A program for computing magnetic dipole and electric quadrupole hyperfine constants from MCHF wavefunctions

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Given an electronic wave function, generated by the MCHF program (LS format) or the MCHF_CI program (LSJ format), this program computes the hyperfine interaction constants, $A_J$ and $B_J$. In strong experimental magnetic fields, the splitting is also affected by the off-diagonal hyperfine constants $A_{J,J-1}$, $B_{J,J-1}$, and $B_{J,J-2}$ and these are computed as well, depending on the input data.

PROGRAM SUMMARY

Title of program: MCHF_HFS

Catalogue number: ACLE

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Licensing provisions: none

Computer for which the program is designed and others on which it has been tested:
Computer: VAX 11/780, DEC 3100, SUN SPARC-station 330; Installation: Lund University, Vanderbilt University

Operating system under which the program is executed: VMS, ULTRIX, Sun UNIX

Programming languages used: FORTRAN77

Memory required to execute with typical data: 210K words

No. of bits in a word: 32

Peripherals used: terminal; disk

No. of lines in distributed program, including test data, etc.: 3291

CPC program Library subroutines used:

Catalogue number Title Ref in CPC
ABBY NJGRAF 50 (1988) 375
ABZU MCHF_LIBRARIES 64 (1991) 399

Keywords: hyperfine structure, $A$ factor, $B$ factor, orbital term, spin-dipole term, Fermi contact term, electric quadrupole term, MCHF calculation, CI calculation

Nature of physical problem
The atomic hyperfine splitting is determined by the hyperfine interaction constants $A_J$ and $B_J$ [1]. In strong external
magnetic fields, where \( J \) is no longer a good quantum number, the splitting is also affected by the off-diagonal hyperfine constants \( A_{J-1}, B_{J-1} \) and \( B_{J+1} \) [2–4]. This program calculates the hyperfine constants using an electronic wavefunction generated with the MCHF or MCHF CI programs of Froese Fischer [5].

Method of solution
The electronic wavefunction, \( \Psi \), for a state labelled \( \gamma J \) can be expanded in terms of configuration state functions, \( \Psi = \sum_c c_j \phi_j(L_j S_j J) \). The hyperfine constants can then generally be calculated as

\[
\sum_{k,k'} c_{j,k} c_{j,k'} \rightlangle j | T^{(K)} | k \rangle \left| \gamma k L_k S_k \rangle
\]

where \( T^{(K)} \) is a spherical tensor operator of rank \( K \). Evaluation of the reduced matrix element between arbitrarily \( LS \) coupled configurations is done by an extended version of the program TENSOR originally written by Robb [6–8].

Unusual features of the program
The program allows for a limited degree of nonorthogonality between orbitals in the configuration state expansion.

Restrictions on the complexity of the problem
The orthogonality constraints are relaxed only within the restrictions described in ref. [9], giving rise to at most two overlap integrals multiplying the one-electron active radial integral. Any number of s-, p-, or d-electrons are allowed in a configuration subshell, but no more than two electrons in a subshell with \( l \geq 3 \). If \( l \geq 4 \), the \( LS \) term for the subshell is restricted to those allowed for \( l = 4 \). Only the subshells outside a set of closed subshells common to all configurations need to be specified. A maximum of 5 (five) subshells (in addition to common closed subshells) is allowed. This restriction may be removed by changing dimension statements and some format statements.

Typical running time
The CPU time required for the test cases is 0.1 seconds for the first and 0.19 seconds for the second on a SUN SPARC-station 330.

References

LONG WRITE-UP

1. Introduction

The present MCHF_HFS program is closely linked with the MCHF atomic structure package. Therefore, it adheres to the structure and constraints underlying the package. A summary of the data input for the various programs was included with the description of the package [1]. The role of the program is to calculate magnetic dipole and electric quadrupole hyperfine constants from MCHF wavefunctions, either in the nonrelativistic \( LS \) scheme, or in the Breit–Pauli \( LSJ \) scheme.

2. Theory

2.1. Hyperfine interaction

The hyperfine structure of the atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. The contribution to the Hamiltonian can be
represented by an expansion in multipoles of order $K$,
\[
H_{\text{hfs}} = \sum_{K \geq 1} T^{(K)} \cdot M^{(K)},
\]
(1)
where $T^{(K)}$ and $M^{(K)}$ are spherical tensor operators of rank $K$ in the electronic and nuclear space, respectively [2]. The $K = 1$ term represents the magnetic dipole interaction and the $K = 2$ term the electric quadrupole interaction. Higher order terms are much smaller and can often be neglected.

For an $N$-electron atom the electronic tensor operators are, in atomic units,
\[
T^{(1)} = \frac{1}{2} \alpha^2 \sum_{i=1}^{N} \left[ 2 \, t^{(1)}(i) \, r_i^{-3} - g_s \sqrt{10} \left[ C^{(2)}(i) \times s^{(1)}(i) \right] r_i^{-3} + g_s \frac{8}{3} \pi \delta(r_i) \, s^{(1)}(i) \right]
\]
(2)
and
\[
T^{(2)} = - \sum_{i=1}^{N} C^{(2)}(i) \, r_i^{-3},
\]
(3)
where $g_s = 2.00232$ is the electronic $g$ factor and $\delta(r)$ the three-dimensional delta function [3]. $C^{(k)}_q = (4 \pi/(2k+1)) Y_{kq}$, with $Y_{kq}$ being a normalized spherical harmonic with the phase conventions of Condon and Shortley.

The magnetic dipole operator (2) represents the magnetic field due to the electrons at the site of the nucleus. The first term of the operator represents the field caused by orbital motion of the electrons and is called the orbital term. The second term represents the dipole field due to the spin motions of the electron and is called the spin-dipole term. The last term represents the contact interaction between the nucleus and the electron spin and contributes only for $s$ electrons. The electric quadrupole operators (3) represents the electric field gradient at the site of the nucleus.

