HFSZEEMAN—A program for computing weak and intermediate field fine and hyperfine structure Zeeman splittings from MCDHF wave functions [☆]

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Abstract

Given electronic wave functions generated by the grasp2K relativistic atomic structure package, this program calculates diagonal magnetic dipole A_J and electric quadrupole B_J hyperfine interaction constants and Landé g_J factors. In addition the program computes diagonal and off-diagonal reduced hyperfine and Zeeman matrix elements and constructs the total interaction matrix for an atom in an external magnetic field. By diagonalizing the interaction matrix and plotting eigenvalues as functions of the magnetic field, Zeeman splittings of hyperfine levels are obtained. The method is applicable in the weak and intermediate field regions and yields results that are useful when analyzing spectra from e.g. EBIT sources and magnetic stars. The program can also be used in the field free limit to calculate mixing coefficients that determine rates of hyperfine induced transitions. For atoms with zero nuclear spin I the program computes splittings of the fine-structure levels.

Program summary

Program title: HFSZEEMAN

Catalogue identifier: ADZS_v1_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADZS_v1_0.html

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

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

No. of lines in distributed program, including test data, etc.: 1528

No. of bytes in distributed program, including test data, etc.: 294 664

Distribution format: tar.gz

Programming language: Fortran, Matlab

Computer: IBM-compatible PC, unix workstation

Operating system: Unix, Linux

Classification: 11.6

Subprograms used: Cat Id: ADZL_v1_0; Title: grasp2K v1.0; Reference: CPC 177 (2007) 597

Nature of problem: Prediction of weak and intermediate field Zeeman splittings of fine- and hyperfine structure levels using multiconfiguration Dirac–Hartree–Fock wave functions.

Solution method: The electronic wave function for a state labeled ΓJM is expanded in terms of jj -coupled configuration state functions $|\Gamma JM\rangle = \sum_{\gamma} c_{\gamma} |\gamma JM\rangle$. In this representation the reduced matrix elements used to construct the interaction matrix can be computed as sums over one-particle radial integrals. By diagonalizing the interaction matrix and plotting eigenvalue as functions of the magnetic field, Zeeman splittings of fine- and hyperfine structure levels are obtained.

Restrictions: The complexity of the cases that can be handled is entirely determined by the grasp2K package [P. Jönsson, H. Xe, C. Froese Fischer, I.P. Grant, Comput. Phys. Commun. 177 (2007) 597] used for the generation of the electronic wave functions.

[☆] 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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Running time: CPU time required to execute test cases: a few seconds.

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1. Introduction

The present `hfszeeman` program is an extension and update of the old hyperfine structure code `hfs92` [1], that was modified by Froese Fischer and Jönsson to treat Landé g_J factors [2]. The program is a part of the `grasp2K` relativistic atomic structure package [3]. As such it adheres to the structure and constraints underlying the package. The role of the program is to calculate magnetic dipole A_J and electric quadrupole B_J hyperfine interaction constants, Landé g_J factors and to determine Zeeman splittings of hyperfine levels in weak and intermediate magnetic fields. For atoms with zero nuclear spin I the program computes Landé g_J factors and splittings of the fine-structure levels. Given the output files of the `hfszeeman` program the accompanying `mtrans` program [4] can be used to compute transition rates between different magnetic fine- and hyperfine structure sublevels. In the field free limit `mtrans` can also be used to compute rates of hyperfine induced transitions.

2. Theory

2.1. Relativistic wave functions

In the multiconfiguration Dirac–Hartree–Fock method the relativistic electronic wave function, frequently referred to as the atomic state function, for a state labeled ΓJM_J is expanded in jj -coupled configuration state functions (CSFs) which are eigenfunctions of $\mathbf{J}^2$, $\mathbf{J}_z$ and parity

$$|\Gamma JM_J\rangle = \sum_{\gamma} c_{\gamma} |\gamma JM_J\rangle. \quad (1)$$

The label Γ is often the same as the label for the dominating CSF and gives a short description of the state including the configuration and the coupling tree. The configuration state functions are sums of products of four-component spin-orbitals

$$\langle \mathbf{r} | n\kappa m \rangle = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r) \chi_{\kappa m}(\hat{\mathbf{r}}) \\ i Q_{n\kappa}(r) \chi_{-\kappa m}(\hat{\mathbf{r}}) \end{pmatrix}, \quad (2)$$

where n is the principal quantum number and κ is the relativistic angular quantum number $\kappa = \pm(j + \frac{1}{2})$ for $l = j \pm \frac{1}{2}$ with l and j being the orbital and total angular momenta of the electron. $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small component radial wave functions and $\chi_{\kappa m}(\hat{\mathbf{r}})$ are the spinor spherical harmonics in the lsj -coupling scheme

$$\chi_{\kappa m}(\hat{\mathbf{r}}) = \sum_{\sigma} \left\langle lm - \sigma \frac{1}{2} \sigma \left| l \frac{1}{2} j m \right. \right\rangle Y_{lm-\sigma}(\theta, \varphi) \xi(\sigma). \quad (3)$$

The radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are represented on a logarithmic grid and are required to be orthonormal within each κ symmetry. In the multiconfiguration self-consistent field procedure both the radial functions and the expansion coefficients for the configuration state functions are optimized to self-consistency.

