(i, j; i', j'; i_v) = \int_{r_{iv}}^{r_{iv+1}} \frac{1}{r_1^{k+1}} B_i(r_1) B_{i'}(r_1) dr_1 \int_{r_{iv}}^{r_1} r_2^k B_j(r_2) B_{j'}(r_2) dr_2. \quad (81)$$

The routines in the BSR spline libraries (Zatsarinny, 2006) are based on algorithms developed by Qiu (1999), and Qiu and Froese Fischer (1999). They assume that integration with respect to  $r_1$  is a summation over the usual Gaussian points (crosses) and that integration with respect to  $r_2$  is from the boundary of the cell to the diagonal as shown in Fig. 4. This requires the introduction of new Gaussian points (circles). Thus the computational complexity of an integration over a diagonal cell is  $\mathcal{O}(k_s^2)$ . Once the moments and integrals over the diagonal cells have been evaluated, the results are assembled to produce the  $R^k(i, j; i', j')$  array. The computational complexity of this process is  $\mathcal{O}(n_s k_s^2)$ .

Here the logarithmic grid can be used to advantage. In the region where  $t_{i+1} = (1 + h)t_i$ , scaling laws can be derived. Let the leftmost knot defining  $B_i(r)$  be  $t_i$  and let  $r = t_i + s$ , then,

$$B_i(t_i + s) = B_{i+1}((1 + h)(t_i + s)) = B_{i+1}(t_{i+1} + s(1 + h)), \quad (82)$$

and it can be shown that

$$\begin{aligned}
 \langle B_{i+1}(r) | r^k | B_{j+1}(r) \rangle &= (1+h)^{1+k} \langle B_i(r) | r^k | B_j(r) \rangle, \\
 \langle B_{i+1}(r) | 1/r^{k+1} | B_{j+1}(r) \rangle &= (1+h)^{-k} \langle B_i(r) | 1/r^{k+1} | B_j(r) \rangle, \\
 R^k(i+1, j+1; i'+1, j'+1) &= (1+h) R^k(i, j; i', j').
 \end{aligned} \tag{83}$$

The BSR library routines take advantage of scaling laws in generating moments and diagonal contributions but do not use scaling to minimize the assembly time which is the more time-consuming task. Note that for  $k = 0$ ,  $\langle B_i(r) | 1/r^{k+1} | B_j(r) \rangle$  is constant for  $i + k_s \leq j \leq n_s - k_s$ . This can reduce the number of multiplications needed for evaluating Slater integrals, but only when  $k = 0$ .

Assembly can be avoided when the Slater matrix elements are not needed. An example is the calculation of orbital Slater integrals. Zatsarinny (2006) has shown that given the B-spline moments over intervals and diagonal contributions, the orbital Slater integrals are a simple sum of products. Orbital Slater integrals can also be evaluated directly by integrating over cells without the need for introducing the B-spline moments. What is needed are the values of the radial functions at all the Gaussian points (including the triangle ones). An important property can be used to advantage, namely the fact that spline functions can easily be evaluated at any point.

Table I compares the accuracy of differential equation and cell methods. Though the differential equation results are of high accuracy, direct integration is always better. For some Breit–Pauli integrals, the differential equation results suffer a greater loss of accuracy than indicated in Table I for Slater integrals. The integrals in this table are for  $k = 0$  or  $k = 1$ . The factor appearing in Eq. (78), namely

$$\frac{r_{<}^k}{r_{>}^{k+1}} = \frac{1}{r_{>}} \left( \frac{r_{<}}{r_{>}} \right)^k \tag{84}$$

is a product of two weighting factors. The first factor reduces the contribution as  $r_{>}$  increases and the second reduces the contribution as the radial coordinates  $(r_1, r_2)$  move away from the diagonal where  $r_1 = r_2$ . This factor decreases rapidly for large  $k$  making the region near the diagonal the most important region for the Slater integral. More comparisons with exact values may be found in Froese Fischer et al. (1992), Qiu and Froese Fischer (1999).

The same Slater matrix elements can be used in Dirac–Hartree–Fock calculations. What differs is the grid and the definition of the density matrix which now includes both the large and small components of the orbitals (Froese Fischer and Parpia, 1993).

Table I

Comparison of Some Hydrogenic Slater Integrals from Differential Equation (DE) Methods and Cell Integration (Cell) Methods with Exact Values for Some Slater Integrals Using Splines of Order  $k_s = 8$  and  $h = 1/8$  (Qiu and Froese Fischer, 1999)

$F^k / G^k$	Exact value	DE	Cell
$F^0(1s, 1s)$	5/8	-4.2(-15)	4.4(-16)
$F^0(1s, 2s)$	17/81	-1.4(-15)	1.4(-16)
$F^0(1s, 2p)$	59/243	-1.9(-15)	-1.4(-16)
$F^0(2s, 2s)$	77/512	-7.2(-16)	5.6(-17)
$F^0(2s, 2p)$	83/512	-4.7(-16)	1.9(-16)
$F^0(2p, 2p)$	93/512	-8.9(-16)	0.0(+00)
$F^0(4s, 4s)$	19541/524288	-1.6(-14)	-6.8(-16)
$G^0(1s, 2s)$	16/729	-6.6(-17)	2.8(-17)
$G^0(2p, 3p)$	96768/9765625	-1.1(-16)	5.2(-18)
$G^0(2p, 4p)$	560/177147	-7.0(-17)	1.3(-18)
$G^1(1s, 2p)$	112/2187	-5.3(-15)	2.1(-17)
$G^1(2s, 2p)$	45/512	-8.2(-14)	0.0(+00)
$G^1(2p, 3s)$	92016/9765625	-3.0(-15)	2.1(-17)
$G^1(2p, 3d)$	1824768/48828125	-6.9(-14)	-2.1(-17)

## 5. B-Spline Methods for the Many-Electron Hartree-Fock Problem

### 5.1. NOTATION

Let us begin with the assumption that radial functions for orbitals  $a, b, c, d \dots$  are spline functions with expansions

$$P(a; r) = \sum_i a_i B_i(r), \quad P(b, r) = \sum_i b_i B_i(r), \quad \text{etc.} \quad (85)$$

Thus  $a$  is both a reference to  $nl$  quantum numbers and a reference to the column vector of expansion coefficients for the radial function. At this point, it also is convenient to introduce a notation which allows us to relate orbital quantities to basic B-spline matrix elements of operators. Let us define

$$\begin{aligned}
 I(a, b) &= \langle a | \mathcal{I} | b \rangle \\
 &= \sum_i a_i \sum_j b_j \langle B_i(r) | \mathcal{I} | B_j(r) \rangle \\
 &= a^t I(.,.) b \equiv a^t I b,
 \end{aligned} \quad (86)$$

$$\begin{aligned}
S(a, b) &= \langle a|b \rangle \\
&= \sum_i a_i \sum_j b_j \langle B_i(r) | B_j(r) \rangle \\
&= a^t S(.,.) b \equiv a^t S b,
\end{aligned} \tag{87}$$

where  $I(.,.)$  and  $S(.,.)$  are matrices in the B-spline basis usually denoted simply as  $I$  and  $S$ .

In spline expansions, the energy functional  $\mathcal{F}(a, b, \dots)$  needs to be stationary with respect to all variations of the expansion coefficients of orbitals, i.e.  $\partial \mathcal{F} / \partial a_i = 0$  and  $\partial \mathcal{F} / \partial b_i = 0$ , for  $i = 1, \dots, n_s$ . This condition leads to a system of equations that we would like to express in matrix–vector form. Let us represent the partial differentiation with respect to each component of a vector  $a$  simply as the column vector  $\partial \mathcal{F} / \partial a$ . Then, from the definition in terms of summations, it follows that

$$\partial I(a, b) / \partial a = \sum_j b_j I(.,.) = I b. \tag{88}$$

Let us define  $I(.,.)b = I(.,b)$ , so the effect of variation with respect to a vector of values is to remove the expansion vector as an argument and yield a column vector. When the argument occurs twice in an expression, then it can be removed in more than one way. Thus  $\partial I(a, a) / \partial a = 2I(.,a)$ . The summation over the column indices can be replaced by matrix–vector multiplication so that  $2I(.,a) = 2Ia$ . The latter process can be viewed as removing a vector argument to yield a matrix times that vector and does not depend on multiplicity.

This notation is hardly needed for quantities with only two orbital arguments but is particularly convenient when applied in a similar manner to Slater integrals with four arguments. Consider the variation of  $R^k(a, b; c, d)$  with respect to the vector  $a$  which according to Eq. (70) is

$$\sum_j b_j \sum_{i'} c_{i'} \sum_{j'} d_{j'} R^k(i, j; i', j'), \quad i = 1, \dots, n_s.$$

Then it follows that the vector of values, according to our notation, is  $R^k(., b; c, d)$  and can be written in matrix–vector form in three different ways,

$$\begin{aligned}
R^k(., b; c, d) &= R^k(., .; c, d)b \\
&= R^k(., b; ., d)c \\
&= R^k(., b; c, .)d,
\end{aligned}$$

where  $R^k(., .; c, d)$ ,  $R^k(., b; ., d)$ , and  $R^k(., b; c, .)$  are matrices whose elements are linear combinations of Slater matrix elements. The matrices  $R^k(., .; c, d)$  and  $R^k(., b; c, .)$  are full matrices and symmetric only if  $c, d$  or  $b, c$  respectively are equivalent, whereas  $R^k(., b; ., d)$  is symmetric and banded with a bandwidth of

$2k_s - 1$ . It is important that the row-index from the result of variation not be confused with the column index from the removal of an argument. By convention, the leftmost unfilled position designates the row. Thus the variation of  $R^k(a, b; c, d)$  with respect to  $c$  would be the column vector  $R^k(a, b; \cdot, d) = R^k(\cdot, b; a, d)$ , by symmetry of the Slater integral. Then  $R^k(\cdot, b; a, d) = R^k(\cdot, \cdot; a, d)b$ , for example.