The conventional nuclear magnetic dipole moment $\mu_I$ and electric quadrupole moment $Q$ are defined as the expectation values of the nuclear tensor operators $M^{(1)}$ and $M^{(2)}$ in the state with the maximum component of the nuclear spin, $M_I = I$,
\[
\langle \gamma_I I | M^{(1)}_0 | \gamma_I I \rangle = \mu_I,
\]
(4)
\[
\langle \gamma_I I | M^{(2)}_0 | \gamma_I I \rangle = \frac{1}{2} Q.
\]
(5)

When the hyperfine contributions are added to the Hamiltonian, the wavefunction representation for which the total Hamiltonian is diagonal is $| \gamma_I \gamma_J UFM_F \rangle$, where $F = I + J$.

In this representation, perturbation theory gives the following hyperfine corrections to the electronic energy
\[
W_{M1}(J, J') = \langle \gamma_I \gamma_J UFM_F | T^{(1)} \cdot M^{(1)} | \gamma_I \gamma_J U'FM_{F'} \rangle, \quad J' = J, J - 1,
\]
(6)
\[
W_{E2}(J, J') = \langle \gamma_I \gamma_J UFM_F | T^{(2)} \cdot M^{(2)} | \gamma_I \gamma_J U'FM_{F'} \rangle, \quad J' = J, J - 1, J - 2.
\]
(7)

This can, using tensor algebra, also be written as
\[
W_{M1}(J, J') = (-1)^{I+J'-F} W(U'U'; F1) \langle \gamma_J J \parallel T^{(1)} \parallel \gamma_I J' \rangle \langle \gamma_I I \parallel M^{(1)} \parallel \gamma_I I \rangle,
\]
(8)
\[
W_{E2}(J, J') = (-1)^{I+J'-F} W(U'U'; F2) \langle \gamma_J J \parallel T^{(2)} \parallel \gamma_I J' \rangle \langle \gamma_I I \parallel M^{(2)} \parallel \gamma_I I \rangle,
\]
(9)
where \(W(\ell' \ell'; F_1)\) and \(W(\ell' \ell'; F_2)\) are \(W\) coefficients of Racah. The reduced matrix elements are defined through the relation

\[
\langle \gamma J M | T_Q^{(K)} | \gamma' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ M & Q & M' \end{pmatrix} \langle \gamma J \parallel T^{(K)} \parallel \gamma' J'. \tag{10} \]

The energies are usually expressed in terms of the hyperfine interaction constants (\(A\) and \(B\) factors)

\[
A_j = \frac{\mu_I}{I} \frac{1}{[J(J+1)(2J+1)]^{1/2}} \langle \gamma_J \parallel T^{(1)} \parallel \gamma_J \rangle, \tag{11} \]

\[
A_{j,J-1} = \frac{\mu_I}{I} \frac{1}{[J(2J-1)(2J+1)]^{1/2}} \langle \gamma_J \parallel T^{(1)} \parallel \gamma_J (J-1) \rangle, \tag{12} \]

\[
B_j = 2Q \left( \frac{J(2J-1)}{(J+1)(2J+1)(2J+3)} \right)^{1/2} \langle \gamma_J \parallel T^{(2)} \parallel \gamma_J \rangle, \tag{13} \]

\[
B_{j,J-1} = \frac{1}{2}Q \left( \frac{J(J-1)}{(J+1)(2J-1)(2J+1)} \right)^{1/2} \langle \gamma_J \parallel T^{(2)} \parallel \gamma_J (J-1) \rangle, \tag{14} \]

\[
B_{j,J-2} = \frac{1}{2}Q \left( \frac{J(J-1)(2J-1)}{(2J-3)(2J+1)} \right)^{1/2} \langle \gamma_J \parallel T^{(2)} \parallel \gamma_J (J-2) \rangle. \tag{15} \]

The energy corrections are then given by

\[
W_{M_1}(J, J) = \frac{1}{2}A_j C, \tag{16} \]

\[
W_{M_1}(j, J-1) = \frac{1}{2}A_{j,J-1} \left[ (K+1)(K-2F)(K-2I)(K-2J+1) \right]^{1/2}, \tag{17} \]

\[
W_{E_2}(J, J) = B_j \frac{\frac{1}{2}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \tag{18} \]

\[
W_{E_2}(J, J-1) = B_{j,J-1} \frac{[F(I+1)(F-I) + \frac{1}{2}][3(K+1)(K-2F)(K-2I)(K-2J+1)]^{1/2}}{2I(2I-1)J(J-1)}, \tag{19} \]

\[
W_{E_2}(J, J-2) = B_{j,J-2} \frac{\left[ 6K(K+1)(K-2I-1)(K-2F-1)(K-2F)(K-2I)(K-2J+1)(K-2J+2) \right]^{1/2}}{2I(2I-1)J(J-1)(2J-1)} \tag{20} \]

where \(C = F(F+1) - J(J+1) - I(I+1)\) and \(K = I + J + F\).

The off-diagonal constant, \(A_{j,J-1}\), can experimentally be determined in strong external magnetic fields, where \(J\) is no longer a good quantum number [4-6]. Using the \(|\gamma_J \gamma_J J M_J M_J\rangle\) representation, this parameter may also be expressed as

\[
A_{j,J-1} = \frac{1}{[J^2 - M_J^2]^{1/2} M_J} \langle \gamma_J \gamma_J J M_J M_J \parallel T^{(1)} \cdot M^{(1)} \parallel \gamma_J \gamma_J (J-1) - I M_J M_J \rangle. \tag{21} \]
2.2. Outline of method

In the MCHF method, the nonrelativistic electronic wavefunction, $\Psi$, for a state labelled $\gamma LSJ$ is expanded in terms of configuration state functions with the same $LS$ term values.

$$\Psi(\gamma LSJ) = \sum_j c_j \Phi_j(\gamma LSJ). \quad (22)$$

The configuration state functions are sums of products of spin-orbitals. The radial parts of the spin-orbitals and the expansion coefficients are determined iteratively by the multiconfiguration self-consistent field method [7]. Relativistic corrections may be included by the Breit–Pauli approximation, where the wavefunction is expanded in terms of configuration state functions with differing $LS$ term values.

$$\Psi(\gamma J) = \sum_j c_j \Phi_j(\gamma J). \quad (23)$$

The $J$ dependent expansion coefficients are then obtained from a configuration interaction (CI) calculation [8].

