



A B-spline Hartree–Fock program [☆]

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ABSTRACT

A B-spline version of a Hartree–Fock program is described. The usual differential equations are replaced by systems of non-linear equations and generalized eigenvalue problems of the form $(H^a - \varepsilon_{aa}B)P_a = 0$, where a designates the orbital. When orbital a is required to be orthogonal to a fixed orbital, this form assumes that a projection operator has been applied to eliminate the Lagrange multiplier. When two orthogonal orbitals are both varied, the energy must also be stationary with respect to orthogonal transformations. At such a stationary point, the matrix of Lagrange multipliers, $\varepsilon_{ab} = (P_b|H^a|P_a)$, is symmetric and the off-diagonal Lagrange multipliers may again be eliminated through projection operators. For multiply occupied shells, convergence problems are avoided by the use of a single-orbital Newton–Raphson method. A self-consistent field procedure based on these two possibilities exhibits excellent convergence. A Newton–Raphson method for updating all orbitals simultaneously has better numerical properties and a more rapid rate of convergence but requires more computer processing time. Both ground and excited states may be computed using a default universal grid. Output from a calculation for Al $3s^23p^2P$ shows the improvement in accuracy that can be achieved by mapping results from low-order splines on a coarse grid to splines of higher order onto a refined grid. The program distribution contains output from additional test cases.

Program summary

Program title: SPHF version 1.00

Catalogue identifier: AEIJ_v1_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEIJ_v1_0.html

Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland

Licensing provisions: Standard CPC license, <http://cpc.cs.qub.ac.uk/licence/licence.html>

No. of lines in distributed program, including test data, etc.: 13 925

No. of bytes in distributed program, including test data, etc.: 714 254

Distribution format: tar.gz

Programming language: Fortran 95

Computer: Any system with a Fortran 95 compiler. Tested on Intel Xeon CPU X5355, 2.66 GHz

Operating system: Any system with a Fortran 95 compiler

Classification: 2.1

External routines: LAPACK (<http://www.netlib.org/lapack/>)

Nature of problem: Non-relativistic Hartree–Fock wavefunctions are determined for atoms in a bound state that may be used to predict a variety atomic properties.

Solution method: The radial functions are expanded in a B-spline basis [1]. The variational principle applied to an energy functional that includes Lagrange multipliers for orthonormal constraints defines the Hartree–Fock matrix for each orbital. Orthogonal transformations symmetrize the matrix of Lagrange multipliers and projection operators eliminate the off-diagonal Lagrange multipliers to yield a generalized eigenvalue problem. For multiply occupied shells, a single-orbital Newton–Raphson (NR) method is used to speed convergence with very little extra computation effort. In a final step, all orbitals are updated simultaneously by a Newton–Raphson method to improve numerical accuracy.

[☆] This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

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Restrictions: There is no restriction on calculations for the average energy of a configuration. As in the earlier HF96 program [2], only one or two open shells are allowed when results are required for a specific LS coupling. These include:

1. $(nl)^N n's$, where $l = 0, 1, 2, 3$
2. $(np)^N n'l$, where $l = 0, 1, 2, 3, \dots$
3. $(nd)(n'f)$

Unusual features: Unlike HF96, the present program is a Fortran 90/95 program without the use of COMMON. It is assumed that Lapack libraries are available.

Running time: For $Ac\ 7s^2 7p^2 P$ the execution time varied from 6.9 s to 9.1 s depending on the iteration method.

References:

[1] C. Froese Fischer, Adv. At. Mol. Phys. 55 (2008) 235.

[2] G. Gaigalas, C. Froese Fischer, Comput. Phys. Commun. 98 (1996) 255.

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LONG WRITE-UP

The HF86 [1] program and its extension HF96 [2], which includes partially filled f-shells, were derived from the MCHF77 [3] program that implemented the numerical procedures described by Hartree [4]. But Hartree's calculations, done with the aid of a desk calculator, were generally developed for ground state or near ground state configurations. A general computer code needs to deal with multiple off-diagonal Lagrange multipliers arising from orthogonality constraints, the fact that the self-consistent field (SCF) process might not converge, and that the equations had multiple solutions. Node counting was introduced as a means of control, but node counting is an art – off-diagonal Lagrange multipliers might produce an extra node with a small amplitude in the tail. Similarly intermediate orbitals with high angular momenta might have an extra node near the origin for a few iterations and then disappear as the solutions converge. Hartree viewed the problem as a system of second-order, homogeneous, integro-differential equations. The SCF process replaced this by a system of second-order differential equations in which off-diagonal Lagrange multipliers and the exchange terms defined the non-homogeneous part of the differential equation, with quite different mathematical properties. These equations could often, but not always, be solved readily using finite differences on equally spaced points. The latter was a limitation that was largely circumvented by transforming the equations to ones where the independent variable was $\rho = \log Zr$ and the dependent variable was $P(nl; r)/\sqrt{r}$, where $P(nl; r)$ is the radial function for an orbital. All this added to the complexity of the program. Users think of the problem in the standard form but need to be aware of the transformations when modifying the code.

With the development of faster computers with considerably more memory, an interesting question arises – what is the best method for solving the Hartree–Fock (HF) equations? A program implementing such a method should be flexible, easy to modify, and allow the user to control the accuracy of the desired solution. The present program, based on the use of B-splines, is an attempt at this goal.

A recent article on B-splines in variational atomic structure calculations [5] begins with a review of Hartree–Fock theory as derived by Hartree and discusses the $1s2s\ ^1S$ case, one of the most difficult to solve by the HF86 program because of the large, off-diagonal Lagrange multiplier. In fact, it is an artificial mathematical problem in that the difficulty disappears as soon as $1s^2$ is included in a multiconfiguration Hartree–Fock (MCHF) calculation making $1s2s$ the second eigenstate. The article then describes the solution of the equations using B-splines together with the Galerkin method [6]. However, differential equations can be avoided entirely, the approach taken in this paper.

For a detailed introduction to the background theory of B-splines and their application to atomic physics, the reader is referred to the review article by Bachau et al. [7].