When the set of radial orbitals has been obtained, relativistic configuration interaction (RCI) calculations can be performed. Here the transverse photon interaction as well as the leading QED effects may be included in the Hamiltonian.

2.2. Hyperfine structure

The hyperfine structure of an atomic energy level is caused by the non-central interaction between the electrons and the electromagnetic multipole moments of the nucleus. The Hamiltonian for the interaction may be written as a multipole expansion

$$H_{hfs} = \sum_{k \geq 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \quad (4)$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k in the electronic and nuclear spaces, respectively [5]. The $k = 1$ term represents the magnetic dipole interaction and the $k = 2$ term the electric quadrupole interaction. Higher order terms are smaller

and can often be neglected. For an N -electron atom the electronic tensor operators are, in atomic units,

$$\mathbf{T}^{(1)} = \sum_{j=1}^N \mathbf{t}^{(1)}(j) = \sum_{j=1}^N -i\sqrt{2}\alpha r_j^{-2}(\boldsymbol{\alpha}_j \mathbf{C}^{(1)}(j))^{(1)}, \quad (5)$$

$$\mathbf{T}^{(2)} = \sum_{j=1}^N \mathbf{t}^{(2)}(j) = \sum_{j=1}^N -r_j^{-3} \mathbf{C}^{(2)}(j). \quad (6)$$

In the formulas above, $i = \sqrt{-1}$ is the imaginary unit, α is the fine-structure constant, $\boldsymbol{\alpha}$ is the Dirac matrix and $\mathbf{C}^{(k)}$ is a spherical tensor operator. The matrix elements of the nuclear tensor operators are related to the conventional nuclear magnetic dipole moment μ_I and electric quadrupole moment Q by

$$\mu_I = \langle \gamma I I | M_0^{(1)} | \gamma I I \rangle = \begin{pmatrix} I & 1 & I \\ -I & 0 & I \end{pmatrix} \sqrt{2I+1} \langle \gamma I | \mathbf{M}^{(1)} | \gamma I \rangle, \quad (7)$$

$$Q = 2 \langle \gamma I I | M_0^{(2)} | \gamma I I \rangle = 2 \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix} \sqrt{2I+1} \langle \gamma I | \mathbf{M}^{(2)} | \gamma I \rangle, \quad (8)$$

where the reduced matrix elements are defined in the Brink and Satchler sense [6]. Evaluating the 3-j symbols we have

$$\langle \gamma I | \mathbf{M}^{(1)} | \gamma I \rangle = \mu_I \sqrt{\frac{I+1}{I}}, \quad (9)$$

$$\langle \gamma I | \mathbf{M}^{(2)} | \gamma I \rangle = \frac{Q}{2} \sqrt{\frac{(2I+3)(I+1)}{I(2I-1)}}. \quad (10)$$

Values of nuclear magnetic dipole and electric quadrupole moments can be found in the recent compilation by Stone [7].

The hyperfine interaction couples the nuclear $\mathbf{I}$ and electronic $\mathbf{J}$ angular momenta to a total momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Denoting the nuclear wave functions by $|\gamma I M_I\rangle$, zero-order wave functions of the coupled states can be written

$$|\gamma \Gamma I J F M_F\rangle = \sum_{M_I, M_J} \langle I J M_I M_J | I J F M_F \rangle |\gamma I M_I\rangle |\Gamma J M_J\rangle. \quad (11)$$

If the hyperfine interaction is weak so that the interaction energy is small compared to the fine-structure separation, H_{hfs} can be treated in first-order perturbation theory. A fine-structure level ΓJ is then split according to

$$\langle \gamma \Gamma I J F M_F | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} + \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} | \gamma \Gamma I J F M_F \rangle. \quad (12)$$

We express this in terms of the reduced electronic and nuclear matrix elements

$$\begin{aligned} & \langle \gamma \Gamma I J F M_F | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | \gamma \Gamma I J F M_F \rangle \\ &= (-1)^{I+J+F} \begin{Bmatrix} I & J & F \\ J & I & 1 \end{Bmatrix} \sqrt{2J+1} \sqrt{2I+1} \langle \Gamma J | \mathbf{T}^{(1)} | \Gamma J \rangle \langle \gamma I | \mathbf{M}^{(1)} | \gamma I \rangle, \end{aligned} \quad (13)$$

$$\begin{aligned} & \langle \gamma \Gamma I J F M_F | \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} | \gamma \Gamma I J F M_F \rangle \\ &= (-1)^{I+J+F} \begin{Bmatrix} I & J & F \\ J & I & 2 \end{Bmatrix} \sqrt{2J+1} \sqrt{2I+1} \langle \Gamma J | \mathbf{T}^{(2)} | \Gamma J \rangle \langle \gamma I | \mathbf{M}^{(2)} | \gamma I \rangle. \end{aligned} \quad (14)$$