The magnetic hyperfine constant $A$ is written as a sum of three terms, $A^{\text{orb}}$, $D^{\text{dip}}$ and $A^{\text{cont}}$, corresponding to the orbital, spin-dipole, and contact term of the Hamiltonian, respectively. Below we derive computable expressions for the different magnetic terms and for the electric quadrupole term $B$, in terms of reduced matrix elements of one-particle tensor operators between the $LS$ coupled configuration state functions in the wavefunction expansion.

2.3. Orbital terms

The orbital terms can, after recoupling of $J$ and $(J - 1)$, be written as

$$A^\text{orb}_J = \frac{\alpha^2}{2} \frac{\mu_J}{I} \left[ \frac{2J + 1}{J(J + 1)} \right]^{1/2} \sum_{j,k} c_j c_k W(L_j S_j I J; JL_k) \langle \gamma J S_j || \sum_i I^{(1)}(i) r_i^{-3} || \gamma J L_k S_k \rangle, \quad (24)$$

$$A^\text{orb}_{J-1} = \frac{\alpha^2}{2} \frac{\mu_J}{I} \sum_{j,k} c_j c_k W(L_j S_j I J - 1; JL_k) \langle \gamma J S_j || \sum_i I^{(1)}(i) r_i^{-3} || \gamma J L_k S_k \rangle. \quad (25)$$

Using an extended version of the program TENSOR [9,10], originally written by Kobb, the reduced matrix element can be calculated as

$$\langle \gamma J S_j || \sum_i I^{(1)}(i) r_i^{-3} || \gamma J L_k S_k \rangle = \sum_{\rho_j} v(\rho_J, \sigma_k) \left( l_{\rho_j} \parallel l^{(1)} \parallel l_{\sigma_k} \right) \left( n_{\rho_j} l_{\rho_j} \parallel r^{-3} \parallel n_{\sigma_k} l_{\sigma_k} \right), \quad (26)$$

$$\langle \gamma J S_j || \sum_i I^{(1)}(i) r_i^{-3} || \gamma J L_k S_k \rangle = \sum_{\rho_j} v(\rho_J, \sigma_k) \left( l_{\rho_j} \parallel l^{(1)} \parallel l_{\rho_j} \right) \left( n_{\rho_j} l_{\rho_j} \parallel r^{-3} \parallel n_{\rho_j} l_{\rho_j} \right), \quad (27)$$

where $\rho$ and $\sigma$ are the different orbitals. The program TENSOR has been adapted for the use of nonorthogonal orbitals [11]. In case of nonorthogonality the one-electron active radial integral, $(n_p l_{\rho} \parallel r^{-3} \parallel n_{\sigma} l_{\sigma})$, is to be multiplied with a number of overlap integral $(n_{\mu} l_{\mu} \parallel n_{\nu} l_{\nu})^n$, $(n_{\mu} l_{\mu} \parallel n_{\nu} l_{\nu})^n$, $\ldots$. The present version of TENSOR allows no more than two overlap integrals to multiply the radial integral [11,12].
2.4. Spin-dipole terms

The spin-dipole terms can, after recoupling of $J$ and $(J-1)$, be written as

$$A_{j\text{dip}}^J = -\frac{\alpha^2 \mu_j}{2} \left[ \frac{30(2J+1)}{J(J+1)} \right] \sum_{j,k} c_j c_k \left( \begin{array}{c} L_j \\ S_j \\ J \\ 2 \\ 1 \\ 1 \end{array} \right) \langle \gamma_i L_j S_j || \sum_i (Cs)^{(21)} i || r_i^{-3} \parallel \gamma_k L_k S_k \rangle,$$

$$A_{j,J-1}^\text{dip} = -\frac{\alpha^2 \mu_j}{2} g \left[ \frac{30}{J} \right] \frac{1}{2} \frac{1}{2} \sum_{j,k} c_j c_k \left( \begin{array}{c} L_j \\ S_j \\ J \\ 2 \\ 1 \\ 1 \end{array} \right) \langle \gamma_i L_j S_j || \sum_i (Cs)^{(21)} i || r_i^{-3} \parallel \gamma_k L_k S_k \rangle.$$

The reduced matrix element can be calculated as

$$\langle \gamma_i L_j S_j || \sum_j (Cs)^{(21)} i || r_i^{-3} \parallel \gamma_k L_k S_k \rangle = v(\rho_j \sigma_k) \left( l_{\rho_j} || C^{(2)} || l_{\sigma_k} \right) (s || s^{(1)} || s) \left( n_{\rho_j} l_{\rho_j} || r^{-3} \parallel n_{\sigma_k} l_{\sigma_k} \right),$$

$$\rho_j \neq \sigma_k,$$  

$$\rho_j = \sigma_k.$$  

2.5. Contact terms

Using the relation $4\pi r^2 \delta(r) = \delta(r)$ between the three- and one-dimensional delta functions, the contact terms can, after recoupling of $J$ and $(J-1)$, be written

$$A_{j\text{cont}}^J = \frac{\alpha^2 \mu_j}{2} \frac{2 g_j}{J} \left[ \frac{2J+1}{3} \right] \sum_{j,k} c_j c_k \left( -1 \right) S_k - S_j \chi L_j S_j (J1 \parallel JS_k),$$

$$\times \langle \gamma_i L_j S_j || \sum_j s^{(1)}(i) r_i^{-2} \parallel \gamma_k L_k S_k \rangle,$$

$$A_{j,J-1}^\text{cont} = \frac{\alpha^2 \mu_j}{2} \frac{2 g_j}{J} \left[ \frac{2J+1}{3} \right] \sum_{j,k} c_j c_k \left( -1 \right) S_k - S_j + 1 \chi L_j S_j (J-1 \parallel JS_k),$$

$$\times \langle \gamma_i L_j S_j || \sum_j s^{(1)}(i) r_i^{-2} \parallel \gamma_k L_k S_k \rangle.$$  