1. B-spline methods for Hartree–Fock wavefunction

Given a grid of strictly increasing knots [8], t_i , $i = 0, \dots, n_v$, $t_{i-1} < t_i$, where t_0 and t_{n_v} are knots of multiplicity k_s , the B-spline functions $B_i(r)$, $i = 1, n_s$ form a basis for piecewise polynomial functions that are polynomials of degree $k_s - 1$ in each interval and whose derivatives up to order $k_s - 2$ are continuous at the interior knots. The number of basis elements is $n_s = n_v + k_s - 1$ where each basis function is non-zero over k_s adjacent intervals. Furthermore, only $B_1(r)$ is non-zero at $r = t_0$ and $B_{n_s}(r)$ is non-zero at $r = t_{n_v}$. For atoms, $t_0 = 0$ and the last grid point is referred to as R . Thus the grid defines a sequence of subintervals over the range $[0, R]$.

A radial function for orbital a , say $P(a; r)$, in this piecewise polynomial function space has associated with it a vector $a = (a_1, a_2, \dots, a_{n_s})$ of expansion coefficients so that

$$P(a; r) = \sum_{i=1}^{n_s} a_i B_i(r). \quad (1)$$

Note that as an argument, a simply denotes an orbital, but when orbital properties are described in terms of matrix–vector operations, a refers to the orbital expansion coefficients. For bound orbitals the boundary conditions are $a_1 = a_{n_s} = 0$, but for additional numerical stability we apply two boundary conditions at the end of the range (equivalent to $P(R) = P'(R) = 0$), namely $a_{n_s-1} = a_{n_s} = 0$. Additional boundary conditions could also be applied at the origin to enforce r^{l+1} behavior but has not been applied in this program. The L_2 norm in this function space is

$$|P(a; r)|^2 = a^t B a,$$

where $B = B(i, j)$ is the matrix of overlap integrals,

Table 1

Rules for applying the variational principle to a Hartree–Fock energy functional and the type of contribution.

Integral	$(1/2)\partial/\partial a$	H^a	Type
$I(a, a)$	$I(., a)$	$I(., .)$	banded
$F^k(a, a)$	$2R^k(., a; a, a)$	$2R^k(., a; ., a)$	banded
$F^k(a, b)$	$R^k(., b; a, b)$	$R^k(., b; ., b)$	banded
$G^k(a, b)$	$R^k(., b; b, a)$	$R^k(., b; b, .)$	full

$$B(i, j) = \int B_i(r) B_j(r) dr.$$

It is a symmetric, positive definite, banded matrix of bandwidth $2k_s - 1$.

Let \mathcal{I} be the one-electron radial operator for an orbital with angular momentum l , namely

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

Then the matrix element of this operator between orbitals a and b of the same angular symmetry is

$$\begin{aligned} I(a, b) &= \langle a | \mathcal{I} | b \rangle \\ &= \sum_i a_i \sum_j b_j \langle B_i(r) | \mathcal{I} | B_j(r) \rangle \\ &= a^t I(., .) b \end{aligned} \quad (3)$$

where $I(., .)$ represents matrix elements in the B-spline basis. The notation emphasizes the fact that the matrix elements are between two orbitals. By contrast, Slater integrals depend on four orbitals, namely

$$R^k(a, b; c, d) = \sum_i \sum_j \sum_{i'} \sum_{j'} a_i b_j c_{i'} d_{j'} R^k(i, j; i', j'), \quad (4)$$

where

$$R^k(i, j; i', j') = \int_0^R \int_0^R \frac{r_{\leq}^k}{r_{>}^{k+1}} B_i(r_1) B_j(r_2) B_{i'}(r_1) B_{j'+1}(r_2) dr_1 dr_2 \quad (5)$$

are referred to as B-spline Slater integrals or as Slater matrix elements. The energy functional for a Hartree–Fock wave function is a quartic in the expansion coefficients in that there may be as many as four summations.

The application of the variational principle with respect to a vector of expansion coefficients for a given orbital, eliminates one summation and results in a vector. For example,

$$\partial I(a, b) / \partial a = I(., b) \equiv \sum_j I(., .) b_j = I(., .) b. \quad (6)$$

But the variational principle also takes into account the number of times an orbital appears. Thus

$$\partial I(a, a) / \partial a = 2I(., a) \equiv 2 \sum_j I(., .) a_j = 2I(., .) a. \quad (7)$$

Here the first “dot” refers to the summation eliminated through the variational process, which indicates the row, whereas the application of the definition of matrix–vector multiplication generates the second “dot”. This notation is helpful when dealing with Slater integrals that depend on as many as four radial functions whereas matrices of linear algebra are restricted to two. Table 1 provides the rules for applying the variational principle to Slater integrals in the Hartree–Fock energy expression, eliminating a factor of two in all cases to yield energies in Hartrees (E_h).

Given an energy expression for a Hartree–Fock wavefunction, assuming for the time being that there are no orthogonality constraints, and applying the rules of Table 1 for orbital a , yields the generalized eigenvalue problem

$$(H^a - \varepsilon_{aa} B) a = 0, \quad (8)$$

where H^a and B are matrices of size $n_s \times n_s$ before boundary conditions are applied. When exchange terms are present the matrix H^a is a full matrix. Thus a is the m th eigenvector of the generalized eigenvalue problem, where m depends on the nl quantum numbers and possible orthogonality constraints with $m = 1$ being the lowest eigenvalue satisfying the orthogonality constraints.

When two orbitals, a and b , are constrained through orthogonality and both are varied, Lagrange multipliers $\varepsilon_{aa}, \varepsilon_{ab} = \varepsilon_{ba}, \varepsilon_{bb}$ must be introduced and the equations for the pair become [5]

$$\begin{bmatrix} H^a \\ H^b \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} - \begin{bmatrix} \varepsilon_{aa} & \varepsilon_{ab} \\ \varepsilon_{ba} & \varepsilon_{bb} \end{bmatrix} \begin{bmatrix} Ba \\ Bb \end{bmatrix} = 0, \quad (9)$$

from which it follows that

Table 2Contributions to g and g' for the rotation of orbitals a and b .