## 5.2. DERIVATION OF B-SPLINE EQUATIONS

### 5.2.1. Case without Orthogonality Constraints

Now let us consider the  $1s^2 2p^2 P$  configuration state. The energy expression for this three-electron system is

$$\begin{aligned} \mathcal{E}(1s^2 2p^2 P) = & 2I(a, a) + I(b, b) + F^0(a, a) + 2F^0(a, b) \\ & - (1/3)G^1(a, b), \end{aligned} \quad (89)$$

where  $1s$  and  $2p$  are denoted by  $a$  and  $b$  respectively. Since there are only normalization constraints, the energy functional can be written as

$$\begin{aligned} \mathcal{F}(a, b, \varepsilon_{aa}, \varepsilon_{bb}) = & \mathcal{E}(1s^2 2p^2 P) + \varepsilon_{aa}(1 - S(a, a)) \\ & + \varepsilon_{bb}(1 - S(b, b)). \end{aligned} \quad (90)$$

Applying the variational procedure to this functional (and dividing by two), we get two generalized matrix-eigenvalue problems,

$$\begin{aligned} [2I + 2R^0(\cdot, a; \cdot, a) + 2R^0(\cdot, b; \cdot, b) - (1/3)R^1(\cdot, b; b, \cdot) - \varepsilon_{aa}S]a &= 0, \\ [I + 2R^0(\cdot, a; \cdot, a) - (1/3)R^1(\cdot, a; a, \cdot) - \varepsilon_{bb}S]b &= 0, \end{aligned} \quad (91)$$

where the exchange contribution makes each matrix a full matrix.

However, the equations could also have been written as one system of equations with banded submatrices, namely

$$\begin{bmatrix} 2I + D^a - \varepsilon_{aa}S & X^a \\ X^b & I + D^b - \varepsilon_{bb}S \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0, \quad (92)$$

where  $D^a$ ,  $D^b$  represent the contributions from the direct  $F^k$  integrals and  $X^a$ ,  $X^b$  those from the  $G^k$  integrals. In the present case,

$$\begin{aligned} D^a &= 2R^0(\cdot, a; \cdot, a) + 2R^0(\cdot, b; \cdot, b), \\ D^b &= 2R^0(\cdot, a; \cdot, a), \\ X^a &= -(1/3)R^1(\cdot, b; \cdot, a), \\ X^b &= -(1/3)R^1(\cdot, a; \cdot, b). \end{aligned} \quad (93)$$

In this form, all submatrices are symmetric and banded, and the coefficient matrix itself for the pair of orbitals is symmetric since  $(X^b)^t = X^a$ . This symmetry would have been destroyed if, as has been the practice in differential equation methods, the equations for an orbital were divided by the orbital occupation. Solutions of these equations can be obtained through singular-value decomposition (SVD) (Press et al., 1992).

Equation (92) can be rewritten as one matrix-eigenvalue problem by using Eq. (24) to define a deviation  $d_{aa}$  for each diagonal energy parameter, namely  $d_{aa} = E - \varepsilon_{aa}$ . In the case of  $1s^2 2p^2 P$ ,

$$d_{aa} = I(b, b) - F^0(a, a) \quad \text{and} \quad d_{bb} = 2I(a, a) + F^0(a, a). \quad (94)$$

Substituting into Eq. (92) we get one generalized symmetric eigenvalue problem for the pair of orbitals,

$$\left( \begin{bmatrix} 2I + D^a + d_{aa}S & X^a \\ X^b & I + D^b + d_{bb}S \end{bmatrix} - E \begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix} \right) \begin{bmatrix} a \\ b \end{bmatrix} = 0. \quad (95)$$

Let  $\mathbf{a}$  be the column vector  $(a^t, b^t)^t$ . Then these equations have the form

$$(\mathbf{H} - E\mathbf{S})\mathbf{a} = 0, \quad (96)$$

where  $\mathbf{H}$  is a matrix of dimension  $2n_s \times 2n_s$  that consists of banded blocks. and  $\mathbf{S}$  is a block matrix whose diagonal blocks are the overlap matrix  $S$ .

Thus the orbitals are solutions of either implicitly coupled generalized eigenvalue problems of full matrices that can be solved independently or explicitly coupled equations consisting of banded blocks of matrices that are solved simultaneously by either singular value decomposition or a generalized eigenvalue problem. It will be shown later that the two variations of the latter expressed by Eqs. (92) and (95) are closely related.

### 5.2.2. Case with Orthogonality Constraints

The Hartree–Fock energy expression for  $1s2s^{1,3}S$  is

$$\mathcal{E}(1s2s^3S) = I(a, a) + I(b, b) + F^0(a, b) \pm G^1(a, b). \quad (97)$$

In addition to normalization constraints, there also is an orthogonality constraint so the energy functional becomes

$$\begin{aligned} \mathcal{F}(a, b, \varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{ab}) = & \mathcal{E}(1s2s^{1,3}S) + \varepsilon_{aa}(1 - S(a, a)) \\ & + \varepsilon_{bb}(1 - S(b, b)) - 2\varepsilon_{ab}S(a, b) \end{aligned} \quad (98)$$

and in matrix-eigenvalue form, the equations become

$$[I + R^0(., b; ., b) \pm R^0(., b; b, .) - \varepsilon_{aa}S]a - \varepsilon_{ab}Sb = 0,$$

$$[I + R^0(., a; ., a) \pm R^0(., a; a, .) - \varepsilon_{bb}S]b - \varepsilon_{ba}Sa = 0 \quad (99)$$

or

$$\begin{bmatrix} H^a & \\ & H^b \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} - \begin{bmatrix} \varepsilon_{aa}S & \varepsilon_{ab}S \\ \varepsilon_{ba}S & \varepsilon_{bb}S \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0. \quad (100)$$

From the orthonormality of solutions, it follows that

$$\begin{aligned} \varepsilon_{aa} &= a^t H^a a, & \varepsilon_{ab} &= b^t H^a a, \\ \varepsilon_{ba} &= a^t H^b b, & \varepsilon_{bb} &= b^t H^b b, \end{aligned} \quad (101)$$

and from the requirement  $\varepsilon_{ab} = \varepsilon_{ba}$ , the condition that

$$b^t H^a a - a^t H^b b = 0. \quad (102)$$

In the present case, since  $I(a, b) = I(b, a)$ , this condition becomes

$$\begin{aligned} &[R^0(b, b; a, b) \pm R^0(b, b; b, a)] \\ &- [R^0(a, a; b, a) \pm R^0(a, a; a, b)] = 0. \end{aligned} \quad (103)$$

For the  $^3S$  where the minus sign applies, the condition is satisfied by any pair of orthogonal orbitals. In this case, by Koopmans' theorem, the physically meaningful solutions are the extremum eigenvalues of the  $\varepsilon$ -matrix characterized by  $\varepsilon_{ab} = \varepsilon_{ba} = 0$ . This choice uncouples the two equations and makes each a generalized matrix-eigenvalue problem.

However, the situation is different for  $1s2s\ ^1S$ . A stationary solution requires that

$$R^0(a, b; b, b) - R^0(a, a; a, b) = 0, \quad (104)$$

and can be satisfied through rotation (see Section 2.2.2). When the condition is satisfied and  $\varepsilon_{ab} = \varepsilon_{ba}$ , the off-diagonal Lagrange multipliers can be eliminated (Bentley, 1994). Using first the fact that  $\varepsilon_{ab}$  is a constant, and then that  $\varepsilon_{ab} = b^t H^a a$ , we have

$$\varepsilon_{ab}Sb = Sb\varepsilon_{ab} = Sbb^t H^a a. \quad (105)$$

When  $a$  and  $b$  are orthogonal,  $b^t Sa = 0$  so that

$$a = (I - b b^t S)a, \quad (106)$$

where  $I$  is the identity operator (not to be confused with  $I$ ). With similar results when  $a$  and  $b$  are interchanged, it follows that Eq. (100) can be rewritten as

$$\begin{aligned} &[(I - Sbb^t)H^a(I - bb^tS) - \varepsilon_{aa}S]a = 0, \\ &[(I - Saa^t)H^b(I - aa^tS) - \varepsilon_{bb}S]b = 0. \end{aligned} \quad (107)$$

This transformation uses both Eqs. (105) and (106), thereby preserving the symmetry of the generalized eigenvalue problems. Earlier methods (Brage and Froese Fischer, 1994a) only eliminated the off-diagonal Lagrange multiplier thereby destroying the symmetry. This matrix method of enforcing orthogonality, does not require that  $\varepsilon_{ab} = \varepsilon_{ba}$ . It simply defines the new orbital  $a$  to be orthogonal to an existing orbital  $b$  (or vice versa). If orbital  $a$  is fixed, this would be an effective method for obtaining orbital  $b$  subject to orthogonality to orbital  $a$ , but when both orbitals are varied, the total energy would not be a stationary point unless  $\varepsilon_{ab} = \varepsilon_{ba}$ .

### 5.3. ITERATIVE SOLUTIONS OF B-SPLINE EQUATIONS

#### 5.3.1. Updating Single Orbitals Successively

We have shown that the radial orbital for a Hartree–Fock wave function can be formulated as a solution of a generalized matrix-eigenvalue problem, one for each orbital. This orbital Hartree–Fock Hamiltonian matrix, however, is defined in terms of radial distributions of other orbitals and thus the systems of equations are coupled implicitly and need to be solved iteratively by a self-consistent field (SCF) process. Basically, after orbitals have been rotated (if necessary), for each orbital  $a$  in the orbital set,  $H^a$  is computed from current estimates of all orbitals, projection operators are applied to ensure orthogonality (as needed), and the generalized eigenvalue problem is solved for the desired eigensolution. The eigenvalue of the solution defines the diagonal energy parameter and the eigenvector the improved expansion coefficients for the orbital. Such a process may converge or diverge.

Table II shows convergence by reporting the change,  $\Delta E = E_i - E_{i-1}$ , from one iteration to the next as the iteration number  $i$  increases for cases where no off-diagonal energy parameters were needed. In all cases, the initial estimates of orbitals were unscreened hydrogenic functions. This facilitates the checking of the calculations since the values of Slater integrals are then known. The calculations for  $1s2p\ ^1P$  and  $1s2s\ ^3S$  converge rapidly and quadratically with the results reaching the round-off limit in 4 or 5 iterations. Convergence for  $1s^22s^2\ ^1S$  is linear but with the accuracy of the total energy increasing by about one digit per iteration. Calculations for the  $1s^22s^22p^5$  ground state of fluorine are different in that convergence is much slower.

