

BSR_MCHF: A B-spline Hartree-Fock program

This program is version of the Splines_MCHF program of Charlotte Froese Fischer, *Towards B-spline Multiconfiguration Hartree-Fock calculations* (2010), unpublished, and designed to more close connection with BSR complex. For some specific features I also refer the reader to another publication of Charlotte Froese Fischer, *B-splines in variational atomic structure calculations*, Advances in atomic, molecular and optical physics, vol. 55, 235 (2008). I thankful Charlotte to strong cooperation in B-spline applications.

Belove description is close to the description of the BSR_HF program, and I suppose the reader will read it first to avoid repetitions. I also use the same notations as in the BSR_HF write-up.

1. General remarks

In the multiconfiguration Hartree-Fock (MCHF) method, the wave function is approximated by a linear combination of orthogonal configuration state functions (CSFs) so that

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

and the energy is required to be stationary both with respect to the variation of the radial functions and the expansion coefficients c_i . The energy of the $\Psi(\gamma LS)$ can then be expressed as

$$E(\gamma LS) = \sum_{i=1}^M \sum_{j=1}^M c_i c_j H_{ij}, \text{ where } H_{ij} = \langle \Phi(\gamma_i LS) | H | \Phi(\gamma_j LS) \rangle. \quad (2)$$

The matrix $\mathbf{H}=\{H_{ij}\}$ is called as the *interaction matrix*. The set of expansion coefficients $\mathbf{c}=\{c_{ij}\}$ are also called *mixing 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 \mathbf{H} for an N -electron Hamiltonian.

Using the integration over angular variables, the matrix elements H_{ij} can be expressed though the radial integrals (see BSR_BREIT) as

$$H_{ij} = \sum_{ab} q_{ab}^{ij} L(a, b) + \sum_{abcd} \sum_k r_{abcd,k}^{ij} R_k(abcd) \quad (3)$$

where the sum on ab and $abcd$ is over the orbitals occupied in either configuration state. Then we get

$$E(\gamma LS) = \sum_{ab} q_{ab} L(a, b) + \sum_{abcd} \sum_k r_{abcd,k} R_k(abcd) \quad (4)$$

where

$$q_{ab} = \sum_{i=1}^M \sum_{j=1}^M c_i c_j q_{ab}^{ij} \quad \text{and} \quad r_{abcd,k} = \sum_{i=1}^M \sum_{j=1}^M c_i c_j r_{abcd,k}^{ij} \quad (5)$$

We see that the energy depends both on the radial integrals and expansion coefficients.

In general, 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 procedure, for example, is referred to as “extended optimal level” in the general relativistic atomic structure package (GRASP). 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 may prevent an accurate prediction of level separation. In this procedure, the angular coefficients have the form

$$q_{ab} = \sum_{l=1}^N w_l \sum_{i=1}^{M^l} \sum_{j=1}^{M^l} c_i^l c_j^l q_{ab}^{ij} \quad \text{and} \quad r_{abcd,k} = \sum_{l=1}^N w_l \sum_{i=1}^{M^l} \sum_{j=1}^{M^l} c_i^l c_j^l r_{abcd,k}^{ij} \quad (6)$$

Additional summation is over set of included levels and w_l are their weights.

At derivation of the MCHF equations, the functional should contain energy and Lagrange multipliers for all the constraints. Thus the full functional has the form

$$F(\{P(a;r)\}, \{c_i\}) = E(\gamma LS) + \sum_{a \leq b} \delta_{l_a l_b} \langle a | b \rangle - E \sum_{i=1}^M c_i^2, \quad (7)$$

where $\{P(a;r)\}$ denotes the set of involved one-electron radial functions. Variations in c_i leads to secular equation

$$\mathbf{Hc} = E\mathbf{c}. \quad (8)$$

We will use the Bently's projection procedure (see BSR_HF) to sure orthogonality all radial functions, so we will exclude the corresponding Lagrange multipliers from further consideration. The requirement of a stationary condition with respect to variations in the radial functions $P(a;r)$ leads to a system of equations, one for each radial function to be varied.