Usually the dependence on the F quantum number is factored out and the energies are written in terms of the hyperfine interaction constants

$$A_J = \frac{\mu_I}{I} \frac{1}{\sqrt{J(J+1)}} \langle \Gamma J | \mathbf{T}^{(1)} | \Gamma J \rangle, \quad (15)$$

$$B_J = 2Q \sqrt{\frac{J(2J-1)}{(J+1)(2J+3)}} \langle \Gamma J | \mathbf{T}^{(2)} | \Gamma J \rangle. \quad (16)$$

The hyperfine energies are then given by

$$\frac{1}{2} A_J C + B_J \frac{\frac{3}{4} C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \quad (17)$$

where $C = F(F+1) - J(J+1) - I(I+1)$. To account for off-diagonal hyperfine effects we consider the total Hamiltonian

$$H = H_{fs} + H_{hfs}, \quad (18)$$

where H_{fs} is the relativistic fine-structure Hamiltonian that may include the Breit interaction. Now only F and M_F are good quantum numbers and we represent the wave function by an expansion

$$|\Upsilon \tilde{F} M_F\rangle = \sum_{\Gamma J} d_{\Gamma J} |\Upsilon \Gamma I J F M_F\rangle. \quad (19)$$

This leads to the matrix eigenvalue problem

$$\mathbf{H}\mathbf{d} = E\mathbf{d}, \quad (20)$$

where $\mathbf{H}$ is the matrix with elements

$$H_{\Gamma J, \Gamma' J'} = \langle \Upsilon \Gamma I J F M_F | H_{fs} + \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} + \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} | \Upsilon \Gamma' I J' F M_F \rangle. \quad (21)$$

The matrix elements of the fine-structure Hamiltonian H_{fs} are diagonal in all quantum numbers and equals the calculated fine-structure energies $E_{\Gamma J}$. The hyperfine interaction matrix elements can be expressed in terms of reduced electronic and nuclear matrix elements. The relevant matrix elements are

$$\begin{aligned} & \langle \Upsilon \Gamma I J F M_F | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | \Upsilon \Gamma' I J' F M_F \rangle \\ &= (-1)^{I+J+F} \begin{Bmatrix} I & J & F \\ J' & I & 1 \end{Bmatrix} \sqrt{2J+1} \sqrt{2I+1} \langle \Gamma J \| \mathbf{T}^{(1)} \| \Gamma' J' \rangle \langle \Upsilon I \| \mathbf{M}^{(1)} \| \Upsilon I \rangle, \end{aligned} \quad (22)$$

where $J' = J-1, J, J+1$ and

$$\begin{aligned} & \langle \Upsilon \Gamma I J F M_F | \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} | \Upsilon \Gamma' I J' F M_F \rangle \\ &= (-1)^{I+J+F} \begin{Bmatrix} I & J & F \\ J' & I & 2 \end{Bmatrix} \sqrt{2J+1} \sqrt{2I+1} \langle \Gamma J \| \mathbf{T}^{(2)} \| \Gamma' J' \rangle \langle \Upsilon I \| \mathbf{M}^{(2)} \| \Upsilon I \rangle, \end{aligned} \quad (23)$$

where $J' = J-2, J-1, J, J+1, J+2$. Explicit formulas for the Wigner 6-j symbols can be found in [8].

2.3. Zeeman effect of fine-structure levels

If we choose the direction of the magnetic field as the z -direction the interaction, neglecting diamagnetic contributions, can be written

$$H_m = (N_0^{(1)} + \Delta N_0^{(1)})B, \quad (24)$$

where the last term is the so called Schwinger QED correction. For an N -electron atom the electronic tensor operators are [10], in atomic units,

$$\mathbf{N}^{(1)} = \sum_{j=1}^N \mathbf{n}^{(1)}(j) = \sum_{j=1}^N -i \frac{\sqrt{2}}{2\alpha} r_j (\boldsymbol{\alpha}_j \mathbf{C}^{(1)}(j))^{(1)}, \quad (25)$$

$$\Delta \mathbf{N}^{(1)} = \sum_{j=1}^N \Delta \mathbf{n}^{(1)}(j) = \sum_{j=1}^N \frac{g_s - 2}{2} \beta_j \boldsymbol{\Sigma}_j, \quad (26)$$