Integral	g	g'
$F^k(a, a)$	$-4R^k(a, a; a, b)$	$2F^k(a, b) + 4G^k(a, b) - 2F^k(a, a)$
$F^k(b, b)$	$4R^k(a, b; b, b)$	$2F^k(a, b) + 4F^k(a, b) - 2F^k(b, b)$
$F^k(a, b)$	$2[R^k(a, a; a, b) - R^k(a, b; b, b)]$	$F^k(a, a) + F^k(b, b) - 2F^k(a, b) - 4G^k(a, b)$
$G^k(a, b)$	$2[R^k(a, a; a, b) - R^k(a, b; b, b)]$	$F^k(a, a) + F^k(b, b) - 2F^k(a, b)$
$F^k(a, m)$	$-2R^k(a, m; b, m)$	$F^k(b, m) - F^k(a, m)$
$F^k(b, m)$	$2R^k(a, m; b, m)$	$F^k(a, m) - F^k(b, m)$
$G^k(a, m)$	$-2R^k(a, b; m, m)$	$G^k(b, m) - G^k(a, m)$
$G^k(b, m)$	$2R^k(a, b; m, m)$	$G^k(a, m) - G^k(b, m)$

$$\begin{aligned} \varepsilon_{aa} &= a^t H^a a, & \varepsilon_{ab} &= b^t H^a a, \\ \varepsilon_{ba} &= a^t H^b b, & \varepsilon_{bb} &= b^t H^b b. \end{aligned} \quad (10)$$

The requirement that $\varepsilon_{ab} = \varepsilon_{ba}$ places a condition on the solution, in that it must be stationary with respect to all first order variations. These include excitations but also include perturbations that are orthogonal transformations. They represent the “rotation” of orbitals in orbital space that in 2-dimensional space can be defined in terms of a single parameter $\epsilon \in [-1, 1]$ as in

$$\mathbf{O} = \begin{bmatrix} 1 & -\epsilon \\ \epsilon & 1 \end{bmatrix} / \sqrt{1 + \epsilon^2}, \quad (11)$$

where $1/\sqrt{1 + \epsilon^2} = \cos(\theta)$ and θ represents the angle of rotation. Values of ϵ outside the range $[-1, 1]$ correspond to an interchange of the orbitals. The transformation

$$\begin{bmatrix} P^*(a; r) \\ P^*(b; r) \end{bmatrix} = \begin{bmatrix} 1 & -\epsilon \\ \epsilon & 1 \end{bmatrix} \begin{bmatrix} P(a; r) \\ P(b; r) \end{bmatrix} / \sqrt{1 + \epsilon^2}, \quad (12)$$

allows the effect of a rotation on the energy to be expanded in powers of ϵ , namely

$$E(\epsilon) = E(0) + g\epsilon + g'\epsilon^2 + \text{higher-order terms},$$

where g represents the gradient of the energy with respect to rotation. Then the stationary condition,

$$\partial E / \partial \epsilon = 0 = g + 2g'\epsilon,$$

leads to $\epsilon = -g/(2g')$ as the rotation required for the stationary condition, given the current estimates. Once the orbitals satisfy this condition, the Lagrange multipliers can be eliminated through projection operators [9] leading to a pair of generalized eigenvalue problems:

$$\begin{aligned} [(1 - Bbb^t)H^a(1 - bb^t B) - \varepsilon_{aa}B]a &= 0, \\ [(1 - Baa^t)H^b(1 - aa^t B) - \varepsilon_{bb}B]b &= 0. \end{aligned} \quad (13)$$

Some special cases need to be mentioned. For orthogonality between orbitals of filled shells of the same symmetry, the diagonal energies should be extremum values, for which off-diagonal energies are zero by Koopmans' theorem [10]. When g , and g' are both zero, the energy is invariant under rotations and the same theorem applies. An example is the $1s2s^3S$ wave function.

The contributions to g and g' from the rotation of a pair of orbitals, a and b of the same symmetry, and a spectator orbital m of arbitrary symmetry is shown in Table 2. As iterations converge, a previously computed value of g' may be used, but g needs to be recomputed.

When orbital a is constrained to be orthogonal to a fixed orbital b , the projection operator can be applied directly.

For a singly occupied orbital a , the matrix H^a depends only on other orbitals, and the orbital expansion is an eigenvector of Eq. (8). Multiply occupied orbitals differ in that H^a now also depends on a and the SCF process may not converge [5]. An example is the $2p^5$ configuration in fluorine. If the initial estimate for the $P(2p; r)$ is too contracted, the $2p$ charge distribution will be too contracted and shield the nucleus too much, resulting in an orbital that is too expanded, a process that leads to oscillations. In HF86 an “accelerating” parameter was introduced when oscillations were encountered. In B-spline methods, the Newton–Raphson (NR) method can be used to deal with the “self-interaction”, but the correction to the orbital now comes from a system of linear equations rather than an eigenvalue problem. Furthermore, the NR method converges to the “nearest” energy solution and can be used safely only when reasonably accurate estimates are available. For a single-orbital update process this requirement would be particularly important for multiply occupied excited states.

The SCF process in which orbitals are updated one at a time and $q_{\text{sum}}(i)$ is the occupation number of orbital i , has been implemented as follows:

```

For each orbital i = 1,nwf
  For each orbital j = 1,nwf
    call rotate (i,j), if needed
  compute H
  if qsum(i) =1 or orbital estimates are not accurate,
    call hf_eiv
  else
    call hf_nr

```

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

The stationary condition requires that the gradient vector of the energy functional be zero. If there are 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). Furthermore, each block can be defined to included only banded contributions. The gradient vector for orbital a contains contributions from $I(., a)$, $B(., a)$, $R^k(., b; a, b)$, and $R^k(., b; b, a)$. Then $I(., a) = I(., .)a$, $B(., a) = B(., .)a$, $R^k(., b; a, b) = R^k(., b; ., b)a$ all lead to symmetric, banded matrices, but the contribution from the exchange term can only be expressed in banded form as $R^k(., b; b, a) = R^k(., b; ., a)b$ that requires an off-diagonal block and both a and b must be determined simultaneously.

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

$$\begin{bmatrix} F^{11} & F^{12} & \dots & F^{1m} \\ F^{21} & F^{22} & \dots & F^{2m} \\ \dots & \dots & \dots & \dots \\ F^{m1} & F^{m2} & \dots & F^{mm} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ \dots \\ A_m \end{bmatrix} = 0, \quad (14)$$

where F^{ii} contains the contributions from one-electron integrals, the direct Slater integrals for orbital i , as well as $-\varepsilon_{ii}B$, and F^{ij} ($i \neq j$) contains the contribution from exchange integrals between orbitals i and j and possible orthogonality constraints $-\varepsilon_{ij}B$.