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} [Z - Y(nl, r) + \frac{l(l+1)}{2r^2} - \varepsilon_{nl, nl}] \right) P(nl; r) = \frac{1}{r} X(nl; r) \quad (9)$$

This system of radial equations has exactly the same form as the Hartree-Fock equations except:

- the function $X(nl;r)$ arises not only from the exchange of electrons within a configuration state, but also from interaction between different configuration states.
- the energy parameters $\varepsilon_{nl, n'l} = \lambda_{nl, n'l} / q_{nl}$ contain the occupation numbers q_{nl} which now are not integers but rather *expected* occupation numbers.

3. B-spline basis

In our implementation, the one-electron radial functions are represented in terms of B-spline basis functions $B_i(r)$, namely

$$P(a;r) = \sum_{i=1}^{n_s} a_i B_i(r). \quad (10)$$

Let us introduce the matrices for the one-electron integrals

$$L_{ij} = L(.,.) = \left\langle B_i(r) \left| -\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2} \right| B_j(r) \right\rangle, \quad (11)$$

and the four-dimensional arrays for Slater integrals between individual B-splines

$$R^k(ij; i' j') = R(.,.,.,.) = \int_0^\infty \int_0^\infty B_i(r_1) B_j(r_2) \frac{r_<^k}{r_>^{k+1}} B_{i'}(r_1) B_{j'}(r_2) dr_1 dr_2. \quad (12)$$

Then

$$L(a,b) = \sum_i^{n_s} a_i b_i L_{ij} = aL(.,.)b = aL(.,b) = L(a,.)b, \quad (14)$$

$$R^k(a,b;c,d) = \sum_i^{n_s} \sum_j^{n_s} \sum_{i'}^{n_s} \sum_{j'}^{n_s} a_i b_j c_{i'} d_{j'} R^k(ij; i' j') = aR(.,b;c,d) = \dots \quad (15)$$

MCHF equations (9) for given orbital are obtained by variation of full functional in the radial functions $P(a;r)$. In B-spline basis, the gradient vector for orbital a leads to contributions of the form

$$L(.,a), \quad B(.,a), \quad R^k(.,b;a,b), \quad R^k(.,b;b,a) \quad \text{or just} \quad R^k(.,b;c,d) \quad \text{and} \quad L(.,b).$$

which can be putted in the matrix form

$$L(.,.)a, \quad B(.,.)a, \quad R^k(.,b;.,b)a, \quad R^k(.,b;b,.)a,$$

except the last terms which are vectors and will be placed in the right side of the equation. We may convert the $R^k(.,b;c,d)$ contribution to the matrix representation, using the trick. Supposed the orbital a are orthogonal: $\langle a|a \rangle = 1$. Then

$$R^k(.,b;c,d) = R^k(.,b;c,d) \langle a|a \rangle = R^k(.,b;c,d) a B(.,.) a = R^k(a,b;c,d) B(.,.) a.$$

The same for the $L(.,b)$ integrals.

Finally, the MCHF matrix, \mathbf{H}^a for orbital a , has the form

$$\mathbf{H}^a = \mathbf{L} + \mathbf{V}_a^{dir} + \mathbf{V}_a^{exc} + \mathbf{V}_a^{int}, \quad (19)$$

where the direct, exchange and interaction potentials are represented by matrices obtained by summation and convolution of the corresponding Slater and L integrals, including the coefficients (5) and divided by

occupation number q_a obtained as coefficient before $L(a,a)$ integral. The \mathbf{V}_a^{int} can be represented as a matrix in \mathbf{H}^a , or as a vector \mathbf{X}_a in the right side .

Solutions then are determined via **SCF** process - orbitals are updated one at a time with following diagonalization of non-relativistic Hamiltonian in the CSF's basis:

$$\begin{cases} \mathbf{H}^a \mathbf{a}_i - \varepsilon_i \mathbf{B} \mathbf{a}_i = \mathbf{X}_i^a, & i = 1, 2, \dots, n_{orb} \\ \mathbf{H}^{nr} \mathbf{c} = E \mathbf{c}, & \mathbf{c} = (c_1, c_2, \dots, c_M)^T \end{cases} \quad (20)$$

4. Program structure

In order to run BSR_MCHF, the user should first make preliminary steps: create the file with the list of CFSs under consideration and obtain the angular coefficients, $r_{abcd,k}^{ij}$, for interaction between involved CFSs. The first step can be done with utilities **zgenconf** and **zgenterm**, second step – with program BSR_BREIT3.