The reduced matrix element can be calculated as

$$\langle \gamma_i L_j S_j || \sum_j s^{(1)}(i) r_i^{-2} \parallel \gamma_k L_k S_k \rangle = v(\rho_j \sigma_k) \left( l_{\rho_j} || s^{(1)} || s \right) \left( n_{\rho_j} l_{\rho_j} || r^{-2} \parallel n_{\sigma_k} l_{\sigma_k} \right),$$

$$\rho_j \neq \sigma_k,$$  

$$\rho_j = \sigma_k.$$  

$$\rho_j = \sigma_k.$$
The radial matrix element is expressed in the radial starting parameter \( AZ(nl) \),

\[
\left( n_{\rho l} \bigg| r^{-2} \delta(r) \bigg| n_{\sigma l} \right) = \frac{P_{nl} A_z}{r} \left. \frac{P_{nl} A_z}{r} \right|_{r \to 0} = \delta_{\rho \sigma} \delta_{l_\rho l_\sigma} AZ(n_{\rho l}) AZ(n_{\sigma l}). \tag{36}
\]

### 2.6. Quadrupole terms

The quadrupole terms can, after recoupling of \( J, (J-1) \), and \( (J-2) \), be written

\[
B_J = -Q \left( \frac{4J(2J-1)(2J+1)}{(J+1)(2J+3)} \right)^{1/2} \sum_{j,k} c_j c_k W(L_j S_j 2J; JL_k) \langle \gamma_j L_j S_j \parallel \sum_i C^{(2)}(i) r_i^{-3} \parallel \gamma_k L_k S_k \rangle,
\]

\[
B_{J,J-1} = -Q \left( \frac{1}{2} \right)^{1/2} \sum_{j,k} c_j c_k W(L_j S_j 2J-1; JL_k) \langle \gamma_j L_j S_j \parallel \sum_i C^{(2)}(i) r_i^{-3} \parallel \gamma_k L_k S_k \rangle,
\]

\[
B_{J,J-2} = -Q \left( \frac{1}{4} \right)^{1/2} \sum_{j,k} c_j c_k W(L_j S_j 2J-2; JL_k)
\times \langle \gamma_j L_j S_j \parallel \sum_i C^{(2)}(i) r_i^{-3} \parallel \gamma_k L_k S_k \rangle.
\]

The reduced matrix element is calculated as

\[
\langle \gamma_j L_j S_j \parallel \sum_i C^{(2)}(i) r_i^{-3} \parallel \gamma_k L_k S_k \rangle = v(\rho_j \sigma_k) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\sigma_k} \right) \langle n_{\rho_j l_{\rho_j}} r_i^{-3} \parallel n_{\sigma_k l_{\sigma_k}} \rangle, \quad \rho_j \neq \sigma_k,
\]

\[
\langle \gamma_j L_j S_j \parallel \sum_i C^{(2)}(i) r_i^{-3} \parallel \gamma_k L_k S_k \rangle = \sum_{\rho_j} v(\rho_j \rho_j) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\rho_j} \right) \langle n_{\rho_j l_{\rho_j}} r_i^{-3} \parallel n_{\rho_j l_{\rho_j}} \rangle, \quad \rho_j = \sigma_k.
\]

### 2.7. Hyperfine parameters in pure LS coupling

For small atoms, in which \( LS \) coupling is valid to a good approximation, the hyperfine constants \( A \) and \( B \) are often expressed in terms of the totally electronic parameters \( a_i, a_d, a_c \) and \( b_q \),

\[
a_i = \langle \gamma LSM L M S \parallel \sum_{i} l_{0}^{(i)}(i) r_i^{-3} \parallel \gamma LSM L M S \rangle,
\]

\[
a_d = \langle \gamma LSM L M S \parallel \sum_{i} 2C_0^{(2)}(i) s_0^{(i)}(i) r_i^{-3} \parallel \gamma LSM L M S \rangle,
\]

\[
a_c = \langle \gamma LSM L M S \parallel \sum_{i} 2s_0^{(1)}(i) r_i^{-2}\delta(r_i) \parallel \gamma LSM L M S \rangle,
\]

\[
b_q = \langle \gamma LSM L M S \parallel \sum_{i} 2C_0^{(2)}(i) r_i^{-3} \parallel \gamma LSM L M S \rangle,
\]

where \( M_L = L \) and \( M_S = S \).

Explicit relations between the hyperfine constants \( A \) and \( B \) and the parameters above are given in refs. [10,13].
2.8. Nonorthogonal orbitals

A totally unrestricted nonorthogonal scheme would lead to a very elaborate computer program. Therefore the present version of TENSOR [11] imposes the following restrictions on the orthogonality of the orbitals in the left hand side configuration, \( \Phi_j \), and the right hand side configuration, \( \Phi_k \), of the reduced matrix element [12].