where $\boldsymbol{\Sigma}_j$ is the relativistic spin-matrix and $g_s = 2.00232$ the g factor of the electron spin corrected for QED effects. If the magnetic field is weak so that the interaction energy is small compared to the fine-structure separation the interaction can be treated in first-order perturbation theory. A fine-structure level ΓJ is then split according to

$$\begin{aligned} & \langle \Gamma J M_J | N_0^{(1)} + \Delta N_0^{(1)} | \Gamma J M_J \rangle B \\ &= (-1)^{J-M_J} \begin{pmatrix} J & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \sqrt{2J+1} \langle \Gamma J \| \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} \| \Gamma J \rangle B \\ &= \frac{M_J}{\sqrt{J(J+1)}} \langle \Gamma J \| \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} \| \Gamma J \rangle B. \end{aligned} \quad (27)$$

Usually the dependence on the M_J quantum number is factored out and the energies are expressed in terms of the Landé g_J factor

$$g_J = 2 \frac{\langle \Gamma J \| \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} \| \Gamma J \rangle}{\sqrt{J(J+1)}}. \quad (28)$$

The energy splittings are then given by

$$g_J M_J \frac{B}{2}. \quad (29)$$

In the intermediate field regime we consider the total Hamiltonian

$$H = H_{fs} + H_m. \quad (30)$$

When the field is included only M_J remain a good quantum number and the wave function is written as an expansion

$$|\tilde{\Gamma} M_J\rangle = \sum_{\Gamma J} d_{\Gamma J} |\Gamma J M_J\rangle. \quad (31)$$

Just as for the hyperfine interaction this leads to a matrix eigenvalue problem

$$\mathbf{H}\mathbf{d} = E\mathbf{d}, \quad (32)$$

where $\mathbf{H}$ is the matrix with elements

$$H_{\Gamma J, \Gamma' J'} = \langle \Gamma J M_J | H_{fs} + (N_0^{(1)} + \Delta N_0^{(1)}) B | \Gamma' J' M_J \rangle. \quad (33)$$

The matrix elements of the fine-structure Hamiltonian H_{fs} are diagonal in all quantum numbers and equals the energies $E_{\Gamma J}$ of the fine-structure levels. The Zeeman interaction matrix elements can be expressed in terms of the reduced electronic matrix elements and the magnetic field

$$\begin{aligned} & \langle \Gamma J M_J | N_0^{(1)} + \Delta N_0^{(1)} | \Gamma' J M_J \rangle \\ &= (-1)^{J-M_J} \begin{pmatrix} J & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \sqrt{2J+1} \langle \Gamma J || \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} || \Gamma' J \rangle \\ &= \frac{M_J}{\sqrt{J(J+1)}} \langle \Gamma J || \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} || \Gamma' J \rangle, \end{aligned} \quad (34)$$

$$\begin{aligned} & \langle \Gamma J M_J | N_0^{(1)} + \Delta N_0^{(1)} | \Gamma' J - 1 M_J \rangle \\ &= (-1)^{J-M_J} \begin{pmatrix} J & 1 & J-1 \\ -M_J & 0 & M_J \end{pmatrix} \sqrt{2J+1} \langle \Gamma J || \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} || \Gamma' J - 1 \rangle \\ &= \sqrt{\frac{J^2 - M_J^2}{J(2J-1)}} \langle \Gamma J || \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} || \Gamma' J - 1 \rangle. \end{aligned} \quad (35)$$

By diagonalizing the interaction matrix and plotting eigenvalues as functions of the magnetic field Zeeman splittings of fine-structure levels are obtained.

2.4. Zeeman effect of hyperfine levels

We now go on to describe the Zeeman effect of hyperfine levels. If we choose the direction of the magnetic field as the z -direction the interaction, again neglecting diamagnetic contributions, can be written

$$H_m = (N_0^{(1)} + \Delta N_0^{(1)}) B + \text{interaction with nucleus}. \quad (36)$$

The interaction with the nucleus is weak and can be neglected. Below we will treat both the weak field limit as well as the intermediate field case.

If the magnetic field is weak so that the interaction energy is small compared to the hyperfine structure separation the interaction can be treated in first-order perturbation theory. A hyperfine level $\gamma \Gamma I J F$ for which off-diagonal effects are small is then split according to

$$\begin{aligned} & \langle \gamma \Gamma I J F M_F | N_0^{(1)} + \Delta N_0^{(1)} | \gamma \Gamma I J F M_F \rangle B \\ &= M_F \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \frac{\langle \Gamma J || \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} || \Gamma J \rangle}{\sqrt{J(J+1)}} B \\ &= M_F \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} g_J \frac{B}{2}. \end{aligned} \quad (37)$$

By defining a Landé g_F factor

$$g_F = \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} g_J, \quad (38)$$

the energy splittings are given by

$$g_F M_F \frac{B}{2} \quad (39)$$

in analogy with the formula for the splitting of the fine-structure levels.