With five equivalent  $2p$  electrons, fluorine has a strong self-interaction. Given estimates of  $2p$  that screen the nucleus too effectively the next  $2p$  orbital will be too diffuse. As a result, the diagonal energy parameter oscillates as shown in Fig. 5. Such oscillations can be reduced through the use of damping factors (also call accelerating factors) and may be needed for convergence. The oscillations can



Table II  
Convergence of the Orbital Generalized Eigenvalue Method for Several Cases without Off-Diagonal Lagrange Multipliers

<i>i</i>	$1s2p^1P$	$1s2s^3S$	$1s^22s^2^1S$	$1s^22s^22p^5^2P$
2	-3.4(-05)	-1.0(-05)	-2.8(-02)	-2.7
3	-1.6(-11)	-4.6(-09)	-1.6(-03)	-4.5(-01)
4	2.2(-14)	-6.5(-12)	-1.2(-04)	-2.5(-01)
5	—	-2.8(-14)	-9.1(-06)	-8.9(-02)
6	—	—	-6.9(-07)	-5.1(-02)
7	—	—	-5.2(-08)	-2.2(-02)
8	—	—	-3.9(-09)	-1.1(-02)
9	—	—	-3.0(-10)	-5.6(-03)
10	—	—	-2.3(-11)	-2.9(-03)

All calculations are for the neutral atom. Shown is the change in the total energy,  $\Delta E_i = E_i - E_{i-1}$ , for iterations  $i = 2, 3, \dots$

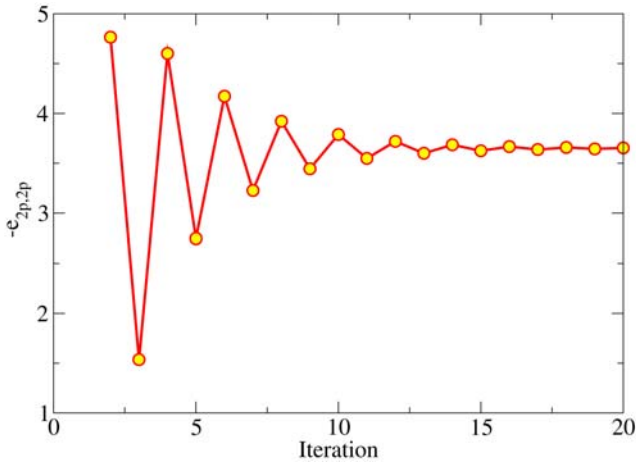


FIG. 5. The oscillating behavior of the value of the diagonal energy parameter,  $-\epsilon_{2p,2p}$ , as a function of the iteration number for the  $1s^22s^22p^5^2P$  ground state of fluorine.

be detected by monitoring the diagonal energy parameter and can be dealt with automatically (Froese Fischer, 1986).

Though it is convenient to pose the orbital problem in terms of an eigenvalue problem where the index of the desired eigenvalue (first, second, etc., with first being the lowest) makes it easy to determine solutions for excited states, explicit rotation is needed to obtain stationary energies when off-diagonal Lagrange

multipliers are needed. Such rotations can be included implicitly when solving simultaneously for orbitals that are connected through orthogonality.

### 5.3.2. Updating Several Orbitals Simultaneously

When all (or several) orbitals are updated simultaneously, there is greater flexibility in how the system of equations are expressed. In particular, it is possible to express the system of equations in terms of only banded  $n_s \times n_s$  submatrices that can be generated more efficiently than full matrices.

The stationary condition requires that the gradient vector of the energy functional be zero. For a CSF with  $m$  radial functions, this leads to a system of  $M \times M$  equations where  $M = m \times n_s$  (before the application of boundary conditions). The gradient vector for each orbital can always be expressed as a sum of matrix–vector operations. The gradient vector for orbital  $a$  contains contributions from  $I(., a)$ ,  $S(., a)$ ,  $R^k(., b; a, b)$ , and  $R^k(., b; b, a)$ . Then  $I(., a) = Ia$ ,  $S(., a) = Sa$ ,  $R^k(., b; a, b) = R^k(., b; ., b)a$  lead to symmetric, banded matrices, but the contribution from the exchange term can only be expressed in banded form as  $R^k(., b; b, a) = R^k(., b; ., a)b$ . For this contribution, an off-diagonal block needs to be introduced and both  $a$  and  $b$  determined simultaneously.

Let  $A_i$  be the expansion vector for orbital  $i$ . Then the system of equations can be written as

$$\begin{bmatrix} F^{11} & F^{12} & \dots & F^{1m} \\ F^{21} & F^{22} & \dots & F^{2m} \\ \dots & \dots & \dots & \dots \\ F^{m1} & F^{m2} & \dots & F^{mm} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ \dots \\ A_m \end{bmatrix} = 0. \quad (108)$$

where  $F^{ii}$  contains the contributions from one-electron integrals, the direct Slater integrals for orbital  $i$ , as well as  $-\varepsilon_{ii}S$ , and  $F^{ij}$  ( $i \neq j$ ) contains the contribution from exchange integrals between orbitals  $i$  and  $j$  and possible orthogonality constraints  $-\varepsilon_{ij}S$ . This method does not require that orbitals be explicitly rotated but the  $\varepsilon$ -matrix used should be symmetric. A possible definition is the average of the two computed values.

This formulation leads to a homogeneous system of equations with a symmetric coefficient matrix and could be solved using singular-value decomposition (SVD). But as long as exchange terms are present, the diagonal matrices,  $F^{ii}$ , will not be singular so that a banded inverse exists and a block LU-factorization scheme may be used. Consider the  $2 \times 2$  case. Multiplying the first row of block matrices, by  $(F^{11})^{-1}$  and subtracting  $F^{21}$  times this row from the second, we get

$$(F^{22} - F^{21}(F^{11})^{-1}F^{12})A_2 = 0, \quad (109)$$

which can be solved either by inverse iteration (Press et al., 1992) or as an eigenvalue problem since  $F^{22}$  includes a  $-\varepsilon_{22}S$  term. Once  $A_2$  is computed

Table III  
Comparison of Convergence of Singular Value Decomposition Methods for  $1s2p^1P$ ,  $1s2s^3S$ ,  
 $1s2s^1S$ , and  $1s^22s^2^1S$

$i$	$1s2p^1P$	$1s2s^3S$	$1s2s^1S$	$1s^22s^2^1S$
1	-2.5(-04)	-4.9(-02)	-4.9(-01)	-4.4(-01)
2	-1.4(-06)	-1.5(-03)	-3.5(-01)	-1.4(-02)
3	-5.2(-09)	-3.16(-06)	-3.0(-02)	-1.6(-04)
4	-2.1(-11)	-1.5(-09)	-5.2(-02)	-8.4(-06)
5	-4.4(-14)	-5.9(-13)	-1.0(-02)	-6.2(-07)
6	-3.0(-14)	-5.8(-15)	-4.0(-03)	-4.7(-08)
7	—	—	-1.7(-03)	-3.7(-09)
8	—	—	-8.8(-04)	-2.9(-10)
9	—	—	-5.0(-04)	-2.2(-11)
10	—	—	-2.6(-04)	-1.8(-12)

Shown are the values of  $\Delta E = E_i - E_{i-1}$  as a function of the iteration  $i$ .

and normalized,  $A_1$  can be determined through back-substitution. A process like LU-decomposition could be used, where the basic quantities are square, banded matrices.

Singular values are closely related to eigenvalues. For a square matrix  $A$ , the singular values of  $A$  are the square roots of the eigenvalues of  $A^t A$ . Should  $A$  be symmetric, then singular values are the absolute value of the eigenvalues and the singular vectors are the eigenvectors of  $A^t A$  which, for symmetric matrices, are eigenvectors of  $A$ . When SVD is used to solve  $Ax = b$ , the computed value of  $x$  is such that  $x$  minimizes  $|Ax - b|$ . Consequently, when  $b = 0$ , the solution is the eigenvector of the eigenvalue nearest to zero and a routine for solving a symmetric eigenvalue problem could be used to solve the system of equations. However, practical aspects need to be considered.

Table III shows the convergence when eigenvalue methods for systems are used. For  $1s2p$  the LAPACK symmetric eigenvalue solver, `dsyev` was used with the desired solution being the one with the smallest eigenvalue (in magnitude). Convergence was rapid and no problems were encountered. It was interesting to observe that the desired solution was the second eigenvalue. There was a solution with a lower eigenvalue, a solution in which  $P_{1s}^{\text{new}} \approx P_{1s}^{\text{previous}}$  but with  $P_{2p}^{\text{new}} \approx -P_{2p}^{\text{previous}}$ . This change in sign in the system of equations is equivalent to changing the coefficient in the energy expression for  $1s2p^1P$  which becomes the energy expression for  $1s2p^3P$ . For the  $1s2s^3S$  case the desired solution is the second eigenvalue since  $2s$  is the second eigenvalue of its orbital equation. With unscreened orbitals as initial estimates the desired solution was the one with the smallest eigenvalue only at the third iteration. The off-diagonal energy parameter was set to zero and no projection operators were applied.

Table IV  
Eigenvalues as a Function of the Iteration Number  $i$  for the Solution of Systems of  
Equations for  $1s2s^1S$

$i$	$E_1$	$E_2$	$E_3$	$E_4$
1	-0.700	-0.032	-0.000	0.058
2	-1.192	-0.531	-0.441	-0.412
3	-0.890	-0.134	-0.032	0.006
4	-0.954	-0.124	-0.009	0.027
5	-0.797	-0.095	-0.001	0.025

The calculations for  $1s2s^1S$  included both diagonal and off-diagonal energy parameters where the value for the latter was the average value computed from current estimates of  $\varepsilon_{ab}$  and  $\varepsilon_{ba}$ . The desired solution is now the eigenvector of the third eigenvalue. Iterative solutions using the `dsyev` symmetric eigenvalue solver failed to converge. This is a case where the implicit rotation of orthogonal orbitals is important and where the orthogonality for expansions in the B-spline basis required the overlap matrix  $S$ . By using the `dsygv` generalized eigenvalue solver for equations of the form

$$\left( \begin{bmatrix} H^{aa} - \varepsilon_{aa}S & H^{ab} - \varepsilon_{ab}S \\ H^{ba} - \varepsilon_{ab}S & H^{bb} - \varepsilon_{bb}S \end{bmatrix} - E \begin{bmatrix} S & 0 \\ 0 & S \end{bmatrix} \right) \begin{bmatrix} a \\ b \end{bmatrix}, \quad (110)$$

where  $H^{aa}$  represents the contributions from  $I(a, a)$  and the direct Slater integrals, and  $H^{ab}$  the contributions from  $G^k(a, b)$ , etc. The self-consistent solution satisfies these equations with  $E = 0$ , but when starting even with screened hydrogenic functions as initial estimates, the first few sets of eigenvalues  $E_i$  resulting from the iterative process may be far from zero. Table IV shows the first few eigenvalues as a function of the iteration number  $i$  for  $1s2s^1S$ . Only at the fourth iteration was the desired solution the one with the smallest eigenvalue. Thus an SVD approach relying only on selecting the solution with the smallest eigenvalue would need to have initial estimates considerably more reliable than screened hydrogenic functions. For cases where orbital rotation through off-diagonal energy parameters are significant, the generalized singular value decomposition needs to be used.