1. The orbitals of a single configuration are mutually orthogonal.
2. There are at most two subshells in \( \Phi_j \) containing spectator electrons whose orbitals are not orthogonal to orbitals in \( \Phi_k \).
3. If all the spectator electrons with nonorthogonal orbitals have the same \( l \)-value, then there are at most two such electrons in each of \( \Phi_j \) and \( \Phi_k \).
4. \( \langle \Phi_j | \Phi_k \rangle = \delta_{jk} \) even if nonorthogonal orbitals are included.

If the user is trying to use expansions with configurations breaking the above restrictions, this program, as well as the other programs in the MCHF package, will stop and give an error message, saying that the nonorthogonality is set up incorrectly.

2.9. General form of the expressions

The contribution to the different \( A \) factors from a pair of configurations \( j \) and \( k \) can in its most basic form be written as

\[
C_A \frac{\mu_j}{I} c_j c_k \sum_{\rho, \sigma, \mu, \nu} \text{coef}(\rho, \sigma) \text{rad}(\rho, \sigma) (\mu | \mu')^{n_1}(\nu | \nu')^{n_2},
\]

(46)

the most basic form of the \( B \) factor

\[
C_B Q c_j c_k \sum_{\rho, \sigma, \mu, \nu} \text{coef}(\rho, \sigma) \text{rad}(\rho, \sigma) (\mu | \mu')^{n_1}(\nu | \nu')^{n_2},
\]

(47)

where the coefficients and the radial matrix elements \( \text{rad}(\rho, \sigma) \) are determined from the expressions above. Most often the \( A \) and \( B \) factors are expressed in the experimentally convenient unit MHz. If the nuclear magnetic moment, \( \mu_j \), is given in nuclear magnetons and the nuclear quadrupole moment, \( Q \), in barns \((10^{-28} \text{ m}^2)\), the conversion factors to MHz are \( C_A = (\frac{1}{2}\alpha^2)2cR_e m_e / M_p = 47.70534 \) and \( C_B = 2cR_e \times 10^{-28} \text{ m}^2/\alpha^2 = 234.9647 \).

3. Program structure

Many of the subroutines used in this program are included in the MCHF program package [1]. Below we describe the subroutines that are specific for the hyperfine code.

3.1. New subroutines

READWT

Reads the weights of all configurations in the wavefunction expansion. If the weights have been obtained from a \( J \) dependent CI calculation they are read from the file \langle name \rangle.j otherwise they are read from \langle name \rangle.l.
**LSJ**

Determines $L$, $S$, $L+S$ and $|L-S|$ for a configuration in the wavefunction expansion.

All the subroutines below are related to a pair of configurations $j$, $k$.

**LSJFACT**

Calculates the $L_j$, $S_j$, $L_k$, $S_k$ and $J$ dependent factors in eqs. (24), (25), (28), (29), (32), (33) and (37–39).

**TENSOR2**

To fit the structure of the hyperfine program the subroutine TENSOR has been modified. TENSOR2 outputs the following information: 

- $\text{IIRHO}(m)$ – the interacting shells in the initial configuration;
- $\text{IISIG}(m)$ – the interacting shells in the final configuration;
- $\text{NNOVLP}$ – the number of overlap integrals;
- $\text{MMU}(m)$ and $\text{MMUP}(m)$ – the shells in the first overlap integral;
- $\text{NNU}(m)$ and $\text{NNUP}(m)$ – The shells in the second overlap integral;
- $\text{IIHSH}$ and $\text{VVSHELL}(m)$ are defined as follows,

$$
\langle \gamma_l L_j \gamma_k S_k \rangle = \sum_{m=1}^{\text{IIHSH}} \text{VVSHELL}(m) \left( \rho \parallel Q^{(\alpha)} \parallel \sigma \right),
$$

where the two cases $\rho \neq \sigma$ and $\rho = \sigma$ are handled on the same footing. In case of nonorthogonality, the reduced one-electron matrix element is to be multiplied with at most two overlap integrals.

**MULTW**

Multiplies the weights of configuration $j$ and $k$.

**ORBITAL**

When $\rho_j \neq \sigma_k$, ORBITAL calculates the following quantity in eq. (26)

$$
v(\rho_j \sigma_k) \left( l_{\rho_j} \parallel t^{(1)} \parallel l_{\sigma_k} \right).
$$

When $\rho_j = \sigma_k$, the following quantities in eq. (27) are calculated:

$$
v(\rho_j \rho_j) \left( l_{\rho_j} \parallel t^{(1)} \parallel l_{\rho_j} \right).
$$

**DIPOLE**

When $\rho_j \neq \sigma_k$, DIPOLE calculates the following quantity in eq. (3):

$$
v(\rho_j \sigma_k) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\sigma_k} \right) \left( s \parallel s^{(\tau)} \parallel s \right).
$$

When $\rho_j = \sigma_k$, the following quantities in eq. (31) are calculated:

$$
v(\rho_j \rho_j) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\rho_j} \right) \left( s \parallel s^{(\tau)} \parallel s \right).
$$

**CONTACT**

When $\rho_j \neq \sigma_k$, CONTACT calculates the following quantity in eq. (34):

$$
v(\rho_j \sigma_k) \left( s \parallel s^{(\tau)} \parallel s \right).
$$
When \( \rho_j = \sigma_k \), the following quantities in eq. (35) are calculated:
\[
v(\rho_j) \left( s \parallel s^{(1)} \parallel s \right).
\] (54)

**QDRPOLE**

When \( \rho_j \neq \sigma_k \), QDRPOLE calculates the following quantity in eq. (40):
\[
v(\rho_j) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\sigma_k} \right).
\] (55)

When \( \rho_j = \sigma_k \), the following quantities in eq. (41) are calculated:
\[
v(\rho_j) \left( l_{\rho_j} \parallel C^{(2)} \parallel l_{\rho_j} \right).
\] (56)

**RADIAL1**

Calculates the one-electron active radial integral \( (n_{\rho_j} l_{\rho_j} r^{-3} | n_{\sigma_k} l_{\sigma_k}) \). In case of nonorthogonality the overlap integrals are calculated and multiplied with the active radial integral.