The block-scheme of the program is shown in the Figure 1, along with optional input/output data files. The primary steps of the program consist of the analysis of input parameters by the module **get_case**, checking of the CFS list, **read_conf**, the definition of the grid and spline parameters by the module **def_spline_param**, the reading of the initial estimations by the module **get_estimates**. Then program prepares radial-function array, **def_orbitals**, the reading or generating of the initial estimations by the module **get_estimates**. All needed angular coefficients are then extract from the **name.bnk** (**int.bnk**) file by subroutine **read_ang_coef**.

The solution of Hartree-Fock equations is driven by the main module **SCF_MCHF**, followed by the output of resulting wavefunctions, **write_bsw**, and summary of results, **summary**.

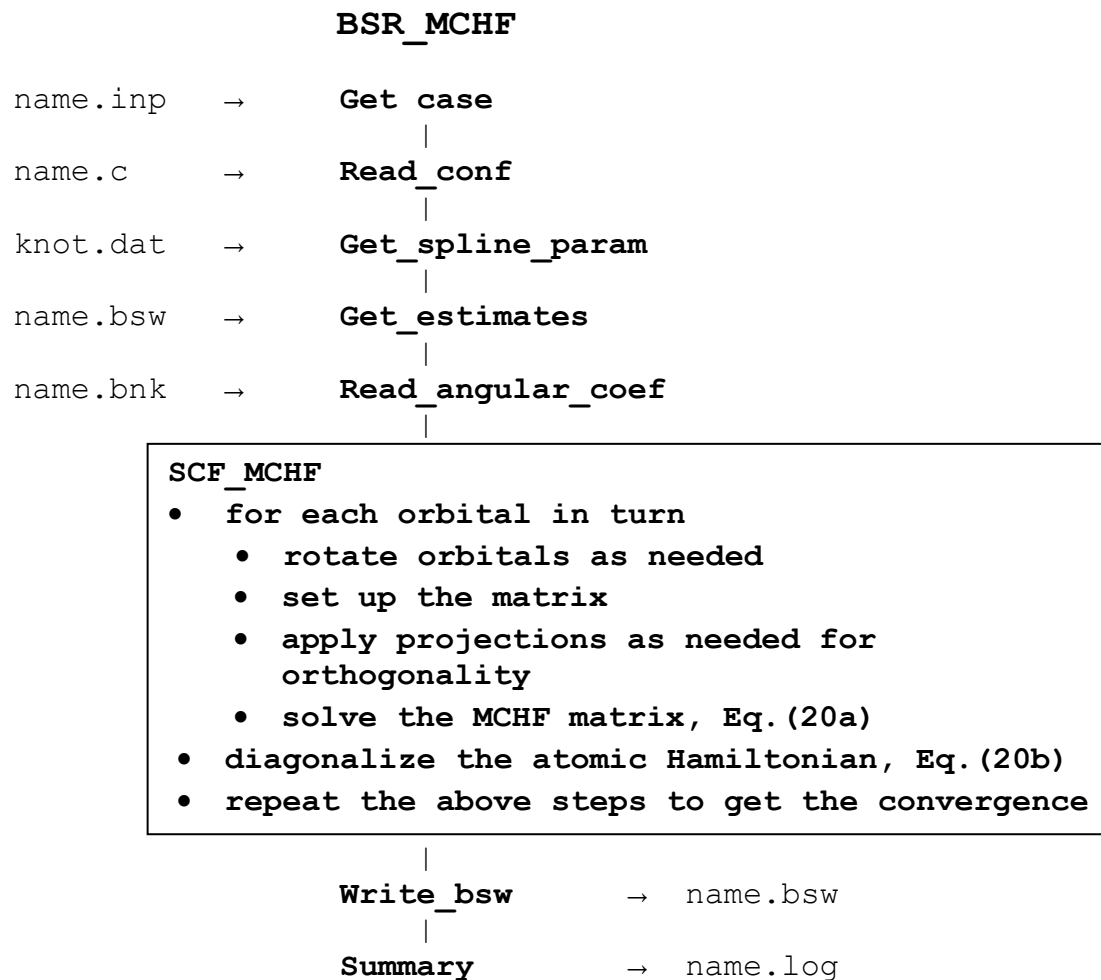


Fig. 1 Block diagram for the program BSR_MCHF and data flow.

4.1. Input parameters

Each calculation is supposed to have its own name, given as the first argument on the command line for which the variable name is not needed. Other input parameters can be given either on the command line or in the file **name.inp** if they differ from the default values. All input parameters are given with their key words as **parameter=value**, and any parameter from the input file can be redefined on the command line with the same construction. The key-word format for input parameters simplifies their preparation: there is no restrictions on their position in the input file. All parameters have their default values, so any missing parameters will not halt the calculations (unless the **name** of the case is missing). Formal detailed description of all input parameters is given in the section 7.

4.2 Spline parameters

The B-splines grid are placed in the files **name.knot** or **knot.dat**. If these files are absent, default grid will be created. Other details about generating B-splines are given in description of BSR_HF.

4.3 Angular coefficients

Angular coefficient are obtained on the based of information recorded in **the int.bnk (name.bnk)** files. Note that the int.bnk contains the data-bank of coefficients when all orbitals considered as non-orthogonal. The program converts this data set in the list of angular coefficients with all orbitals are orthogonal.

4.4 Initial estimations