When Koopmans' theorem is used to express diagonal energy parameters as the total energy minus a deviation, as was done in Eq. (95) for  $1s2p^1P$ , and where the total energy at each iteration is computed from the current orbitals, the generalized eigenvalue problem is equivalent to the method of Eq. (110) except that the eigenvalues have been shifted and the desired solution needs to be specified or known.

Table III also shows the convergence for the three cases  $1s2s^3S$ ,  $1s2s^1S$ , and  $1s^22s^2^1S$  when the generalized SVD method is used.  $1s2s^1S$  has by far

the slowest rate of convergence. Initial estimates were hydrogenic orbitals with effective nuclear charge of (2, 1) for (1s, 2s) respectively. The numerical differential equation Hartree–Fock method was able to solve this problem only with initial estimates from  $1s2s^3S$  and the explicit rotation of orbitals (Froese Fischer, 1986). Comparing the present values with Table II, we see that convergence for  $1s2p^1P$ ,  $1s2s^3S$ , and  $1s^22s^2^1S$  is similar. One question that arises is whether orbitals should be orthogonalized when the off-diagonal energy parameters are zero. In Table III, at the end of each iteration, 2s was made orthogonal to 1s. This orthogonalization can help in some cases, such as  $1s2s^1S$ , but may slow convergence slightly in others.

### 5.3.3. Newton–Raphson Methods

The Newton–Raphson procedure for non-linear systems of equations often exhibits quadratic convergence once an estimate is sufficiently near a solution. Consider the system of  $n$  equations  $F_i(x) = 0$ ,  $i = 1, \dots, n$  in  $n$  unknowns,  $x = (x_1, \dots, x_n)$ . Let  $F(x) = 0$  be the column vector of equations and the vector  $x^m$  an estimate of a solution. Expanding in a Taylor's series,

$$F(x) = 0 = F(x^{(m)}) + (\partial F / \partial x) \Delta x + \text{higher order terms}, \quad (111)$$

where  $(\partial F / \partial x)$  is the Jacobian matrix with elements  $(\partial F_i / \partial x_j)$ . Then the iterative process:

$$\begin{aligned} (\partial F / \partial x) \Delta x &= -F(x^{(m)}), \\ x^{(m+1)} &= x^m + \Delta x \end{aligned} \quad (112)$$

can be shown to have quadratic convergence in many circumstances. Notice that  $F(x^{(m)})$  is the residual or amount by which the equations are not satisfied by the current estimate. In the following discussion the residual for equations for orbital  $a$  will be denoted  $\text{res}_a$ , etc., and the residual for constraints will be given explicitly.

This process was applied to  $1s2s^3S$  and  $^1S$  (Froese Fischer et al., 1992). For the latter the unknowns were  $(a, b, \varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{ab})$  and the systems of equations are the stationary conditions of Eq. (99) along with the three orthonormality conditions that are part of the energy functional. Let  $(a, b)$  be the current estimates which are used to evaluate the  $\varepsilon$ -matrix. If symmetry conditions are not satisfied, we can use the average value,

$$\varepsilon_{ab} = \varepsilon_{ba} = (b^t H^a a + a^t H^b b) / 2. \quad (113)$$

Then  $\Delta a$  and  $\Delta b$  are solutions of

Table V  
The Orbital Self-Consistency ( $\Delta P$ ) and the Deviation from the Virial Theorem ( $VT + 2$ ) as a Function the Number of Iterations,  $i$ , for  $1s2s$   $1,3S$  States of He with Spline Parameters  $k_s = 6$  and  $h = 1/8$  (Froese Fischer et al., 1992)

$i$	Triplet			Singlet		
	$\Delta P_{1s}$	$\Delta P_{2s}$	$ VT + 2 $	$\Delta P_{1s}$	$\Delta P_{2s}$	$ VT + 2 $
1	9.7(−3)	2.9(−1)		5.7(−2)	1.4(−1)	
2	8.7(−3)	1.1(−2)		6.2(−3)	1.0(−2)	
3	1.7(−5)	3.8(−5)		2.2(−4)	1.3(−4)	
4	3.9(−11)	6.4(−11)	<5(−14)	5.9(−6)	7.3(−6)	
5				3.7(−7)	4.2(−7)	4.0(−7)
6				2.1(−8)	2.4(−8)	4.5(−10)

Initial estimates were screened hydrogenic functions with  $Z_{\text{eff}} = 2$  and 1, respectively, for  $1s$  and  $2s$ , for  $^3S$ . The latter were used as initial estimates for  $^1S$ .

$$\begin{bmatrix} H^a - \varepsilon_{aa}S & H^{ab} - \varepsilon_{ab}S & -Sa & -Sb \\ H^{ba} - \varepsilon_{ab}S & H^b - \varepsilon_{bb}S & -Sb & -Sa \\ -(Sa)^t & & & \\ & -(Sb)^t & & \\ -(Sb)^t & -(Sa)^t & & \end{bmatrix} \begin{bmatrix} \Delta a \\ \Delta b \\ \Delta \varepsilon_{aa} \\ \Delta \varepsilon_{bb} \\ \Delta \varepsilon_{ab} \end{bmatrix} = \begin{bmatrix} -\text{res}_a \\ -\text{res}_b \\ S(a, a) - 1 \\ S(b, b) - 1 \\ S(a, b) \end{bmatrix} \tag{114}$$

where  $H^a$  and  $H^b$  in this case are the matrices of Eq. (100) and

$$H^{ab} = (H^{ba})^t = 2R^0(., .; a, b) \pm R^0(., a; ., b) \pm R^0(., .; b, a).$$

With orthonormal initial estimates, the conditions for the last three equations would be zero. The performance of this method is shown in Table V where the maximum change in an orbital  $\Delta P$  is shown at the end of each iteration. By the Virial theorem (VT), the ratio of the potential energy and kinetic energy should be exactly  $-2.0$ . In Table V the deviation of this ratio is also reported. Clearly, the  $^3S$  calculations converge quadratically, with the  $\Delta P$  for each orbital, effectively squared in going from one iteration to the next. Convergence for the  $^1S$  is considerably slower, though converging without explicit rotations (Froese Fischer et al., 1992). The price for the faster convergence is the extra computation needed to generate the Jacobian matrix and the time needed to solve full systems of equations.

The Newton–Raphson method generally requires considerably more computation for setting up the system of equations than the orbital or SVD methods. Thus

Table VI  
Comparison of Convergence for  $2p^5$  ( $Z = 5$ ) for the Orbital  
Hamiltonian Method (Orbital) and the Newton–Raphson (NR)  
Method

$i$	Orbital	NR
1	-3.9(-01)	-3.8(-01)
2	+3.6(-01)	-7.8(-03)
3	-3.3(-01)	-2.1(-06)
4	+3.8(-01)	-1.4(-12)
5	-3.6(-01)	4.4(-14)

Shown are the values of  $\Delta E = E_i - E_{i-1}$  as a function of the iteration  $i$ .

it is not always the method of choice. However, for multiply occupied shells such as  $2p^5\ ^2P$  it can be extremely effective with a minimum of overhead. The energy functional is

$$\mathcal{F}(2p^5) = 5I(a, a) + 10F^0(a, a) - 0.8F^2(a, a) + \varepsilon_{aa}(1 - S(a, a)), \quad (115)$$

from which it follows that

$$\begin{aligned} H^a &= 5I + 20R^0(., a; ., a) - 1.6R^2(., a; ., a), \\ \varepsilon_{aa} &= a^t H^a a, \\ \text{res}_a &= (H^a - \varepsilon_{aa}S)a, \\ H^{aa} &= H^a + 40R^0(., .; a, a) - 3.2R^2(., .; a, a) - \varepsilon_{aa}S, \end{aligned} \quad (116)$$

where  $H^{aa}$  is the second-order variation of  $\mathcal{E}$  with respect to  $a$  and is a full matrix. Then the Newton–Raphson equations are

$$\begin{bmatrix} H^{aa} & -Sa \\ -(Sa)^t & 0 \end{bmatrix} \begin{bmatrix} \Delta a \\ \Delta \varepsilon_{aa} \end{bmatrix} = \begin{bmatrix} -\text{res}_a \\ S(a, a) - 1 \end{bmatrix}. \quad (117)$$

Thus with the addition of the extra  $R^k(., .; a, a)$  full matrix contributions, quadratic convergence of the iterative process is achieved. Though this process solves only a single orbital equation, it avoids the necessity of introducing damping factors for oscillations.

Table VI compares the convergence of the total energy as a function of the iteration number for  $2p^5$  and  $Z = 5$ . In the single orbital method, the total energy oscillates and actually diverges. With the Newton–Raphson method convergence is rapid and quadratic. The important contributors are the contributions to the equations from the second-order variation of  $F^k(a, a)$  integrals in the energy expression which will always be present when a shell is multiply occupied.

It needs to be remembered that the Newton–Raphson method for non-linear equations such as the HF equations, converges to the nearest energy solution. Consequently, with reasonably good initial estimates for  $1s$  and  $2s$ , this method applied to  $1s^2 2s$  may converge rapidly to  $1s^2 3s$ . In other words, the orbital properties of the initial estimates do not control the solution obtained by the Newton–Raphson method. This difficulty applies primarily to the application of the method to systems with singly occupied orbitals in that eigenvalues can be closely spaced.

#### 5.3.4. Summary of Methods

In summary, three different iterative methods for solving the Hartree–Fock equations have been identified.