This formulation leads to a homogeneous system of equations with a symmetric coefficient matrix and could be solved using singular-value decomposition (SVD). Simple tests have shown the method to have linear convergence [5]. 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 2×2 case. Multiplying the first row of block matrices, by $(F^{11})^{-1}$ and subtracting F^{21} times this row from the second, we get

$$(F^{22} - F^{21}(F^{11})^{-1}F^{12})A_2 = 0, \quad (15)$$

which can be solved either by inverse iteration or as an eigenvalue problem since F^{22} includes a $-\varepsilon_{22}B$ term. Once A_2 is computed 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. No tests for such a numerical procedure have been performed but, like SVD, the convergence would be linear, in general.

For larger matrices the faster rate of convergence of the NR methods is attractive. When applied to all the orbitals, it is particularly important to have good estimates since small errors in the closed shells have a large effect on the total energy. For example, with screened hydrogenic initial estimates for $3p^2 \ ^3P$ of Mg, the NR method converged *rapidly* to the $4p^2$ energy, this being the nearest total energy from the initial estimates.

The NR procedure for non-linear systems of equations usually 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,

$$F(x) = 0 = F(x^{(m)}) + (\partial F / \partial x) \Delta x + \text{higher-order terms}, \quad (16)$$

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

$$(\partial F / \partial x) \Delta x = -F(x^{(m)}), \quad x^{(m+1)} = x^{(m)} + \Delta x \quad (17)$$

can be shown to have quadratic convergence in most 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 res_a , etc., and the assumption made that estimates are orthonormal.

Consider the case of two orbitals a and b , with an orthogonality constraint between them. Then the unknowns are $(a, b, \varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{ab})$ and the systems of equations are Eq. (9) 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 ε -matrix. If symmetry conditions are not satisfied exactly, we can use the average value,

$$\varepsilon_{ab} = \varepsilon_{ba} = (b^t H^a a + a^t H^b b) / 2. \quad (18)$$

Then Δa and Δb are solutions of

$$\begin{bmatrix} H^{aa} - \varepsilon_{aa}B & H^{ab} - \varepsilon_{ab}B & -Ba & -Bb \\ H^{ba} - \varepsilon_{ab}B & H^{bb} - \varepsilon_{bb}B & -Bb & -Ba \\ -(Ba)^t & & & \\ & -(Bb)^t & & \\ -(Bb)^t & & -(Ba)^t & \end{bmatrix} \begin{bmatrix} \Delta a \\ \Delta b \\ \Delta \varepsilon_{aa} \\ \Delta \varepsilon_{bb} \\ \Delta \varepsilon_{ab} \end{bmatrix} = \begin{bmatrix} -\text{res}_a \\ -\text{res}_b \\ 0 \\ 0 \\ 0 \end{bmatrix}. \quad (19)$$

The NR method allows for some rotation of orbitals but convergence is greatly improved when explicit rotations are performed. The rules for generating H^{aa} , H^{ab} , H^{bb} are presented in Table 3.

The present SPHF program is based on both the SCF process and the NR method in which all orbitals are improved simultaneously. To speed up the calculation, the arrays of Slater matrix elements are stored so that they need to be computed only once for each grid.

Table 3Rules of generating H^{aa} , H^{ab} , H^{bb} for the NR method and the type of matrix contribution: d – banded, x – full.

Integral	$(1/2)\partial/\partial a$	H^a	H^{aa}	Type	H^{ab}	Type
$F^k(a, a)$	$2R^k(., a; a, a)$	$2R^k(., a; ., a)$	$4R^k(., a; ., a)$ $+2R^k(., .; a, a)$	d x		
$F^k(a, b)$	$R^k(., b; a, b)$	$R^k(., b; ., b)$	$R^k(., b; ., b)$	d	$2R^k(., .; a, b)$	x
$G^k(a, b)$	$R^k(., b; b, a)$	$R^k(., b; b, .)$	$R^k(., b; b, .)$ $+R^k(., b; ., a)$	x d	$R^k(., .; b, a)$	x

2. Program structure

The main program, `sphf` defines the various stages of the calculation:

- (1) `open_files` determines whether certain files exist and opens all needed files.
- (2) `read_hf_param` determines parameters that control the calculation. If the file `hf_param` exists, they will be read from the file. Otherwise the values are set to default values found in `MODULE hf_param`.
- (3) `get_case` obtains information about the problem to be solved:
 - (a) `get_atom` obtains information about the atom. If the file `bsw.c` exists, it is read from the file. Otherwise the user is prompted for the name of the atom, LS term (or AV for average energy), the atomic number, the list of closed shells, and the configuration. One of the symbols [He], [Be], [Ne], [Ar], [Kr], [Xe], or [Rn] may be used to designate some or all of the closed shells. The file `bsw.c` will be written for this data so that it does not need to be re-entered when the calculation is rerun. The orbitals are ordered by increasing n and within a given n , by increasing l . If the file `hf_param` does not exist, the program prompts the user for the orbitals to be varied. The responses are keywords `all`, `none` or `=n` where n refers to the last n orbitals in the list, or a space delimited list of orbitals. This may require a re-ordering so that all the fixed orbitals appear before the list of orbitals to be varied in the order specified.
 - (b) `get_energy` determines the energy expression from the configuration and the LS term. The average energy as defined by Slater [11] can be computed for any configuration containing s –, p –, d –, f –, g – electrons. What is needed for specified LS terms is the deviation from the average energy. Tables are used for deviations but are restricted to a single open s –, p –, d –, f – shell or a single s -electron and an open shell. Open p -shells and a single electron are allowed as well as the df configuration.
 - (c) `get_spline_param` determines the grid for spline calculations. If the file `hf_param` exists, parameters h , ks , ns will be read from the file. Otherwise the values are set to default values: $h=0.25$; $ks=4$; $ns=30+2*\text{sqrt}(z)$. The routine `mkgrid` determines a grid with two regions in terms of the variable $t = Zr$, namely:
 - an equally spaced region, $t_i = t_{i-1} + h$ starting at the nucleus and terminating near the maximum of the hydrogenic $1s$ orbital,
 - an exponential region, $t_i = t_{i-1}(1 + h)$.
 The range is extended until a basis of size ns has been achieved. For numerical accuracy, it is recommended that h be an exact binary number. Values of $h = 1/4$ and $h = 1/8$ are default values. A common modification for continuum calculations is to have a third region where the knots are again equally spaced [12].
 - (d) `allocate_orbital_arrays` allocates memory for arrays of orbitals.
- (4) `define_spline` sets up all the spline arrays needed for the spline Galerkin method. These routines are part of the `BSPLINE LIBRARY` [12] with a few modifications.
- (5) For `acc=1`, `acc_max`: This loop controls the accuracy levels of the calculation. In the default mode, the program solves the HF problem for two levels of accuracy. The first level calls `get_estimates` for initial estimates that are of uncertain accuracy, whereas the second level refines the results of the first:
 - (a) `get_estimates` searches for estimates in `bsw.inp`. If the results are for a different Z or from different spline parameters, the data is mapped onto the current spline grid. If the orbital is not found or if `bsw.inp` does not exist, then screened hydrogenic functions are used and orthogonalized to orbitals already found.
 - (b) `refine_grid` uses the results from the current grid where the range is expected to be too large to a more accurate range and, at the same time, refines the grid in a manner that essentially doubles the number of intervals by setting $h = h/2$ and $ks = ks+2$. The latter significantly improves the accuracy of orbitals at the origin. The change of grid requires that spline arrays need to be deallocated and regenerated for the new grid. Slater matrix elements need to be re-evaluated as well.
 - (c) `write_spline_param` displays grid and tolerance parameters to the screen and to the `sphf.log` file.
 - (d) `solve_HF_equations`.
The HF equations are solved mainly by a single-orbital SCF process that calls `rotate`, `hf_matrix`, and either `hf_eiv` or `hf_nr`. In the first iteration when initial estimates are not accurate, `hf_eiv` is preferred in that with this routine the solution is controlled to be a particular eigenvalue whereas the NR method of `hf_nr` converges to the “nearest” solution. The SCF iterations are limited to at most 6 iterations after which, provided all orbitals are to be varied, the program calls `hfall_nr` that updates all orbitals simultaneously until convergence. Finally, for the highest levels of accuracy, the radial functions are written to the file `bsw.out`. If the last orbital is singly occupied, the program writes the one-electron energies and the orbital expansions for the fixed core Rydberg series of the last electron to the file `ryd.bsw`.
- (6) `write_hf_param` writes parameters to the `hf_param` file. This file can then be edited for a rerun without the need for additional input.

3. Example

Our example is an HF calculation for Al [Ne]3s²3p ²P using `sphf_all` where [Ne] designates the neon-like core. Fig. 1 displays the screen output when no input data comes from files (i.e. `bsw.c`, `bsw.inp`, `hf_param` do not exist). Input is provided in response

```

=====
S P L I N E   H A R T R E E - F O C K : 2010
=====

Enter ATOM,TERM,Z (separated by blanks)
>Al 2P 13.

List the CLOSED shells (separated by blanks, * for none)
>[Ne] 3s

Enter electrons outside CLOSED shells (blank line if none)
Example: 2s(1)2p(3)
>3p(1)

WAVE FUNCTIONS FOR      Al    2P    Z = 13.0

      Core = 1s(  2) 2s(  2) 2p(  6) 3s(  2)
Configuration = 3p( 1.0)

There is(are)  5 orbital(s) as follows:
 1s 2s 2p 3s 3p

Orbitals to be varied: ALL/NONE/=i (last i) or "LIST"
>all

Level 1: HF_parameters
-----
Step-size (h)                0.25000
Spline order (ks)             4
Size of basis (ns)            37
Maximum radius                62.14
SCF convergence tolerance     1.00D-12
Orbital convergence tolerance 1.00D-06
Orbital tail cut-off          1.00D-06
Orbitals varied               all

Level  1
-----

Total energy from initial estimates =  -236.053385622390

Iteration 1.01
-----

      nl      E(nl)              AZ          DPM          MAXR
1s   -62.335187696592          91.0927616727      1.29D-02         22
2s   -6.649254832131          25.0383952907      1.03D-01         30
2p   -4.954053720000          76.8639216739      4.60D-01         33
3s   -0.694984930564           5.9733137863      1.24D+00         33
3p   -0.185840491472           7.8160439924      1.09D+00         32

SCF convergence (diff vs tol)          2.11D-02      1.00D-12
Orbital convergence (diff vs tol)       1.24D+00      1.00D-06
Tail cut-off (orbital nwf)              -6.37D-05      1.00D-06
Total energy =  -241.150670172580

Iteration 1.02
-----

      nl      E(nl)              AZ          DPM          MAXR
1s   -57.015473671696          90.4849709655      7.58D-03         24
2s   -4.458329773467          22.9382065849      8.16D-02         29
2p   -3.225857746672          66.6785614672      9.05D-02         31
3s   -0.402972841243           5.5403916219      1.19D-01         32
3p   -0.212802121580          13.4635520589      6.28D-02         32

SCF convergence (diff vs tol)          2.92D-03      1.00D-12
Orbital convergence (diff vs tol)       1.19D-01      1.00D-06
Tail cut-off (orbital nwf)              -2.46D-05      1.00D-06
Total energy =  -241.856754259442

...

```

Fig. 1. Interactive run of SPHF for Al $3s^23p\ ^2P$. Input data is indicated by the > symbol.

Iteration 1.05

nl	E(nl)	AZ	DPM	MAXR
1s	-58.500731992210	90.6573979733	1.64D-06	24
2s	-4.910650695353	23.5691061423	6.53D-05	28
2p	-3.218335167852	66.8223086903	4.22D-06	29
3s	-0.393420344536	5.4418307402	3.01D-05	31
3p	-0.209951121886	12.0098733045	1.10D-05	32

SCF convergence (diff vs tol) 4.26D-10 1.00D-12
 Orbital convergence (diff vs tol) 6.53D-05 1.00D-06
 Tail cut-off (orbital nwf) -2.67D-05 1.00D-06
 Total energy = -241.876624465694

The first phase of Level 1 has converged
 it_max for the second phase set to 0

TOTAL ENERGY (a.u.)	-241.876624465694300
Kinetic	241.876372409537300
Potential	-483.752996875231600
Ratio	-2.000001042086726