Initial estimations for the radial functions are obtained either from screened hydrogen functions or from reading the file specified by the **inp=<filename>** parameter. This file should contain the B-spline expansions for the radial functions, obtained from a previous calculation. These files may have the default extension **.bsw** and contain, along with the radial functions, also the B-spline grid used in their calculation. Should this B-spline grid not coincide with the grid used in the current calculations, the corresponding B-spline expansions will be converted to the current grid.

4.5 SCF procedure

The central routine of the program is the **SCF_NCHF** subroutine, which runs the SCF procedure for solution of MCHF equations and diagonalization of the atomic Hamiltonian.

When several radial functions with the same orbital symmetry are present, the solutions of the MCHF equations not only are stationary with respect to single excitations to unoccupied radial functions, they also are stationary with respect to orthonormal transformations. Such transformations represent the rotation of orbitals and are provided, if needed, in the same way as in the BSR_HF program.

Then the program, for each optimized orbital, sets up the MCHF matrixes, Eq.(19), and solve them by different methods, depending on the V_{int} potentials. (These methods are similar to DBSR_MCHF program and will not described here). Then the program diagonalizes the atomic Hamiltonian to get the expansion coefficients. This procedure is repeated up to reaching the convergence. Here we may use the "acceleration" procedure described in the BSR_HF.

4.7 Output of results

The essential information about the calculation is summarized in the **<name>.log** file, which contains the parameters of the computational model, B-spline parameters, the final results of the SCF iteration process, convergence estimates, and final energies in atomic unites (au) and (eV) . Below is a typical example of final results for Al.

ATOM: Al TERM: 2P

Convergence (latest difference):

Orbital diff. = 5.46D-06
SCF diff. = 1.15D-13

nl	E(nl)	1/R	R	R**2	dmp	ns	max_R
1s	0.00000000	12.589	0.120	0.019	0.00E+00	52	12.55
2s	0.00000000	2.349	0.620	0.459	0.00E+00	59	19.55
2p	0.00000000	2.205	0.600	0.455	0.00E+00	58	18.55
3s	-0.41606057	0.502	2.612	7.950	5.46E-06	64	24.55
3p	-0.27715896	0.413	3.126	11.430	8.06E-07	68	28.55
3d	-0.50966995	0.382	3.022	10.366	1.15E-06	65	25.55