- (1) The single-orbital Hartree–Fock Hamiltonian method is straight forward to apply and leads to a generalized eigenvalue problem for which the matrix is a full matrix except when no exchange is present. The matrix is of size  $n_s \times n_s$ . Projection operators can readily be incorporated for orthogonality constraints, though they do not result in orbital rotations. The index of the eigenvalue for a given orbital is known. However, without orbital rotations the final energy may not be a stationary energy. Also, the iterative process is not guaranteed to converge for multiply occupied shells, though damping factors can be introduced to eliminate oscillations in diagonal energy parameters if needed.
- (2) Systems of equations for two or more orbitals can be solved by generalized singular value decomposition methods. Orbital rotations are included implicitly but initial estimates need to be sufficiently accurate so that the eigenvalue nearest to zero is associated with the desired solution. Otherwise, the index of the eigenvalue needs to be known in advance. The size of the matrix for  $m$  orbitals is  $m n_s \times m n_s$  and consists of banded blocks of size  $n_s \times n_s$ . By rearranging the order of the matrix, it would be a banded matrix of bandwidth  $m \times (2k_s - 1)$ .
- (3) Newton–Raphson methods may be used for quadratic convergence but become computationally intensive as the number of orbitals computed simultaneously increases. For  $m$  orbitals, a Jacobian matrix needs to be computed and a full system of equations of size  $M \times M$  needs to be solved where  $M = m n_s + n_c$ , where  $n_c$  is the number of orthonormalization constraints. Orbital rotations are included. For the case of a single, multiply occupied orbital, the Newton–Raphson method may eliminate the need for damping factors. Accurate initial estimates may be needed to ensure that the Newton–Raphson method converges to the desired solution.

Thus a number of options are available. More study is needed for determining the most efficient combination of methods.



In this discussion we have mentioned only methods based on homogeneous equations. It is always possible to express a contribution determined from current estimates as defining a “right-hand side” for the system of equations in which case eigenvalue methods can no longer be used.

## 6. B-Spline MCHF Equations

### 6.1. WITH ORTHONORMALITY CONSTRAINTS

Traditionally, MCHF calculations obtain a solution through an iterative process that

- improves the radial functions, then
- finds the CSF expansion coefficients.

These two phases differ in their view of angular data.

Finding the CSF expansion coefficients is a configuration-interaction (CI) problem which requires computing the matrix elements of  $H = (H_{ij})$ , where  $H_{ij} = \langle \Phi(\gamma_i LS) | \mathcal{H} | \Phi(\gamma_j LS) \rangle$ . The latter can be expressed in the form

$$H_{ij} = \sum_{ab} w_{ab}^{ij} I(a, b) + \sum_{abcd;k} v_{abcd;k}^{ij} R^k(a, b; c, d), \quad (118)$$

where  $w_{ab}$  and  $v_{abcd;k}$  are angular coefficients obtained from integrating over all angular coordinates (Hibbert and Froese Fischer, 1991; Cowan, 1981; Gaigalas, 1999). The total energy  $E$  and the CSF expansion coefficients are eigenvalues and eigenvectors, respectively, of the real, symmetric, matrix-eigenvalue problem  $(H - E)c = 0$ . For large expansions, this interaction matrix is sparse and can be solved using the Davidson algorithm (Stathopoulos and Froese Fischer, 1994). In fact, generating the interaction matrix can easily be done in parallel by distributing the work by columns with excellent performance. Finding eigenvalues and eigenvectors using Davidson’s algorithm is based on parallel matrix–vector multiplication with the interaction matrix distributed. Considerable communication is needed in this stage and performance is not as impressive, but solving the eigenvalue problem is a relatively small portion of the overall task (Froese Fischer et al., 1994; Stathopoulos et al., 1996).

When radial functions are improved, the energy expression is needed, namely

$$\mathcal{E}(\gamma LS) = \sum_{ab} w_{ab} I(a, b) + \sum_{abcd;k} v_{abcd;k} R^k(a, b; c, d), \quad (119)$$

where the coefficients  $w_{ab}$  and  $v_{abcd;k}$  are obtained by summing over all contributions to the energy expression so that

$$w_{ab} = \sum_i^M \sum_j^M c_i c_j w_{ab}^{ij} \quad \text{and} \quad v_{abcd;k} = \sum_i^M \sum_j^M c_i c_j v_{abcd;k}^{ij}. \quad (120)$$

One obvious difference from the HF problem is the fact that not all Slater integrals are either  $F^k(a, b)$  or  $G^k(a, b)$  integrals. This means that the orbital equation for a single orbital cannot always be expressed as a generalized eigenvalue problem though it can be expressed as a system of equations.

Consider the case of

$$\Psi = c_1 \Phi(3p^2 1D) + c_2 \Phi(3s3d 1D), \quad (121)$$

for which (ignoring any possible core)

$$\begin{aligned} \mathcal{E}(1D) &= c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}, \\ \text{where } H_{11} &= 2I(p, p) + F^0(p, p) + 0.04F^2(p, p), \\ H_{12} &= (2/\sqrt{15})R^1(s, d; p, p), \\ H_{22} &= I(s, s) + I(d, d) + F^0(s, d) + 0.2G^2(s, d), \end{aligned} \quad (122)$$

and where  $p, s, d$  are expansion vectors for  $3p, 3s, 3d$  respectively. The gradient vector of  $R^1(s, d; pp)$  with respect to orbital  $s$  is  $R^1(., d; p, p)$ , a vector that cannot be written as a matrix times the vector  $s$  and so a single orbital Hamiltonian matrix is not possible for the  $s$  and  $d$  orbitals. All gradients for the variation of  $p, s, d$  can, however, be written as a system of equations in terms of banded submatrices:

$$\begin{bmatrix} H^{pp} & H^{ps} & H^{pd} \\ H^{sp} & H^{ss} & H^{sd} \\ H^{dp} & H^{ds} & H^{dd} \end{bmatrix} \begin{bmatrix} p \\ s \\ d \end{bmatrix} = 0, \quad (123)$$

where

$$\begin{aligned} H^{pp} &= c_1^2 (2I + 2R^0(., p; ., p) + 0.08R^2(., p; ., p)) - \varepsilon_{pp} S, \\ H^{ps} &= (2c_1 c_2 / \sqrt{15}) R^1(., p; ., d), \\ H^{pd} &= (2c_1 c_2 / \sqrt{15}) R^1(., p; ., s), \\ H^{ss} &= c_2^2 (I + R^0(., d; ., d)) - \varepsilon_{ss} S, \\ H^{sd} &= 0.2c_2^2 R^2(., d; ., s), \\ H^{dd} &= c_2^2 (I + R^0(., s; ., s)) - \varepsilon_{dd} S \end{aligned} \quad (124)$$

and

$$H^{sp} = (H^{ps})^t, \quad H^{dp} = (H^{pd})^t, \quad H^{ds} = (H^{sd})^t.$$

This symmetric system of equations can be solved by the singular value decomposition method.

Through a generalization of Koopmans' theorem, we have

$$\varepsilon_{aa} = E(\gamma LS) - d_{aa} \quad (125)$$

where now  $d_{aa}$  includes not only the  $E(\gamma; \underline{a})$  and self-energy corrections, but corrections from Slater integrals with one- or three occurrences of orbital  $a$ . Substituting for diagonal energy parameters, Eq. (123) can be cast in the form

$$(\mathbf{H} - E\mathbf{S})\mathbf{a} = 0, \quad (126)$$

where  $\mathbf{H}$  and  $\mathbf{S}$  are matrices of dimension  $3n_s \times 3n_s$  and consist of banded blocks.

Of course, the Newton–Raphson method could also be used but overall quadratic convergence can be achieved only if the expansion coefficients  $c_1, c_2$  are included among the set of unknowns to be determined.

In theory, the orbital expansion coefficients and the CSF expansion coefficients could be improved simultaneously but such an approach has not been tested. Certainly it is feasible for small expansions but for large MCHF CSF expansions of 1–100 thousand configuration states, sparse matrix methods for finding the eigenvalue are preferred.

## 6.2. WITHOUT NORMALIZATION CONSTRAINTS

### 6.2.1. Correlation in the $1s^2$ Ground State

The normalization constraint can readily be removed from the derivation of the HF equations (Froese Fischer, 1977). In fact, unconstrained forms are an easy way of interpreting the meaning of the diagonal energy parameter in an MCHF expansion (Froese Fischer, 2005).

Consider the correlation contribution of  $4f^2$  to the ground state energy of  $1s^2$  from a variational calculation. When orbitals and CSFs are orthonormal, the wave function has the form

$$\Psi = c_1 |1s^2\rangle + c_2 |4f^2\rangle, \quad \text{where } c_1^2 + c_2^2 = 1. \quad (127)$$

In Condon and Shortley phases (Cowan, 1981), the interaction  $\langle 1s^2 {}^1S | \mathcal{H} | 4f^2 {}^1S \rangle$  is negative. Since correlation lowers the energy, the expansion coefficients  $c_1, c_2$  must have the same sign and can be chosen to be positive. Consequently the square root of these coefficients can be absorbed into the definition of the radial function so that the wave function can be written in the unnormalized orbital form as

$$\Psi = |1s^2\rangle + |4f^2\rangle, \quad \text{where } \langle 1s | 1s \rangle^2 + \langle 4f | 4f \rangle^2 = 1. \quad (128)$$

With the constraint that  $\Psi$  be normalized, the energy functional becomes

$$\begin{aligned}\mathcal{F}(\Psi) = & 2S(s, s)I(s, s) + F^0(s, s) + 2S(f, f)I(f, f) + F^0(f, f) \\ & + cG^3(s, f) - E[S(s, s)^2 + S(f, f)^2],\end{aligned}\quad (129)$$

where  $c = -2/\sqrt{7}$  and only the lowest multipole of the  $4f^2$  self-interaction has been included for brevity. The variational equations (in symmetric banded form) become

$$\begin{aligned}& [2S(s, s)I + 2R^0(., s; ., s)]s - [2E S(s, s) - 2I(s, s)]Ss \\ & + cR^3(., s; ., f)f = 0, \\ & cR^3(., f; ., s)s + [2S(f, f)I + 2R^0(., f; ., f)]f \\ & - [2E S(f, f) - 2I(f, f)]Sf = 0.\end{aligned}\quad (130)$$