**RADIAL2**

Calculates the one-electron active radial integral \( (n_{\rho_j} l_{\rho_j} r^{-3} \delta(r) | n_{\sigma_k} l_{\sigma_k}) \). In case of nonorthogonality the overlap integrals are calculated and multiplied with the active radial integral.

**PRINT**

Dependent on the responses to the prompts in the beginning of the program, this subroutine prints out parameters from the matrix element calculations between configuration \( j \) and \( k \).

### 3.2. New common blocks

A series of COMMON blocks arising from the original cfp packages and from Robb's tensor program have been redefined in the write-up of the MCHF_LIB_COM, MCHF_LIB_ANG, MCHF_RAD3 and NJGRAF libraries. The common blocks OVRINT and OVRLAP are related to the non-orthogonality feature and are described in the write-up of MCHF_NONH [14].

**COEF**

ORBF(n), DIPF(n), CONTF(n), QUADF(n) contains the \( L_j, S_j, L_k, S_k, J \) dependent coefficients in eqs. (24), (25), (28), (32), (33) and (37–39), where \( n \) is a parameter ordering the different combinations of \( J \) and \( J' \).

\( J(n), JP(n) \) are used in the printout to give \( J \) and \( J' \) as rational numbers. JJMAX, JJMIN are twice the maximum and minimum \( J \) quantum numbers, respectively, for the wavefunction \( \Psi(\gamma_j LSJ) \) in eqs. (22) and (23). LL1, SS1, JJ1MAX, JJ1MIN correspond to \( 2L_{j'}, 2S_{j'}, 2 | L_{j'} + S_{j'} |, 2 | L_{j'} - S_{j'} | \). LL2, SS2, JJ2MAX, JJ2MIN correspond to \( 2L_k, 2S_k, 2 | L_k + S_k |, 2 | L_k - S_k | \).

**TENSOR**

This common block holds the output from TENSOR2.

**HYPER**

Quantities in this common block are closely linked to the output from TENSOR. After the subroutine ORBITAL has been called the quantities in the common block will be defined as follows:

\( \text{NHY} = \text{JIHSH} \),
\[ \text{VHY}(m) = \text{VVSH}(m)(I_\alpha \| t^{(1)}\| I_\alpha), \]
\[ \text{IRHY}(m) = \text{IIFUL}(\text{IRHO}(m)), \]
\[ \text{ISHY}(m) = \text{IIFUL}(\text{ISIG}(m)), \]
\[ \text{JRHY}(m) = \text{IAJCMP}(\text{IRHY}(m)), \]
\[ \text{JSHY}(m) = \text{IAJCMP}(\text{ISHY}(m)), \]
\[ \text{JMUHY}(m) = \text{IIFUL}(\text{MMU}(m)), \]
\[ \text{JMUHY}(m) = \text{IAJCMP}(\text{IMUHY}(m)), \]
\[ \text{JNUHY}(m) = \text{IAJCMP}(\text{INUHY}(m)), \]
\[ \text{JNUHY}(m) = \text{IAJCMP}(\text{INUHY}(m)), \]
\[ \text{JMUHY}(m) = \text{IAJCMP}(\text{IMUHY}(m)), \]
\[ \text{JNUHY}(m) = \text{IAJCMP}(\text{INUHY}(m)), \]
\[ \text{JNUHY}(m) = \text{IAJCMP}(\text{INUHY}(m)), \]

where \( m = 1, \ldots, \text{IIHSH} \).

In the same way the quantities above can be inferred from eqs. (51)-(56) after the subroutines DIPOLE, CONTACT and QDRPOLE have been called.

**PRINTA**

This common block supplies the subroutine PRINT with many of the quantities needed for the printout. For every pair of configurations \( j, k \) the following quantities are supplied:

- \( \text{ORB} = \text{ORBF}(n)\text{VHY}(N) \), where \( \text{VHY}(N) \) is the output from the subroutine ORBITAL.
- \( \text{DIP} = \text{DIPF}(n)\text{VHY}(N) \), where \( \text{VHY}(N) \) is the output from the subroutine DIPOLE.
- \( \text{CONT} = \text{CONTF}(n)\text{VHY}(N) \), where \( \text{VHY}(N) \) is the output from the subroutine CONTACT.
- \( \text{QUAD} = \text{QUADF}(n)\text{VHY}(N) \), where \( \text{VHY}(N) \) is the output from the subroutine QDRPOLE.
- \( \text{RADINT} = \text{QUADR} (\text{IRHY}(N), \text{ISHY}(N), -3) \).
- \( \text{AZSQR} = \text{AZ}(\text{IRHY}(N))\text{AZ}(\text{ISHY}(N)) \).
- \( \text{INTGR} = 1 \) if radial integration has been performed and 0 otherwise.
- \( \text{OVLINT1} = \text{QUADR}(\text{IMUHY}(N), \text{IMUPHY}(N), 0)^*\text{IOVEP}(1) \).
- \( \text{OVLINT2} = \text{QUADR}(\text{INUHY}(N), \text{INUHY}(N), 0)^*\text{IOVEP}(2) \).
- \( \text{CONTRI} \) the contribution to the \( A \) and \( B \) factors.

IREPRI, ICOPRI and IDOPRI are parameters controlling the write-out.

4. Input data

To describe how the calculations are to be done, a few prompts for data have to be answered.

1. **Name of state**

   This program assumes the naming conventions described in the paper on the atomic-structure package [1], and the \langle name \rangle of the state has to be specified.

2. **Type**

   This prompt asks you to specify the different constants that are to be calculated. The options are
   - only diagonal \( A \) and \( B \) factors,
   - both diagonal and off-diagonal \( A \) and \( B \) factors,
   - only the coefficients of the radial matrix elements.