Refined grid orbital

1s	max. diff.	1.01D-04	at r =	1.89
2s	max. diff.	1.01D-04	at r =	8.95
2p	max. diff.	5.47D-05	at r =	20.42
3s	max. diff.	5.07D-05	at r =	25.85
3p	max. diff.	3.99D-05	at r =	106.22

Level 2: HF_parameters

Step-size (h)	0.12500
Spline order (ks)	6
Size of basis (ns)	66
Maximum radius	39.55
SCF convergence tolerance	1.00D-15
Orbital convergence tolerance	1.00D-09
Orbital tail cut-off	1.00D-09
Orbitals varied	all

Total energy from initial estimates = -241.876660570345

Iteration 1.01

nl	E(nl)	AZ	DPM	MAXR
1s	-58.501036672967	90.7126103214	3.31D-04	55
2s	-4.910674734267	23.5781014601	7.02D-04	58
2p	-3.218303425684	67.3851912362	4.32D-04	65
3s	-0.393420812639	5.4437999969	9.53D-04	65
3p	-0.209950620081	12.1091451891	6.91D-04	65

SCF convergence (diff vs tol) 1.93D-07 1.00D-15
 Orbital convergence (diff vs tol) 9.53D-04 1.00D-09
 Tail cut-off (orbital nwf) -5.83D-09 1.00D-09
 Total energy = -241.876707250666

Iteration 1.02

nl	E(nl)	AZ	DPM	MAXR
1s	-58.501026523640	90.7126100006	3.40D-08	55
2s	-4.910671664663	23.5780984941	7.83D-07	58
2p	-3.218302973882	67.3852026487	1.74D-07	60
3s	-0.393420422348	5.4437974050	1.08D-06	62
3p	-0.209950740363	12.1091925831	2.59D-07	65

SCF convergence (diff vs tol) 4.63D-14 1.00D-15
 Orbital convergence (diff vs tol) 1.08D-06 1.00D-09
 Tail cut-off (orbital nwf) -5.84D-09 1.00D-09
 Total energy = -241.876707250677

The first phase of Level 2 has converged
 it_max for the second phase set to 2

Fig. 1. (continued)


```

Iteration 2.01
-----
SCF convergence (diff vs tol)      5.41D-14    1.00D-15
Orbital convergence (diff vs tol)  2.26D-08    1.00D-09
Tail cut-off (orbital nwf)        -5.84D-09    1.00D-09
Total energy = -241.876707250679

Iteration 2.02
-----
SCF convergence (diff vs tol)      2.70D-15    1.00D-15
Orbital convergence (diff vs tol)  7.77D-11    1.00D-09
Tail cut-off (orbital nwf)        -5.84D-09    1.00D-09
Total energy = -241.876707250678

TOTAL ENERGY (a.u.)              -241.876707250678000
Kinetic                           241.876707250674100
Potential                         -483.753414501352000
Ratio                             -2.0000000000000016

```

Fig. 1. (continued)

to prompts. Note that the occupation number is not an integer but a real number. The present program has inherited the capability of computing orbitals for a combination of two configurations but without any interaction between them. The configuration $3p(0.5)3d(0.5)$ would be interpreted as an average of $3p$ and $3d$. The LS term would now have to be AV (see [1] for more details).

The default parameters assume the purpose of the first level is to get reasonable estimates and determine the range for the orbitals. The convergence parameters are modest. Note that the basis size is 37. The SCF iterations of the first level display the orbital parameters, $E(nl) = \varepsilon_{aa}/q\text{sum}(a)$, $AZ = P_a(r)/r^{a+1}$, $r = 0$, $DPM = \max |P(\text{new}) - P(\text{old})| / \max |P(\text{old})|$ and $MAXR = i$ where $i - 1$ is the last value for which a_{i-1} is greater than the tail cut-off parameter and the expansion coefficients a_j , $j = i, \dots, n_s$ are set to zero. Parameters summarizing convergence are displayed: SCF convergence is the relative change in energy, orbital difference the largest DPM relative to the largest value of the orbital, and tail cut-off the last value of the orbital greater than the tail cut-off parameter. The maximum iterations of the SCF phase is 6 iterations: if the calculations have converged in Level 1, then the number of iterations for the NR phase is set to zero. Total energy information and the ratio of the potential energy to kinetic energy are displayed.

The second level maps the orbital expansions to a finer grid and re-defines the range. The largest change in each orbital from the old and the new grid is reported. Level 2 parameters are displayed as well as the total energy from the new orbital expansions. Convergence for the SCF phase is $1000 \times \text{scf_tol}$ for the level. Two SCF iterations have been applied and two NR iterations in which all orbitals were varied. The change in the total energy is small and could be defined as having converged because of the limitation on numerical accuracy but note that small changes are occurring in the orbital expansions which result in the excellent agreement with the exact ratio (Potential/Kinetic) of -2.0 .

The essential information about the calculation is summarized in the `sphf.log` file: atom, closed shells, configuration, followed by parameters, orbital properties, and total energy information for each level. This file is listed in Fig. 2, the `bsw.c` in Fig. 3, and `hf_param` in Fig. 4.

Not shown here is the output from a modification of `sphf_all` that, if the last orbital is singly occupied, displays all the eigenvalues and the mean radii of orbitals that define the fixed-core Hartree–Fock wave functions of the entire Rydberg series. For a calculation such as $[\text{Ar}]4s$, there will be three eigenstates with zero eigenvalues. These are the eigenvectors that have been shifted to zero by the application of the orthogonality constraints, namely $1s$, $2s$, and $3s$, in this case. In many-body perturbation theory [13], the eigenvectors for the Rydberg series define an effectively complete orbital basis. A difference, however, is how the range is determined and the boundary conditions. In variational methods, the range is determined by the outermost Hartree–Fock orbital. The boundary condition $P'(r) = 0$ in addition to $P(r) = 0$ at large r has a large effect. Typically, there are a relatively small number of bound orbitals whose mean radii are increasing, followed by the zero energy states already explained, and then orbitals in the continuum with decreasing mean radii, similar to correlation orbitals [14]. The orbitals are appended to `bsw.out`.