More generally we will look at hyperfine structure, including off-diagonal contributions, in an intermediate field. The total Hamiltonian is now given by

$$H = H_{fs} + H_{hfs} + H_m. \quad (40)$$

In this case M_F is the only good quantum number and we represent the wave function by the expansion

$$|\gamma \tilde{I} M_F\rangle = \sum_{\Gamma J F} d_{\Gamma J F} |\gamma \Gamma I J F M_F\rangle. \quad (41)$$

This leads to the matrix eigenvalue problem

$$\mathbf{H}\mathbf{d} = E\mathbf{d}, \quad (42)$$

where $\mathbf{H}$ is the matrix with elements

$$H_{\Gamma J F, \Gamma' J' F'} = \langle \gamma \Gamma I J F M_F | H_{fs} + \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} + \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} + (N_0^{(1)} + \Delta N_0^{(1)}) B | \gamma \Gamma' I J' F' M_F \rangle. \quad (43)$$

The matrix elements of the hyperfine operator are diagonal in F and have been treated in a previous section. The Zeeman matrix elements between the coupled atomic and nuclear wave functions are given by

$$\begin{aligned} & \langle \gamma \Gamma I J F M_F | N_0^{(1)} + \Delta N_0^{(1)} | \gamma \Gamma' I J' F M_F \rangle \\ &= M_F \sqrt{\frac{2F+1}{F(F+1)}} (-1)^{I+J'+1+F} \begin{Bmatrix} J & F & I \\ F & J' & 1 \end{Bmatrix} \sqrt{2J+1} \langle \Gamma J \| \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} \| \Gamma' J' \rangle, \end{aligned} \quad (44)$$

where $J' = J - 1, J, J + 1$ and

$$\begin{aligned} & \langle \gamma \Gamma I J F M_F | N_0^{(1)} + \Delta N_0^{(1)} | \gamma \Gamma' I J' F - 1 M_F \rangle \\ &= \sqrt{\frac{F^2 - M_F^2}{F}} (-1)^{I+J'+1+F} \begin{Bmatrix} J & F & I \\ F-1 & J' & 1 \end{Bmatrix} \sqrt{2J+1} \langle \Gamma J \| \mathbf{N}^{(1)} + \Delta \mathbf{N}^{(1)} \| \Gamma' J' \rangle, \end{aligned} \quad (45)$$

where $J' = J - 1, J, J + 1$.

2.5. Computation of reduced matrix elements

In the multiconfiguration approximation

$$|\Gamma J M_J\rangle = \sum_{\gamma} c_{\gamma} |\gamma J M_J\rangle \quad (46)$$

a general electronic matrix element can be written

$$\langle \Gamma J \| \mathbf{W}^{(k)} \| \Gamma' J' \rangle = \sum_{\gamma, \gamma'} c_{\gamma} c_{\gamma'} \langle \gamma J \| \mathbf{W}^{(k)} \| \gamma' J' \rangle. \quad (47)$$

The evaluation of the electronic matrix element between configuration state functions is done using a program originally written by Pyper, Grant and Beatham, [9] where angular recoupling programs are set up to reduce the matrix element $\langle \gamma J \| \mathbf{W}^{(k)} \| \gamma' J' \rangle$ to terms that involve single-particle orbitals only

$$\langle \gamma J \| \mathbf{W}^{(k)} \| \gamma' J' \rangle = \sum_{a,b} d_{ab}^k \langle n_a \kappa_a \| \mathbf{w}^{(k)} \| n_b \kappa_b \rangle. \quad (48)$$

The single-particle matrix elements $\langle n_a \kappa_a \| \mathbf{w}^{(k)} \| n_b \kappa_b \rangle$, in turn, can be factorized into a reduced angular matrix elements and radial integrals. Here we give the factorization of the single-particle matrix elements corresponding to the electronic magnetic dipole and electric quadrupole hyperfine operators and to the magnetic operators [10]

$$\langle n_a \kappa_a \| \mathbf{t}^{(1)} \| n_b \kappa_b \rangle = -\alpha (\kappa_a + \kappa_b) \langle -\kappa_a \| \mathbf{C}^{(1)} \| \kappa_b \rangle [r^{-2}]_{n_a \kappa_a n_b \kappa_b}, \quad (49)$$

$$\langle n_a \kappa_a \| \mathbf{t}^{(2)} \| n_b \kappa_b \rangle = -\langle \kappa_a \| \mathbf{C}^{(2)} \| \kappa_b \rangle \langle r^{-3} \rangle_{n_a \kappa_a n_b \kappa_b}, \quad (50)$$