For the last option all needed input data is in the configuration input file \langle name \rangle.c.
3. **Hyperfine parameters**

The hyperfine parameters $a_t$, $a_d$, $a_c$ and $b_q$ can be printed out. This is only meaningful for pure $LS$ terms.

4. **Input**

This prompt inquires if the wavefunctions expansion has been obtained from an MCHF or CI calculation. In case of an MCHF calculation, configuration weights are read from the configuration input file ⟨name⟩.c. If the expansion has been obtained from a CI calculation, weights are read from the eigenvector file ⟨name⟩.j or ⟨name⟩.l, dependent on whether the CI Hamiltonian is $J$ dependent or not.

5. **Number**

In general the eigenvector files ⟨name⟩.j or ⟨name⟩.l from a CI calculation contain wavefunction expansions for many different states. Thus, the particular states for which the $A$ and $B$ factors are to be calculated have to be specified. Suppose, in a $J$ dependent CI calculation, that the expansion in the file ⟨name⟩.c consists of the following four CSFs

\[
\begin{align*}
&1s(2) \ 2p(1) \\
&1s0 \ 2p1 \ 2p \\
&1s(1) \ 2s(1) \ 2p(1) \\
&2s1 \ 2s1 \ 2p1 \ 1s \ 2p \\
&1s(1) \ 2s(1) \ 2p(1) \\
&2s1 \ 2s1 \ 2p1 \ 3s \ 2p \\
&1s(1) \ 2s(1) \ 2p(1) \\
&2s1 \ 2s1 \ 2p1 \ 2s \ 4p
\end{align*}
\]

and that the hyperfine structure is to be calculated for the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ states of the third CSF

\[
\begin{align*}
&1s(1) \ 2s(1) \ 2p(1) \\
&2s1 \ 2s1 \ 2p1 \ 3s \ 2p
\end{align*}
\]

Then, by replying 3 to the number prompt the program searches for the two wavefunction expansions (one for the $J = \frac{1}{2}$ state and one for the $J = \frac{3}{2}$ state) in the file ⟨name⟩.j, having the third CSF as the dominant component. If no state has the third CSF as the dominant component the program stops and an error message is written out, telling the user how to proceed. This is also the case when more than one state for a given $J$ value has the third CSF as the dominant component in the expansion.

6. **Print-out**

In a calculation of the $A$ and $B$ factors, values of the $A_{\text{orb}}$, $A_{\text{dip}}$, $A_{\text{cont}}$, and $B$ terms are written to the file ⟨name⟩.h. If in this case a full print-out is requested, values of coefficients and radial matrix elements as well as the contribution to the different $A$ and $B$ factors are printed for every pair of configurations.

7. **Tolerance for printing**

In the case of a full print-out it is possible to set a tolerance for printing. If the contribution to a term is less than the tolerance, then it will not be printed.

8. **Nuclear data**

The last prompt asks for the following nuclear data:

- $2I$,
- $\mu_I$ in nuclear magnetons,
- $Q$ in barns.
A recent compilation of experimental data on nuclear magnetic dipole and electric quadrupole moments for ground and excited states can be found in ref. [15].

5. Output data

When the program is running $J_a = 1$, $J_a = 2, \ldots, J_a = N$, where $N$ is the number of CFSs in the wavefunction expansion, is written out on the screen, indicating how far the program has executed. Output from the program is written to a file <name>.h. If a full print-out is requested, the program outputs the following data from eqs. (46) and (47) for a pair of configurations $j$ and $k$.

1. $J_J'$ – the $J$ values for which the matrix element has been calculated.
2. Weight – the configuration weight $c_j c_k$.
3. Coeff – the coefficient $\text{coeff}(\rho, \sigma)$.
4. Radial matrix elements – values of the radial matrix elements $\text{rad}(\rho, \sigma)$, $(\mu | \mu')^u_1$ and $(\nu | \nu')^u_2$
5. $A$(MHz), $B$(MHz) – the contribution in MHz to the different $A$ and $B$ factors from this pair of configurations.

6. Examples

The Test Run Output contains full print-outs from two different hyperfine structure calculations of $2p^2P$ in $^7\text{Li}$. Diagonal $A$ and $B$ factors are calculated as well as the hyperfine parameters $a_\rho$, $a_d$, $a_c$ and $b_d$. The wavefunctions have been obtained from a HF and a non-orthogonal MCHF calculation, respectively. Nuclear data has been supplied by the user.

Acknowledgements

The authors wish to acknowledge the assistance given to this project by K.M.S. Saxena who shared an early version of a hyperfine program with us, based on parts of Alan Hibbert's CIV3 program.

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References

TEST RUN OUTPUT

>> cat cfg.inp

1s(2) 2p1(1)
1 3 120 2 1 2 70

===> Case #1.

Display cfg.inp

===> Obtain Energy Expression

Full print-out ? (Y/N)

Tolerance for printing (in MHz)

>0.0

Give 2p1 and nuclear dipole and quadrupole moments (in n.m. and barns)

>3.256000 -0.040000

The configuration set

STATE (WITH 1 CONFIGURATIONS):

THERE ARE 2 ORBITALS AS FOLLOWS:

ls 2p1

CONFIGURATION 1 ( OCCUPIED ORBITALS= 2 ): 1s( 2) 2p1( 1)

COUPLING SCHEME: ISO 2P1

Ja= 1

>> cat lit.h

Display lit.h file

Hyperfine structure calculation

1il.c

Tolerance for printing 0.000000 MHz

Nuclear dipole moment 3.256000 n.m.