In this expression,  $E \equiv E(\Psi)$  is the energy of the correlated state. Dividing the first set of equations by  $S(s, s)$  and the second by  $S(f, f)$  in order to put them in the same form as normalized equations, we can identify the coefficient of the  $S$  matrix as the diagonal energy parameter, namely

$$\begin{aligned}\varepsilon_{ss} &= 2[E(\Psi) - I(s, s)/S(s, s)] = 2[E(\Psi) - I(\underline{s}, \underline{s})], \\ \varepsilon_{ff} &= 2[E(\Psi) - I(f, f)/S(f, f)] = 2[E(\Psi) - I(\underline{f}, \underline{f})],\end{aligned}\quad (131)$$

where  $\underline{s}$  and  $\underline{f}$  are the normalized  $s$  and  $f$  orbitals respectively. Along the iso-electronic sequence as  $Z$  increases, the effect of correlation decreases so that  $\underline{s} \rightarrow s$ . Thus, in the limit of infinite  $Z$ ,  $E(\Psi) = E(1s^2)$ , and by definition  $E(1s^2) = I(1s, 1s) + F^0(1s, 1s)$ , from which it follows that

$$2[E(1s^2) - I(s, s)] = E(1s^2) + F^0(1s, 1s),\quad (132)$$

in agreement with the definition of Eq. (24) for  $\varepsilon_{ss}$ . Associated with the  $\underline{f}$  orbital is a pseudo-state,  $|\underline{f}\rangle^2 F$ , for which  $E(\underline{f}) = I(\underline{f}, \underline{f})$ . Then

$$\varepsilon_{ff}/2 = [E(\Psi) - E(\underline{f})]\quad (133)$$

represents the distance of this pseudo-state from the correlated ground state and clearly is not a binding energy. Figure 6 shows that  $I(\underline{f}, \underline{f})$  is a positive and increasing function of  $Z$  as the nuclear charge increases. Thus the one-electron  $4f$  pseudo-state lies in the continuum for all  $Z$ .

As another example, consider the natural orbital expansion of the two-electron  $^1S$  ground state of Eq. (54), generalized to include a sum on  $l$ . With a positive coefficient for  $\Phi(1s^2)$ , the expansion coefficients have the sign  $(-1)^l$  in Condon and Shortley phases. As a result, the wave function can be expression in terms of

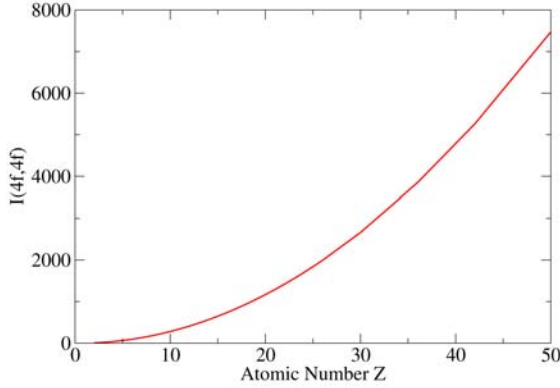


FIG. 6. The value of  $I(4f, 4f)$  for the correlation orbital of the  $4f^2\ ^1S$  CSF representing correlation in the  $1s^2\ ^1S$  ground state of the He-like isoelectronic sequence.

unnormalized orbitals as

$$\Psi(1s^2\ ^1S) = \Phi(1s^2\ ^1S) + \sum_{n>2} \sum_l (-1)^{l+1} \Phi(nl^2\ ^1S), \quad (134)$$

without the need for matrix diagonalization. If the wave function is not normalized, the variational condition needs to be applied to

$$\langle \Psi(1s^2) | \mathcal{H} | \Psi(1s^2) \rangle / \langle \Psi(1s^2) | \Psi(1s^2) \rangle,$$

augmented with off-diagonal Lagrange multipliers for orthogonality. This is equivalent to introducing the total energy  $E$  as a Lagrange multiplier for the normalization constraint on the wave function. In the simple case where only  $1s^2$  and  $2s^2$  are included in the expansion, the expression for the energy functional becomes (Froese Fischer et al., 1992):

$$\begin{aligned} \mathcal{F}(a, b, E, \varepsilon_{ab}) = & 2S(a, a)I(a, a) + 2S(b, b)I(b, b) \\ & + F^0(a, a) + F^0(b, b) - 2G^0(a, b) \\ & - E[S(a, a)^2 + S(b, b)^2] - 2\varepsilon_{ab}S(a, b). \end{aligned} \quad (135)$$

Table VII shows the rapid convergence for He and  $H^-$ . Initial estimates were assumed to be hydrogenic orbitals with charge  $Z = 2$  for He, and  $Z = 0.5$  for  $H^-$ . No explicit rotations were imposed. But this is a rather special case.

### 6.2.2. Singly Occupied Shells and Rydberg Series

The expansion coefficient of a CSF can always be absorbed into the definition of one singly occupied orbital of the CSF, provided the orbital is not occupied in any

Table VII  
Convergence of the Newton–Raphson Method for  $(1s^2, 2s^2)$  Approximation to  
the  $1s^2$  Ground State of He and  $H^-$  with  $k_s = 6$  and  $h = 1/8$  (from Froese  
Fischer et al., 1992)

Iteration	He		$H^-$	
	$\Delta P$	$ VT + 2 $	$\Delta P$	$ VT + 2 $
1	1.6(−1)		2.0(−1)	
2	2.1(−2)		2.6(−2)	
3	3.8(−4)	1.2(−7)	1.0(−3)	
4	7.8(−8)	2.0(−13)	5.2(−6)	
5	5.3(−15)	2.0(−13)	1.8(−10)	3.0(−13)

other CSF of the MCHF expansion. The orbital then is no longer normalized. Let us reconsider Eq. (122). Suppose we assume  $3p$  and  $3s$  are known, normalized orbitals and that  $c_2$  is absorbed into the definition of  $d$  so that effectively,  $c_2 = 1$ . What has changed is the definition of  $H_{22}$  in that  $I(s, s)$  must be replaced by  $I(s, s)S(d, d)$  and, for the variational process, the normalization constraint on the  $d$ -orbital needs to be replaced by the normalization constraint on the wave function, namely  $-E[c_1^2 + S(d, d)]$ . In this formulation,  $c_1$  and  $d$  can be determined from a generalized matrix-eigenvalue problem,

$$\left( \begin{bmatrix} H_{11} & (2/\sqrt{15})R^1(., s; p, p)^t \\ (2/\sqrt{15})R^1(., s; p, p) & H_{22} \end{bmatrix} - E \begin{bmatrix} 1 & 0 \\ 0 & S \end{bmatrix} \right) \begin{bmatrix} c_1 \\ d \end{bmatrix} = 0 \quad (136)$$

where  $H_{22} = I(s, s)S + I + R^0(., s; ., s) + 0.2R^2(., s; s, .)$ . The multiple solutions of this eigenvalue problem represent members of the  $3snd$  Rydberg series that include the interaction with  $3p^2$ . For each energy, there will be a different  $c_1$  and  $d$ -expansion for the orbital. It is still possible to obtain variational solutions for  $p, s$  orbitals, but it will be necessary to decide how many members of the Rydberg series are to be considered. For only one, say  $d^{(1)}$ , we could define  $c_2 = \sqrt{S(d^{(1)}, d^{(1)})}$  and  $d = d^{(1)}/c_2$  and solve the equations for  $p, s$  orbitals of Eq. (123) with  $d$  known. If the  $s, p$  orbitals are to be optimized on more than one eigenstate, it is necessary to generalize the optimization process. If in the present case,  $s, p$  are to be optimized for the first two members of the Rydberg series, then two Rydberg orbitals need to be normalized, and the energy expression assumed to be a linear combination of two energy expressions, one for the lowest state and one for the second.

This method can be generalized to wave functions with interacting Rydberg series as in

$$\begin{aligned} \Psi(^{1,3}P) = & c_1 \Phi(3s3p^3\ ^{1,3}P) + \Phi(3s^23pns\ ^{1,3}P) \\ & + \Phi(3s^23pn'd\ ^{1,3}P), \end{aligned} \quad (137)$$

where now  $ns$  and  $n'd$  refer to Rydberg orbitals. Such calculations are performed with the orbitals for the  $3s3p^3$  “perturber” and the  $3s^2$  “target” fixed (not varied). This case differs from the previous one in that the  $ns$  Rydberg orbitals need to be orthogonal to the fixed  $3s$  orbital. Applying the variational procedure of Eq. (129) and that of the approximation of Eq. (121) ignoring orthogonality initially, leads to equations of the form

$$\left( \begin{bmatrix} H_{11} & (H_{21}^s)^t & (H_{31}^d)^t \\ H_{21}^s & H_{22}^{ss} & H_{23}^{sd} \\ H_{31}^d & H_{32}^{ds} & H_{33}^{dd} \end{bmatrix} - E \begin{bmatrix} 1 & 0 & 0 \\ 0 & S & 0 \\ 0 & 0 & S \end{bmatrix} \right) \begin{bmatrix} c_1 \\ s \\ d \end{bmatrix} = 0. \quad (138)$$

In this notation, the matrices  $H_{ij}^{ab}$  are such that  $H_{ij}^{ab}b = H_{ij}^a$  where the latter is the column vector obtained by varying the matrix element  $\langle i|\mathcal{H}|j \rangle$  with respect to orbital  $a$ . The orthogonality between the Rydberg orbital  $ns$  and the fixed  $3s$  orbital can readily be included through the use of projection operators. Let  $a$  refer to  $3s$  orbital. The Lagrange multiplier for the orthogonality condition  $S(a, s) = 0$ , can again be eliminated by multiplying the second “superrow” of submatrices for the  $s$  row by  $(1 - Saa^t)$  on the left. To symmetrize we can multiply the second “supercolumn” of submatrices by  $(1 - aa^t S)$  since this column is multiplied by the vector  $s$  and  $(1 - aa^t S)s = s$ .