$$\langle n_a \kappa_a \| \mathbf{n}^{(1)} \| n_b \kappa_b \rangle = -\frac{1}{2\alpha} \langle -\kappa_a \| \mathbf{C}^{(1)} \| \kappa_b \rangle [r]_{n_a \kappa_a n_b \kappa_b}, \quad (51)$$

$$\langle n_a \kappa_a \| \Delta \mathbf{n}^{(1)} \| n_b \kappa_b \rangle = \frac{g_s - 2}{2} (\kappa_a + \kappa_b - 1) \langle -\kappa_a \| \mathbf{C}^{(1)} \| \kappa_b \rangle \langle r^0 \rangle_{n_a \kappa_a n_b \kappa_b}, \quad (52)$$

where

$$\langle \kappa \| \mathbf{C}^{(k)} \| \kappa' \rangle = (-1)^{j'-k-1/2} \sqrt{2j'+1} \begin{pmatrix} j & j' & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \pi(l, k, l'),$$

$$\pi(l, k, l') = \begin{cases} 1 & \text{if } l + k + l' \text{ even,} \\ 0 & \text{otherwise} \end{cases} \quad (53)$$

and

$$[r^k]_{n\kappa n'\kappa'} = \int_0^\infty r^k [P_{n\kappa}(r) Q_{n'\kappa'}(r) + Q_{n\kappa}(r) P_{n'\kappa'}(r)] dr, \quad (54)$$

$$\langle r^k \rangle_{n\kappa n'\kappa'} = \int_0^\infty r^k [P_{n\kappa}(r) P_{n'\kappa'}(r) + Q_{n\kappa}(r) Q_{n'\kappa'}(r)] dr. \quad (55)$$

3. Installation of programs

The hyperfine Zeeman package consists of a Fortran program `hfszeeman` and a Matlab¹ program `plothfszeeman` that allows the computed energy structure to be plotted. Installation of the programs assumes that the `grasp2K` package is available and that a number of environment variables have been set as described in [3].

Start the installation procedure by copying the `hfszeeman.tar.gz` file to the `grasp2K/src/app1/v2` directory. Uncompress the tar file and give the unix `tar xvf` command. This will build the Fortran source code under the directory `hfszeeman`. The Matlab source code is in the subdirectory `hfszeeman/matlab` and data files needed to run the test cases appear in the subdirectories `hfszeeman/data_Ge` and `hfszeeman/data_He`.

Once the environment variables are properly set up, the making of the `hfszeeman` executable is straightforward. Simply change to the `hfszeeman` directory and issue the `make` command. If the compilation and linking is successful the executable will automatically be transferred to the `grasp2K/bin` directory. Changing to the data directories, test runs described later in the article can now be executed to make sure the `hfszeeman` program works correctly.

Matlab is a interpreting language and there is no need for compilation for this part. To make sure that the `plothfszeeman` program is working start Matlab and add the `hfszeeman/matlab` directory to the path. Change to the data directories and execute the test runs.

Fig. 1. Program operation and data flow for `hfszeeman` and `plothfszeeman`.

¹ Matlab is a registered trademark of The MathWorks, Inc.

```

> hfszeeman

HFSZEEMAN: Execution begins...
Default settings?
> y
Name of state
> 2Fn5
Mixing coefficients from a CI calc.?
> y
Calculate off-diagonal matrix elements?
> y
NPLANTS:          121          590          120          30
Loading Configuration Symmetry List File...
There are 25 relativistic subshells;
There are 1850 relativistic CSFs;
... load complete;
2Fn5.wsetrwfa
Loading Radial WaveFunction File...
Block format?
> y

nelec  =          31
ncftot =          1850
nw     =           25
nblock =           2

block   ncf   nev   2j+1  parity
   1     922     1     6    -1
   2     928     1     8    -1
Column 100 complete;
Column 200 complete;

.....

Column 1700 complete;
Column 1800 complete;

HFSZEEMAN: Execution complete.
FORTRAN STOP

```

Fig. 2. Session log for the hfszeeman program. The nuclear spin and magnetic dipole and quadrupole moments are read from the file isodata.

```

Number of relativistic eigenvalues
2
Lev   J  Parity      E
  1   3.5  -  -2095.248432236
  1   2.5  -  -2095.248428981
Zeeman interaction matrix
0.22684E+01 -0.32809E+00
0.37884E+00  0.12672E+01
HFI-matrix for the magnetic dipole operator
0.73508E-03 -0.27772E-03
0.32069E-03  0.20511E-03
HFI-matrix for the electric quadrupole operator
0.61308E-02  0.20658E-02
-0.23854E-02  0.59418E-02

```

Fig. 3. The hfszeeman output file 2Fn5.cgjhfs containing J quantum numbers and energies for the fine-structure levels $4s^2 4f^2 F_{5/2,7/2}$ together with reduced electronic matrix elements of the magnetic interaction.