The CPU time of a calculation depends on the size of the basis which defines the size of the SCF matrix and the number of blocks. For accuracy, the size should be sufficiently large. In this example the basis size is 66 whereas $MAXR$ for the outermost orbital was 65, the largest value that allows for the zero boundary conditions. As a check the `hf_param` file can be edited by increasing the order of the spline approximation k_s and the range n_s to $ks=8$, $ns=67$. If `bsw.out` is moved to `bsw.inp` and the program rerun, Fig. 5 displays the screen output. The program reports the difference in grid for each orbital and shows that the SCF and NR iterations each converge in one iteration, that the deviation of the ratio from -2.0 becomes a bit smaller, and that the total energy changes by an amount consistent with the deviation from -2.0 . The results are close to the limits of a double precision calculation and the CPU time was 0.240 s. In this case, the CPU time for `sphf_scf` is 0.300 s and the final ratio of -1.999999999951167 is not as accurate.

Table 4 shows the accuracy by comparing the ratio of the kinetic to potential energy which, by the virial theorem, should be exactly -2.0 and the CPU time in seconds for a series of examples of the `sphf_all` and `sphf_scf` iteration process. On the whole `sphf_all` has the better accuracy but for large closed shell systems such as $\text{Ra} [\text{Rn}]7s^2 1S$ updating all orbitals simultaneously is not necessary. A feature of the exchange interaction matrix $K^k(.,., a, b)$ is that coefficients of Slater matrix elements depend on the product of expansion coefficients of the orbitals a and b . In a large atom, such as Ac ($Z = 89$) this product may quickly become negligible the radius increases. By modifying the routine `add_rkm_x` to the range where this product is $< 10^{-18}$, the CPU time was reduced by about 30% with little change in accuracy as shown in Table 4.

4. Program compilation

The program is submitted as a stand-alone program that links to the Lapack and Blas library. The Makefile uses environment variables that can be defined in the Makefile (see the file for details). Two versions of the program are installed: `sphf_scf` that uses the SCF itera-

```

HARTREE-FOCK WAVE FUNCTIONS FOR      Al    2P    Z = 13.0

      Core = 1s(  2) 2s(  2) 2p(  6) 3s(  2)
Configuration = 3p( 1.0)

Level 1: HF_parameters
-----
      Step-size (h)                0.25000
      Spline order (ks)              4
      Size of basis (ns)             37
      Maximum radius                 62.14
      SCF convergence tolerance      1.00D-12
      Orbital convergence tolerance  1.00D-06
      Orbital tail cut-off           1.00D-06
      Orbitals varied                all

Convergence (latest difference)
      SCF diff. = 4.262D-10
      Orbital diff. = 6.528D-05
      Tail cut-off = 4.408D-02

      ATOM      Al    TERM      2P

nl      E(nl)      I(nl)      KE(nl)      S(nl)      Az(nl)      MAXR      MAXP
1s      -58.50073199  -84.39586731  79.26418026  0.527      90.657398      24       6
2s      -4.91065070  -19.65255555  10.88443408  3.323      23.569106      28      14
2p      -3.21833517  -18.81038691  9.85602792  4.674      66.822309      29      14
3s      -0.39342034  -5.65223092  0.93596923  7.806      5.441831      31      21
3p      -0.20995112  -4.35963275  0.57103775  9.360      12.009873      32      22

nl      Delta(r)      1/R**3      1/R      R      R**2
1s      654.028443      0.000000      12.589234  0.12025852  0.019459
2s      44.205505      0.000000      2.348999  0.62002768  0.458900
2p      0.000000      34.938598      2.205109  0.60054223  0.455356
3s      2.356569      0.000000      0.506785  2.59928400  7.890709
3p      0.000000      1.088340      0.379282  3.43389422  14.006318

TOTAL ENERGY (a.u.)      -241.876624465694300
      Kinetic      241.876372409537300
      Potential      -483.752996875231600
      Ratio      -2.000001042086726

Level 2: HF_parameters
-----
      Step-size (h)                0.12500
      Spline order (ks)              6
      Size of basis (ns)             66
      Maximum radius                 39.55
      SCF convergence tolerance      1.00D-15
      Orbital convergence tolerance  1.00D-09
      Orbital tail cut-off           1.00D-09
      Orbitals varied                all

Convergence (latest difference)
      SCF diff. = 2.703D-15
      Orbital diff. = 7.768D-11
      Tail cut-off = -5.837D-09

      ATOM      Al    TERM      2P

nl      E(nl)      I(nl)      KE(nl)      S(nl)      Az(nl)      MAXR      MAXP
1s      -58.50102657  -84.39589925  79.26432704  0.527      90.712610      55      11
2s      -4.91067188  -19.65259238  10.88449349  3.323      23.578098      58      27
2p      -3.21830326  -18.81038418  9.85601446  4.674      67.385203      60      26
3s      -0.39342039  -5.65224188  0.93597027  7.806      5.443797      62      39
3p      -0.20995075  -4.35963442  0.57103891  9.360      12.109194      65      41

nl      Delta(r)      1/R**3      1/R      R      R**2
1s      654.825314      0.000000      12.589248  0.12025840  0.019459
2s      44.239242      0.000000      2.349007  0.62002551  0.458897
2p      0.000000      34.938537      2.205108  0.60054252  0.455357
3s      2.358273      0.000000      0.506786  2.59927819  7.890676
3p      0.000000      1.088344      0.379283  3.43389299  14.006309

TOTAL ENERGY (a.u.)      -241.876707250678000
      Kinetic      241.876707250674100
      Potential      -483.753414501352000
      Ratio      -2.000000000000016

```

Fig. 2. Listing of the sphf.log file.

```

      A1      2P  13.0      4      5
    1s 2s 2p 3s
    3p(1)

```

Fig. 3. Listing of bsw.c file.

```

HF_parameters
-----
h      =      0.125000
ks     =      6
ns     =      66
scf_tol =      1.00D-15
orb_tol =      1.00D-09
end_tol =      1.00D-09
acc_max =      1
varied =      all