In general, this method assumes that there are a set of orbitals that appear in many CSFs, say the orbital set, and Rydberg “channels” which are singly occupied and appear in some subset of CSFs. Let us refer to the  $(N - 1)$  electron CSFs that couple to a Rydberg channel as a “target” state and the unnormalized channel function as  $|n_j l_j\rangle$ . Then, the wave function expansion consists of  $N$ -electron CSFs or “pseudo-states” defined in terms of normalized radial functions, and targets coupled with channel functions, namely

$$\Psi(\gamma LS) = \sum_i^{M_p} c_i \Phi(\gamma_i LS) + \sum_j^{M_c} \underline{\Phi}(t_j LS), \quad (139)$$

where  $M_p$  and  $M_c$  are the number of pseudo-states and channel functions, respectively, and

$$\underline{\Phi}(t_j LS) = |(\text{target})_j \cdot |n_j l_j\rangle LS\rangle. \quad (140)$$

Our notation implies that the channel function is coupled to the target function according to the usual angular momentum rules to form an anti-symmetric eigenfunction of the total  $L$  and  $S$ . With the orbitals of the  $N - 1$  targets fixed, this method is referred to as the “frozen cores” approximation (Creels et al., 1978), but the term “target” is preferred here since in many calculations it is convenient to

have only one common “core”. In this method, a wave function typically has many targets. A description of the application of this method to the study of Rydberg series in Ca, extended to the Breit–Pauli Hamiltonian and neglecting the background interaction with the continuum, can be found in [Brage and Froese Fischer \(1994a, 1994b\)](#) where orthogonality constraints are imposed without symmetrization. It has also been applied by [Brage et al. \(1992\)](#) to the study of photodetachment and photoionization cross-sections for  $H^-$  and He for the excited states in the continuum and by Xi et al. to photodetachment in both  $He^-$  ([Xi and Froese Fischer, 1999a](#)) and  $Be^-$  ([Xi and Froese Fischer, 1999b](#)). Besides the grid which needs to be equally spaced at large  $r$  for continuum wave functions, what distinguishes the continuum problem is that there is a boundary condition only at the nucleus for a given orbital, the wave function is not normalized, and the energy is specified. By applying the Galerkin method to the Schrödinger equation

$$(\mathcal{H} - E)\Psi = 0, \quad (141)$$

equations similar to those derived by variational methods are obtained (see [Froese Fischer and Idrees, 1989](#), where the simple case for hydrogen scattering is explained). With no boundary condition at a large radius, the coefficient matrix is not quite symmetric. Though in these early publications the systems of equations were solved by inverse iteration, they could be solved by singular value decomposition, the solution being the one for the eigenvalue nearest to zero.

### 6.3. WITHOUT ORTHOGONALITY CONSTRAINTS

Relaxation of the orthogonality constraint can have large benefits with a modest increase in complexity, provided non-orthogonality is used judiciously. For example, in a study of Rydberg series between the  $4s^2S$  and  $3d^2D$  ionization limits of calcium, six targets were identified ([Brage and Froese Fischer, 1994a](#)):

$$3d^2D, \quad 4p^2P, \quad 5s^2S, \quad 4d^2D, 5p^2P, \quad 4f^2F$$

which are the six lowest levels above  $4s$  in  $Ca^+$ . The channel functions included  $3dns_1$  and  $5sns_2$  where  $\langle ns_1 | ns_2 \rangle \neq 0$ . Because of the different targets, much better results are obtained if  $ns_1$  is not required to be the same as  $ns_2$ . The 1991 version of MCHF ([Froese Fischer, 1991a](#)) allowed a limited amount of non-orthogonality for which the energy expressions never required more than two overlap integrals and was sufficient for the calcium study. Calculations were done in the Breit–Pauli approximation. Methods for computing Breit–Pauli integrals are discussed in [Brage and Froese Fischer \(1994b\)](#). More recently, [Zatsarinny \(2006\)](#) has developed determinantal methods where many constraints are removed. In particular, channel functions are not required to be orthogonal to the core with the consequence that the target functions may be MCHF wave functions



for an  $(N - 1)$ -electron state. Typically the orbitals and expansion coefficients for targets are not varied. The Slater matrix element cell methods have been extended to the Breit–Pauli integrals.

#### 6.4. SPLINE ORBITAL BASIS METHODS: CI AND PERTURBATION THEORY

One advantage of spline orbitals is related to the fact that they form an effectively complete, orthonormal set of relatively modest size (Johnson and Saperstein, 1986). Variational methods usually find only one or possibly a few eigenvalues of an orbital Hamiltonian  $H^a$  but the equation for any singly occupied orbital can be used to generate an orthonormal spline basis. Landtman and Hansen (1993) used this basis to study the strong interactions between perturbers and Rydberg series such as between the perturber  $3s3p^5\ ^3P$  and the  $3s^23p^3ns\ ^3P$  and  $3s^23p^3n'd\ ^3P$  Rydberg series in SI. In the Hartree–Fock approximation  $3s3p^5\ ^3P$  is predicted to lie above the  $3s^23p^3\ ^4S$  limit but correlation with the continuum lowers the energy to where it becomes a bound state. They claim that starting with a fixed Hartree–Fock core is preferable to a model potential.

Alternatively, the variational methods could be used to determine major components of a wave function, and then a spline orbital basis could be used to determine small corrections to first-order. Vilkas et al. (1998) use multi-reference Möller–Plesset many-body perturbation theory for relativistic calculations Vilkas and Ishikawa (2004a, 2004b) to improve variational results.

Another way of combining variational calculations with perturbation theory is to modify the CI process. In fact, this would stabilize the variational calculation where convergence slows down significantly when many small effects need to be determined. Let  $x$  be the CSF expansion vector for a variational calculation where  $H^{00}x = E^0x$  defines the zero-order approximation with  $x^tx = 1$ . The CSFs in this expansion are the zero-order set of CSFs. Let  $y$  be the CSF expansion vector for the first-order approximation determined to first order. The CSFs in this expansion are in the first-order set. Then the CI problem for the combined set is

$$\begin{bmatrix} H^{00} & H^{01} \\ H^{10} & H^{11} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = (E^0 + E^1) \begin{bmatrix} x \\ y \end{bmatrix}, \quad (142)$$

where  $H^{01}$  is the matrix of interaction matrix elements between the zero-order and first-order sets, and  $H^{11}$  the matrix of interaction matrix elements within the first-order set. In a first-order calculation the latter may be replaced by the diagonal matrix  $D$  for which  $D_{ii} = H_{ii}^{11}$ . Retaining terms to first-order we get

$$\begin{aligned} H^{00}x + H^{01}y &= (E^0 + E^1)x \quad \text{or} \quad E^1 = x^t H^{01}y, \\ H^{10}x + Dy &= E^0y \quad \text{or} \quad y = (E^0 - D)^{-1} H^{10}x. \end{aligned} \quad (143)$$

The CSFs in the first-order set could include all CSFs that can be constructed by the excitation of one or two orbitals from the zero-order to the first-order orbital set. Since angular data is independent of the principle quantum number, considerable simplification can be introduced as shown by Ellis et al. (2004).

Once the first-order corrections have been determined, the CSF expansions can be normalized and used in the calculation of other atomic properties.

## 6.5. DIRECT EXPANSIONS IN PRODUCTS OF B-SPLINES FOR THE MANY-ELECTRON CASE

Traditional multiconfiguration configuration-interaction methods expand a wave function in terms of orbitals that are orthonormal. This approach provides physical insight about a state in that often a wave function can be labelled by its dominant component and its properties predicted in qualitative (though not quantitative) manner. Orthonormality also provides mathematical convenience.

Direct expansions in a basis consisting of products of B-splines have not been carefully investigated. Such methods would have to deal with non-orthogonal basis functions, but could have advantages. Given a zero-order approximation, the first-order corrections consist of excitations  $(a, b) \rightarrow (v, v')$  where  $(a, b)$  are occupied orbitals and  $(v, v')$  are virtual orbitals. The sum of CSFs for the excitation from a given pair of occupied orbitals can be expressed as symmetry adapted, two-electron, pair-correlation functions. These are linear combinations of two-electron partial waves  $\Psi^P$  characterized by the orbital angular momenta and their LS coupling, namely

$$\Psi^P(l'l'LS) = \sum_v \sum_{v'} c_{vv'l'l'} |vlv'l'LS\rangle. \quad (144)$$

By definition,

$$|vlv'l'LS\rangle = \mathcal{N} \frac{1}{r_1 r_2} (1 - \mathcal{P}_{12}) P(vl; r_1) P(v'l'; r_2) |l'l'LS\rangle, \quad (145)$$

where  $\mathcal{N}$  is a normalization factor that may depend on symmetry,  $\mathcal{P}_{12}$  a permutation operator,  $|l'l'LS\rangle$  a spin-angular factor, and  $P(vl; r)$  and  $P(v'l'; r)$  are orbital radial functions. Substituting into Eq. (144) and noting that each term has the same spin-angular factor, that the double sum is an expansion in a basis of a function of two variables, we get

$$\Psi^P(l'l'LS) = \mathcal{N} \frac{1}{r_1 r_2} (1 - \mathcal{P}_{1,2}) p(r_1, r_2) |l'l'LS\rangle. \quad (146)$$

We can treat  $p(r_1, r_2)$  as a general two-dimensional function, usually expanded in terms of orbitals but one that could also be expanded in terms of tensor products

of B-spline basis functions, namely

$$T_{ij}(r_1, r_2) = B_i(r_1)B_j(r_2). \quad (147)$$

The advantage of this basis is the local support (non-zero region) compared with products of orbitals which extend over the entire two-dimensional region.

A 1974 correlation study of the  $1s^2 2s^2 \text{Be } ^1S$  ground state used a pair-correlation approach in terms of orbitals that were non-orthogonal between different pairs (Saxena and Froese Fischer, 1974). SD-excitations from this zero-order approximation lead to four pair-correlation functions depending on the two occupied orbitals and their coupling that enter into the excitation, namely  $1s^2 ^1S$ ,  $1s2s ^1S$ ,  $1s2s ^3S$ , and  $2s^2 ^1S$ . For each expansion, a reduced form (like the natural orbital expansion for the  $1s^2$  ground state of helium) was used. By this method, 99.1% of the correlation energy was accounted for in 52 CSFs yielding a total energy of  $-14.66587$  au. The best estimate today is  $-14.667355748$  au from an exponentially correlated Gaussian wave function (Pachuki and Komasa, 2006).