4. Program structure

4.1. HFSZEEMAN

hfszeeman computes and outputs the Landé g_J factors for all states $\Gamma J M_J$ in a multiconfiguration Dirac–Hartree–Fock (MCDHF) or relativistic configuration interaction (RCI) calculation. If the nuclear spin, I , is non-zero hfszeeman also computes and outputs the hyperfine interaction constants A_J and B_J . In addition the program computes and outputs the reduced electronic hyperfine and magnetic matrix elements between the states in three different matrices. To the output from the hfszeeman program, J quantum numbers and energies $E_{\Gamma J}$ of all the fine-structure states from the preceding MCDHF or RCI calculations are added.

Nuclear spin	0.000000000000000D+00	au
Nuclear magnetic dipole moment	0.000000000000000D+00	n.m.
Nuclear electric quadrupole moment	0.000000000000000D+00	barns

Eigenenergies:

Level	J	Parity	Hartrees	Kaysers	eV
1	5/2	-	-2.09524842898071D+03	-4.59853875133393D+08	-5.70146351384218D+04
1	7/2	-	-2.09524843223598D+03	-4.59853875847841D+08	-5.70146352270022D+04

Energy of each level relative to immediately lower level:

Level	J	Parity	Hartrees	Kaysers	eV
1	7/2	-	-3.25526889355388D-06	-7.14448938176829D-01	-8.85804116000301D-05

Energy of each level relative to lowest level:

Level	J	Parity	Hartrees	Kaysers	eV
1	7/2	-	-3.25526889355388D-06	-7.14448938176829D-01	-8.85804116000301D-05

Interaction constants:

Level1	J	Parity	g_J	delta g_J	total g_J
1	5/2	-	8.5713571855D-01	-3.3142670393D-04	8.5680429184D-01
1	7/2	-	1.1428503195D+00	3.3143002543D-04	1.1431817495D+00

Fig. 4. The hfszeeman output file 2Fn5.ch with nuclear data, J quantum numbers, energies and Landé g_J factors the for fine-structure levels $4s^2 4f^2 F_{5/2,7/2}$.

```

> plothfszeeman

Name of the file
> 2Fn5
Are the calculations based on a relativistic CI calculation? (Y/N)
> y
Nuclear spin I
> 0
B-field in Tesla (0) or Gauss (1) ?
> 1
Give the upper limit for the B-field.
> 40000
Energies in a.u. (0), cm-1 (1) or MHz (2) ?
> 1

level    E_fs (a.u.)    J
-----
1        -2095.248432236    7/2
2        -2095.248428981    5/2

Would you like a plot? (Y/N)
> y
Give an index vector of the levels for which the
zeeman patterns should be plotted
> [1 2]
Energies and the J-value printed in the plot ? (Y/N)
> y
More plots ? (Y/N)
> n

PLOTHFSZEEMAN finished

```

Fig. 5. Session log for the plothfszeeman program. Magnetic sublevels are plotted for $4s^2 4f^2 F_{5/2,7/2}$.

4.2. PLOTHFSZEEMAN

plthfszeeman reads the nuclear spin I , the nuclear magnetic dipole moment μ_I , the nuclear electric quadrupole moment Q and the maximum magnetic field B from the terminal and the reduced matrix elements from the hfszeeman output file. From the list of atomic states and the nuclear spin I the program determines the basis functions for the calculation. If the nuclear spin I

Fig. 6. Magnetic sublevels of $4s^2 4f^2 F_{5/2, 7/2}$ as functions of the magnetic field. The displayed energy levels are relative to the weighted energy average at zero field.

is non-zero the basis functions are

$$|\Upsilon \Gamma I J F M_F\rangle = \sum_{M_I, M_J} \langle I J M_I M_J | I J F M_F \rangle |\Upsilon I M_I\rangle |\Gamma J M_J\rangle \quad (56)$$

with $|I - J| \leq F \leq I + J$. In cases where the nuclear spin I is zero the basis functions are instead given by the atomic state functions $|\Gamma J M_J\rangle$. The program goes on and constructs and diagonalizes the interaction matrix for different values B of the magnetic field and plots the energies of the magnetic sublevels as functions of B . For the largest specified value of the magnetic field the energies of the magnetic sublevels and the expansion coefficients $d_{\Gamma J F}$ (or $d_{\Gamma J}$ when the nuclear spin I is zero) for the basis functions are written to file.

The calculations in `plothfszeeman` are normally done in double precision arithmetic. In some case it may, however, be necessary to switch to variable precision arithmetics which gives more digits.

The operation and data flow (see next section) of `hfszeeman` and `plothfszeeman` is schematically shown in Fig. 1.