Nuclear quadrupole moment -0.040000 barns

2p1 3

Li 2p -7.3650696

(config 1|hfs|config 1 )

Orbital term

matrix element <2p1|ls|--3|2p1> matrix element values Aorb(MHz)

J J' weight coeff matrix element values Aorb(MHz)

1/2 1/2 1.000000 2.666667 0.0686 16.173963

3/2 3/2 1.000000 1.333333 0.0586 8.086976

Spin-dipole term

matrix element <2p1|ls|--3|2p1> matrix element values Adip(MHz)

J J' weight coeff matrix element values Adip(MHz)

1/2 1/2 1.000000 2.666667 0.0686 16.173963

3/2 3/2 1.000000 -0.266667 0.0686 -1.619271

Quadrupole term

matrix element <2p1|ls|--3|2p1> matrix element values B(NHz)

J J' weight coeff matrix element values B(NHz)

3/2 3/2 1.000000 0.400000 0.0686 -0.220196
There are 6 orbitals as follows:
1s 2p1 2s2 2p2 2s3 2p3
Enter orbitals to be varied: (ALL,NONE,SONE,WIT=,comma delimited list)
>2p1.2s2.2p2.2s3.2p3
Default electron parameters ? (Y/N)
>y
Default values (RU,REL,STRAIN) ? (Y/N)
>y
Default values for other parameters ? (Y/N)
>y
Do you wish to continue along the sequence ?
>n
>mv cfg.out 112.c
>> mv wfn.out 112.w
>> hfs
hyperfine calculation

**

Hyperfine parameters in a.u.
al ad ac bq
0.06867 -0.01171 0.00000 -0.02343

**

Hyperfine parameters in a.u.
al ad ac bq
0.06867 -0.01171 0.00000 -0.02343

**

Name of state
>112
Indicate the type of calculation
0 => diagonal A and B factors only;
1 => diagonal and off-diagonal A and B factors;
2 => coefficients of the radial matrix elements only:
>1
Hyperfine parameters al,ad,ac and bq ? (Y/N)
>y
Input from an MCHF (M) or CI (C) calculation ?
>m
Full print-out ? (Y/N)
>y
Tolerance for printing (in MHz)
>1.0
Give 2I and nuclear dipole and quadrupole moments (in n.m. and barns)
>2,3.266,-0.046

The configuration set

STATE (WITH 3 CONFIGURATIONS):

 THERE ARE 6 ORBITALS AS FOLLOWS:
1s 2p1 2s2 2p2 2s3 2p3

CONFIGURATION 1 (OCCUPIED ORBITALS=2): 1s(2) 2p1(1)
COUPLING SCHEME: 150 2p1

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### Configuration 2 (Occupied Orbitals = 3)

<table>
<thead>
<tr>
<th>J</th>
<th>J'</th>
<th>Orbital</th>
<th>Spin-dip</th>
<th>Cont</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>2p0</td>
<td>16.84626</td>
<td>16.78143</td>
<td>11.45731</td>
</tr>
</tbody>
</table>

**Coupling Scheme:**

\[
\begin{align*}
2s1 & \quad 2s1 \quad 2p1 \\
& \quad 150 \quad 2p0
\end{align*}
\]

### Configuration 3 (Occupied Orbitals = 3)

<table>
<thead>
<tr>
<th>J</th>
<th>J'</th>
<th>Orbital</th>
<th>Spin-dip</th>
<th>Cont</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>3/2</td>
<td>2p0</td>
<td>8.42313</td>
<td>-1.67815</td>
<td>-11.45731</td>
</tr>
</tbody>
</table>

**Coupling Scheme:**

\[
\begin{align*}
2s1 & \quad 2s1 \quad 2p1 \\
& \quad 350 \quad 2p0
\end{align*}
\]

### Hyperfine Structure Calculation

**B factors in MHz**

\[
\begin{align*}
J \quad J' \quad Quadrupole
\end{align*}
\]

\[
\begin{align*}
1/2 & \quad 1/2 & \quad 0.000000
\end{align*}
\]

**A factors in MHz**

\[
\begin{align*}
J \quad J' \quad Spin-dip & \quad Total
\end{align*}
\]

### Hyperfine Parameters in a.u.

al & ad & ac & bq

\[
\begin{align*}
0.06101 & \quad -0.01214 & \quad -0.24866 & \quad -0.02440
\end{align*}
\]

**Orbital Term**

<table>
<thead>
<tr>
<th>J</th>
<th>J'</th>
<th>Orbital</th>
<th>Spin-dip</th>
<th>Cont</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>2p0</td>
<td>16.84626</td>
<td>16.78143</td>
<td>11.45731</td>
</tr>
</tbody>
</table>

**Spin-dipole Term**

<table>
<thead>
<tr>
<th>J</th>
<th>J'</th>
<th>Orbital</th>
<th>Spin-dip</th>
<th>Cont</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>3/2</td>
<td>2p0</td>
<td>8.42313</td>
<td>-1.67815</td>
<td>-11.45731</td>
</tr>
</tbody>
</table>

**Fermi-contact Term**

<table>
<thead>
<tr>
<th>J</th>
<th>J'</th>
<th>Orbital</th>
<th>Spin-dip</th>
<th>Cont</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>3/2</td>
<td>2p0</td>
<td>8.42313</td>
<td>-1.67815</td>
<td>-11.45731</td>
</tr>
</tbody>
</table>

**A factors in MHz**

\[
\begin{align*}
J \quad J' \quad Aorb(Kz) & \quad Acont(\Delta E_{2p1})
\end{align*}
\]

\[
\begin{align*}
16.682863 & \quad 5.739065 & \quad 16.702207 & \quad -0.266076 & \quad -0.333720
\end{align*}
\]

**B factors in MHz**

\[
\begin{align*}
J \quad J' \quad Quadrupole
\end{align*}
\]

\[
\begin{align*}
1/2 & \quad 1/2 & \quad 0.000000
\end{align*}
\]

**A factors in MHz**

\[
\begin{align*}
J \quad J' \quad Spin-dip & \quad Total
\end{align*}
\]