Pair functions are similar to wave functions for the 2-electron case. The feasibility of B-spline tensor-product expansions for  $1s^2$ ,  $1s2s ^{1,3}S$ , and  $1s2p ^{1,3}P$  states was studied in 1991 (Froese Fischer, 1991b). Of interest at the time was performance on parallel vector processors. Of greater importance here is the accuracy of the energy as a function of grid parameters. Shown in Fig. 7 is the log

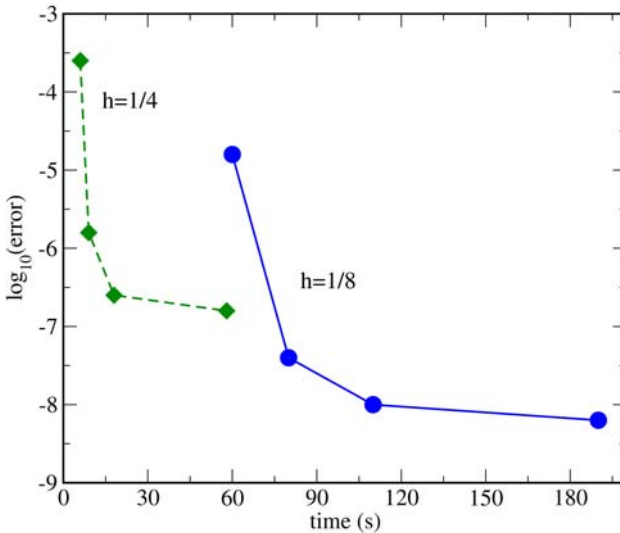


FIG. 7. The accuracy of the total energy for the  $l = 0$  partial wave for the helium  $1s^2$  ground state as a function of CPU time for various grid parameters. The dashed curve shows increasingly more accurate results for  $k_s = 3, 4, 5, 6$  and  $h = 1/4$  whereas the solid curve shows similar results for  $h = 1/8$  (from Froese Fischer, 1991b).

of the error as a function of computer time for various grid parameters. Of particular importance is the size of the step-size parameter  $h$ . Notice the significant improvement in accuracy as the step-size parameter is reduced from  $h = 1/4$  to  $h/8$ . This paper used differential equation methods for computing the B-spline Slater matrix elements which may partly explain this observation.

It is important to remember that correlation is a correction to the wave function that increases the binding of the outer electron. No increase in box-size is needed unless it increases the accuracy of the HF solution. Of particular importance is the region  $r_1 = r_2$ . For states like  $1s^2$  where both electrons share the same region of space, exceedingly high values of  $l$  are needed because of the slow convergence with respect to  $l$ . For expansions up to  $l = 7$  the errors in the total energy (in micro-Hartrees), are (Froese Fischer, 1991b):

State:	$1s^2\ ^1S$	$1s2s\ ^1S$	$1s2s\ ^3S$	$1s2p\ ^1P$	$1s2p\ ^3P$
Error (mH):	50.1	3.0	0.1	2.6	0.1

Considerably more correlation remains for the  $1s^2$  state than for the others and, given slow convergence with  $l$  for the energy of the ground state, computed energies are usually extrapolated. With B-splines, the expansions could be restricted to the correlation region. Consider the wave function for the  $1s2p\ ^1P$  state that can be expressed in terms of partial waves as

$$\Psi(^1P) = \frac{1}{2r_1r_2} \sum_l (1 - \mathcal{P}) p^{(l)}(r_1, r_2) |ll'\ ^1P\rangle, \quad l' = l + 1. \quad (148)$$

In orbital methods,

$$p^{(l)}(r_1, r_2) = \sum_n \sum_{n'} c_{n,n'}^{(l)} P(nl; r_1) P(n'l'; r_2) \quad (149)$$

whereas in a direct B-spline expansion, it is

$$p^{(l)}(r_1, r_2) = \sum_i \sum_j c_{i,j}^{(l)} B_i(r_1) B_j(r_2). \quad (150)$$

These two expressions are equivalent in a complete orbital spline basis expansion, but there will be differences as soon as summations are truncated as is frequently done in spline orbital methods for a many-electron atom (see Chen et al., 2001, as an example).

Figure 8 shows the matrix of coefficients  $c_{i,j}^{(l)}$  for B-spline tensor-product expansions for  $l = 0, 1, 2, 3$  from left to right and top to bottom, respectively. Notice that each subgraph has a different scale with the maximum value decreasing. The modest decrease going from  $l = 2$  to  $l = 3$  is consistent with the slow rate of convergence with  $l$ . For  $l = 0$ , the matrix is approximately the cross-product of the expansions for the  $1s$  and  $2p$  Hartree-Fock orbitals with the maximum at

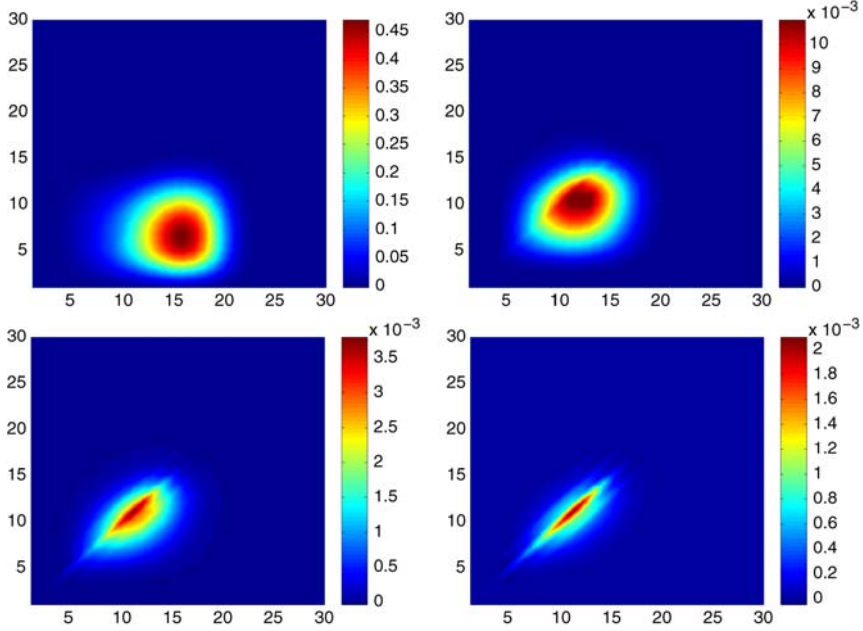


FIG. 8. A visualization of the magnitude of the matrix of expansion coefficients  $c_{i,j}^l$ ,  $\{i, j\} = 1, \dots, 30$  for the  $1s2p^1P$  state of helium. Shown, from left to right and top to bottom, are the expansion coefficients for the  $sp$ ,  $pd$ ,  $df$ , and  $fg$  partial wave functions. The maximum values are 0.45, 0.010, 0.0035, 0.0020, respectively. Note both the changing region and the decreasing maximum magnitude of each partial wave.

$r_1 = 0.707$ ,  $r_2 = 2.05a_0$  resulting in an off-diagonal maximum for the  $l = 0$  partial wave. As  $l$  increases, the maximum coefficient moves closer to  $r_1 = r_2$ . But more importantly, the significant components (that take into account the scale) are concentrated in a smaller and smaller region. In fact, correlation is correcting the electron–electron cusp condition first defined by Kato (1957). For two-electron systems the latter is the condition (Qiu et al., 1997)

$$\left( \frac{\partial(\Psi(\mathbf{r}_1, \mathbf{r}_2))}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \Psi(\mathbf{r}_1 = \mathbf{r}_2, \mathbf{r}_2) \quad (151)$$

and depends on what, in density functional theories (Gori-Giorgi and Savin, 2006), is referred to as “short-range correlation”. This means that orbital expansions, where high- $n$  orbitals oscillate and extend over the entire range, must deal with extensive cancellation in regions where the partial wave is near zero. At the same time, because of their local support, B-spline tensor-products can safely be restricted to the region of importance. First-order perturbation theory could be used to determine in advance whether a certain basis element should be included.

At the same time, this example shows why numerical accuracy is so important for correlation contributions. As  $l$  increases, the region around  $r_1 = r_2$  contributes most to the correlation correction, and the accuracy depends more and more on the accuracy of the contribution from the diagonal cells to the Slater matrix elements. Thus the inclusion of the B-spline tensor-product basis provides a number of computational advantages that could be exploited.

## 7. Conclusion

This paper has reviewed variational methods in atomic structure calculations. It has been shown that differential equations with their many special cases can be eliminated and replaced by more robust linear algebra and symmetric eigenvalue problems. Through the use of B-spline expansions, Hartree–Fock orbitals can be defined as solutions of a generalized eigenvalue problem,  $(H^a - \varepsilon_{aa}S)a = 0$ , once orthogonality issues have been dealt with. Iterative self-consistent methods are still needed in that the “Hartree–Fock Hamiltonians”  $H^a$  depend on the other orbitals. When orthogonality conditions are significant or excited states are needed, this would be the most effective method for getting good estimates of orbitals. Once such estimates have been obtained, a number of orbitals may be updated simultaneously by expressing the equations in terms of blocks of banded submatrices for which the generation of submatrices is most efficient. Methods based on generalized singular decomposition may be used that are able to incorporate orbital rotations. For special cases, the Newton–Raphson method may be used, but with this method, the submatrices are usually dense. Thus a number of strategies are available for solving the Hartree–Fock problem.

Unlike the Hartree–Fock problem, multiconfiguration Hartree–Fock orbitals cannot always be represented as solutions of a symmetric, generalized eigenvalue problem for a given orbital, but they can be expressed as solutions of systems of banded submatrices. When normalization conditions can be relaxed, calculations for Rydberg series can be expressed as generalized eigenvalue problems, calculations that can be improved significantly through the use of non-orthogonal orbitals as implemented in BSR methods (Zatsarinny, 2006).

B-spline methods present many opportunities. Calculations can be done to low accuracy through the use of larger intervals through the parameter  $h$  and lower spline order  $k_s$ . A variety of methods may be applied. Because a spline function can be evaluated at any point in the interval, a low-order spline approximation can be redefined on a different grid and improved with a higher-order spline calculation, similar to multigrid methods for partial differential equations (Wesseling, 1992). Many options can be applied.

Though this discussion has dealt solely with the non-relativistic case, it applies also to the Dirac–Coulomb Hamiltonian ( $H_{\text{DC}}$ ) and Dirac–Coulomb–Breit

Hamiltonian ( $H_{\text{DCB}}$ ). Many of the convergence problems encountered in the General Relativistic Atomic Structure Package (GRASP92) (Parpia et al., 1996) are associated with initial estimates of inadequate accuracy. The simplest option in this code determines orbitals from a Thomas–Fermi potential. These are not good estimates for correlation orbitals that often may have a high principal quantum number. When instead MCHF (Froese Fischer, 1991a) orbitals are considered, converted to relativistic form to lowest-order, convergence often is achieved. Other problems are associated with node counting, something not needed for solutions of a generalized eigenvalue problem. Spline orbitals for highly excited states can be computed to considerably better accuracy than differential equation methods (Froese Fischer and Parpia, 1993).

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