Total energy -241.920415738981
Kinetic 241.919017246191
Potential -483.839432985172
Ratio -2.000005780830

Optimized states:

Level	Energy	Leading CSFs
1	-241.92041574	1 0.9604 4 0.1903 2 0.1543 3 -0.1149 5 -0.0545

time: 9.06 sec

5 List of input parameters

Input data can be provided in the input file **<name>.inp** or in the command line as **keyword=value** (the data from the command line overrides the data from the input file **<name>.inp**). Below we describe input parameters with their default values indicated in brackets. The zero value for many parameters implies a negative answer.

name	name of the case; it is the first argument in the command line and is given without keyword.
atom	symbolic name of the atom under consideration, may be used to find nuclear charge.
z	nuclear charge.
varied [all]	list of one-electron orbitals included in the SCF optimization; accepted value: all , none , a list of orbitals separated by commas, or =number , where number indicates the number of orbitals involved in the SCF procedure (from the end of the list) .
physical [all]	list of one-electron orbitals included in the SCF optimization; given as a list of orbitals separated by commas.
nlevels [1]	number of levels to be optimized
level	indexes of levels for optimization
weight	weights of levels for optimization
scf_tol [1.0E-10]	energy convergence tolerance.
orb_tol [1.0E-7]	orbital convergence tolerance.
end_tol [1.0E-6]	orbital tail cut-off.
max_it [25]	maximum number of iterations .
rotate [0]	rotations during optimization (0/1 →no/yes).
ilzero [0]	initial zero B-splines (0 means delete $l+1$ B-splines)
ibzero [2]	zero B-splines in the end
aweigh [0.7]	α acceleration parameter, Eq.(34)
bweight [0.7]	β acceleration parameter, Eq.(34)
acc [0]	if not equal 0, acceleration procedure applies every time
debug [0]	additional debug output (0/1 →no/yes).

6 Data files

The program employs the name-driven file convention. All filenames have the structure **<name>.<extension>**, where **<name>** (the value of **name**) identifies the specific calculation. The

list of data files and their description is given in table 1. There is also an option for user-defined filenames that is defined by the corresponding key-words in the command line and can be useful in some specific cases. To keep the knot grid consistent with the previous calculations it is enough to indicate the corresponding knot file through the parameter **knot**, or rename it as the default **knot.dat** file. In this case, all associated calculations for the given atom or ion will be carried out with the same grid.

Table 1 Input/output files.

name.inp	dat=...	File type: formatted sequential input. Written by the user or created by the program if absent. Description: input parameters for the given run.
name.log	log=...	File type: formatted sequential output. Description: Summary of the running information.
name.knot	knot=...	File type: formatted sequential input/output. Written by the user or created by the program if absent. Description: defines the B-spline grid.
name.c	c=...	File type: formatted sequential input/output. Created by the user with utilities <code>zgenconf</code> and <code>zgenterm</code> . Description: input configuration states in BSR/MCHF format.
name.bnk	bnk=	File type: unformatted sequential input. Description: data-bank of angular coefficients. Created by program <code>BSR_BREIT3</code> .
name.bsw	inp=...	File type: unformatted sequential input. Provided by the user or can be created by the program in prior runs. Description: one-electron orbitals in B-spline representation.
name.bsw	out=...	File type: unformatted sequential input. Description: one-electron orbitals in B-spline representation for initial estimations.

8 Program installation and testing

The `BSR_MCHF` program is a part of the BSR complex and extensively uses common routines from the BSR libraries: `ZCONFLS`, `BS`, `ZCOM`. `ZCONFLS` deals with the state description and calculation of the angular coefficients, `BS` contains subroutines for different operations with B-splines, including two-electron integrals, and `ZCOM` contains commonly used subroutines, such as those that read arguments or order arrays. The `BSR_MCHF` program also uses the linear algebra LAPACK and BLAS libraries which are widely used in different applications and freely available at the site: <http://www.netlib.org/lapack/>. It is recommended that users employ the LAPACK and BLAS libraries optimized for the given computer. Makefile contains all needed information for the compilation.

5 Examples

Example are given in several folders together with the source code.