```

Fig. 4. Listing of the hf_param file.

```

=====
S P L I N E   H A R T R E E - F O C K : 2010
=====

WAVE FUNCTIONS FOR      A1      2P  Z = 13.0

      Core = 1s(  2) 2s(  2) 2p(  6) 3s(  2)
Configuration = 3p( 1.0)

Read_bsw: Grid for 1s
  File: 13.0 0.1250      6      66
  Curr: 13.0 0.1250      8      67

Read_bsw: Grid for 2s
  File: 13.0 0.1250      6      66
  Curr: 13.0 0.1250      8      67

Read_bsw: Grid for 2p
  File: 13.0 0.1250      6      66
  Curr: 13.0 0.1250      8      67

Read_bsw: Grid for 3s
  File: 13.0 0.1250      6      66
  Curr: 13.0 0.1250      8      67

Read_bsw: Grid for 3p
  File: 13.0 0.1250      6      66
  Curr: 13.0 0.1250      8      67

Level 1: HF_parameters
-----
  Step-size (h)                      0.12500
  Spline order (ks)                   8
  Size of basis (ns)                   67
  Maximum radius                      35.16
  SCF convergence tolerance            1.00D-15
  Orbital convergence tolerance        1.00D-09
  Orbital tail cut-off                 1.00D-09
  Orbitals varied                      all

Level  1
-----

Total energy from initial estimates =  -241.876707250749

Iteration 1.01
-----

      nl      E(nl)      AZ      DPM      MAXR
    1s  -58.501026568596  90.7126080518  9.70D-09  56
    2s  -4.910671882832  23.5780981545  2.36D-09  59
    2p  -3.218303257151  67.3851736688  3.98D-10  61
    3s  -0.393420387447   5.4437972715  1.34D-09  63
    3p  -0.209950745995  12.1091888403  1.04D-07  66

      SCF convergence (diff vs tol)      3.64D-15  1.00D-15
      Orbital convergence (diff vs tol)  1.04D-07  1.00D-09
      Tail cut-off (orbital nwf)        -5.58D-08  1.00D-09
Total energy =  -241.876707250750

```

Fig. 5. Output from rerunning the case after copying bsw.out to bsw.inp and editing hf_param so that ns=67 and ks=8.

```

The first phase of Level 1 has converged
it_max for the second phase set to 2

Iteration 2.01
-----
      SCF convergence (diff vs tol)          5.76D-15    1.00D-15
      Orbital convergence (diff vs tol)       8.68D-12    1.00D-09
      Tail cut-off (orbital nwf)             -5.58D-08    1.00D-09
Total energy =    -241.876707250750

TOTAL ENERGY (a.u.)    -241.876707250750400
      Kinetic            241.876707250748900
      Potential          -483.753414501499300
      Ratio              -2.000000000000006

```

Fig. 5. (continued)

Table 4

A comparison of the ratio of the kinetic to potential energy and CPU time (in seconds) for a series of test cases of the `sphf_all` and `sphf_scf` iteration versions.

Atom	sphf_all		sphf_scf	
	Ratio	Time (s)	Ratio	Time (s)
He $1s^2 \ ^1S$	-1.999999999999991	0.008	-1.999999999999991	0.012
Li $1s^2 2s \ ^2S$	-2.000000000000000	0.040	-2.000000000000003	0.028
He $1s 2s \ ^1S$	-2.000000000881988	0.044	-2.000000000056903	0.056
Be $1s^2 2s^2 \ ^1S$	-2.000000000000039	0.036	-2.000000000000097	0.028
F [Ne] $2p^5 \ ^2P$	-2.000000000000001	0.096	-1.999999999996467	0.088
Mg [Ne] $3s 3d \ ^1D$	-1.999999999999968	0.368	-2.000000000079570	0.256
Ra [Rn] $7s^2 \ ^1S$	-2.000000000000023	6.896	-2.000000001520626	2.300
Ac [Rn] $7s^2 7p \ ^2P$	-2.000000000056325	9.085	-2.000000000000294	5.616
(modified exchange)	-2.000000000056322	6.612	-1.999999999998914	3.844

tion process of updating only one orbital at a time, or `sphf_all` that updates all orbitals simultaneously during the Level 2 calculations. It has the better accuracy but, at least in the present version, consumes more CPU time. When the last orbital is singly occupied, the latter version has been modified to report the other members of the Rydberg series for the last electron and append them to `bsw.out`.

The tarfile for the program also contains a test directory with output results from `sphf_all` for the eight test listed in Table 4.

5. Conclusion

Spline methods are accurate and flexible methods for approximating functions. Because the results on one grid may be mapped onto a refined grid, it is possible to quickly obtain rough estimates of solutions and, as needed, refine the calculations for greater accuracy. In the case of the Hartree–Fock problem, it was possible to apply a rotation analysis for stationary solutions when orthogonality constraints are present and eliminate off-diagonal Lagrange multipliers by using projection operators. Though larger ranges are needed, the matrix method can easily obtain solutions for high n Rydberg states. Further studies are under way for the multiconfiguration Hartree–Fock method.

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References

- [1] C. Froese Fischer, *Comput. Phys. Commun.* 43 (1987) 355–365.
- [2] G. Gaigalas, C. Froese Fischer, *Comput. Phys. Commun.* 98 (1996) 255.
- [3] C. Froese Fischer, *Comput. Phys. Commun.* 14 (1978) 145–153.
- [4] D.R. Hartree, *The Calculation of Atomic Structures*, Wiley, New York, 1957.
- [5] C. Froese Fischer, in: E. Arimondo, P.R. Berman, C.C. Lin (Eds.), *Advances in Atomic and Molecular Physics*, vol. 55, 2007, pp. 539–550.
- [6] C.A.J. Fletcher, *Computational Galerkin Methods*, Springer, New York, 1984.
- [7] H. Bachau, E. Cormier, P. Decleva, J.E. Hansen, F. Martin, *Rep. Prog. Phys.* 64 (2001) 1815–1942.
- [8] Spline theory allows for multiple knots at any point but the present code assumes they occur only at the first and last knot.
- [9] M. Bentley, *J. Phys. B: At. Mol. Opt. Phys.* 27 (1994) 637–644.
- [10] T.A. Koopmans, *Physica* 1 (1933) 104.
- [11] J.C. Slater, *Quantum Theory of Atomic Structure*, vol. II, McGraw–Hill, New York, 1960.
- [12] O. Zatsarinny, *Comput. Phys. Commun.* 174 (2006) 273–356.
- [13] J. Sapirstein, W.R. Johnson, *J. Phys. B* 29 (1996) 5213–5225.
- [14] S. Verdebout, P. Jönsson, G. Gaigalas, M. Godefroid, C. Froese Fischer, *J. Phys. B* 43 (2010) 074017.