5. Input and output data

5.1. HFSZEEMAN

This program assumes the naming convention of the `grasp2K` package and the `<name>` of the state has to be specified. The program reads data from the configuration list file `<name>.c`, the wave function file `<name>.w` and, dependent on whether the electronic wave functions originate from a MCDHF or RCI calculation, from the mixing file `<name>.m` or `<name>.cm`. Values of the nuclear spin, magnetic dipole and quadrupole moments are, just as for all programs of the `grasp2K` package, read from the file `isodata`.

The program produces two output files `<name>.(c)gjhfs` and `<name>.(c)h`, where the letter `c` in the extension indicates that the input data were from an RCI calculation. In the file `<name>.(c)gjhfs` the program outputs the J quantum numbers and energies $E_{\Gamma J}$ of the atomic states together with the reduced matrix elements. Note that the reduced matrix elements are not symmetric but related according to (Brink and Satchler [6, p. 61])

$$\sqrt{2J+1} \langle J \| \mathbf{T}^{(k)} \| J' \rangle = (-1)^{J-J'} \sqrt{2J'+1} \langle J' \| \mathbf{T}^{(k)} \| J \rangle. \quad (57)$$

In the file `<name>.(c)h` the program outputs the energies and the diagonal Landé g_J factors, and if the isotope has a nuclear spin, the diagonal A_J and B_J hyperfine constants.

```

B = 40000.0000000 Gauss N_EIGVEC = 2

Eigenv.  J-val    FS-energy

  1      3.5    -2095.248432236
  2      2.5    -2095.248428981

2*M =    7  NUMBER =    1

  1 -2095.248398192
1.000000000  0.000000000

2*M =    5  NUMBER =    2

  2 -2095.248412641
0.53419524  0.84536113
  1 -2095.248406033
0.84536113 -0.53419524

2*M =    3  NUMBER =    2

  2 -2095.248421704
0.68852798  0.72520977
  1 -2095.248413988
0.72520977 -0.68852798

.....

2*M =   -5  NUMBER =    2

  1 -2095.248457425
0.95989923  0.28034527
  2 -2095.248446335
-0.28034527  0.95989923

2*M =   -7  NUMBER =    1

  1 -2095.248466280
1.000000000  0.000000000

```

Fig. 7. The file 2Fn5.czm with energies and mixing coefficients of the magnetic sublevels of the fine-structure levels $4s^2 4f^2 F_{5/2,7/2}$ at a magnetic field of 40 000 Gauss.

```

> hfszeeman

HFSZEEMAN: Execution begins...

Default settings?
> y
Name of state
> 3Pn6
Mixing coefficients from a CI calc.?
> y
Calculate off-diagonal matrix elements?
> y
NPLANTS:          121          590          120          30
Loading Configuration Symmetry List File...
There are 36 relativistic subshells;
There are 472 relativistic CSFs;
... load complete;
2Pn6.wsetrwfa
Loading Radial WaveFunction File...
Block format?
> y

nelec =          2
ncftot =         472
nw =           36
nblock =          3

block   ncf   nev   2j+1  parity
  1      70     1     1     -1
  2     180     2     3     -1
  3     222     1     5     -1
Column 100 complete;
Column 200 complete;
Column 300 complete;
Column 400 complete;

HFSZEEMAN: Execution complete.
FORTRAN STOP

```

Fig. 8. Session log for the hfszeeman program. The nuclear spin and magnetic dipole and quadrupole moments are read from the file isodata.

5.2. PLOTHFSZEEMAN

Given the (name) the program opens and reads (name).(c)gjhs. The program asks for the nuclear spin. If the spin is given a non-zero value, values for the nuclear magnetic dipole and electric quadrupole moments need to be supplied. The maximum magnetic field should be given, in Tesla or Gauss, and the units of energy should be chosen to a.u., cm^{-1} or MHz. The program plots the energy of the magnetic sublevels as a function of the magnetic field for fine- or hyperfine levels selected by the user. The field free energies together with some further information about the fine/hyperfine levels are printed to the file (name).(c)zm, together with the energies and expansion coefficients of the magnetic sublevels for the largest specified value of the magnetic field.

6. Examples

In the test run output we present two different calculations; the first is for an isotope in Ge without nuclear spin where the splittings of two fine-structure levels are plotted as functions of the magnetic field, the second is for ^3He which has a nuclear spin, $I = 1/2$, and here the splittings of a number of hyperfine levels are displayed. This test run was compared to [11], and Fig. 12 was found to be in excellent agreement with the similar plot in [11].

To test the programs additional calculations, not presented in the test run output, have been done. The diagonal and off-diagonal reduced electronic magnetic matrix elements in light atoms were checked against the corresponding elements in pure LS -coupling [12]. A calculation was done to determine the splitting of the two hyperfine levels of $1s^2 2s^2 2p^6 3s^2 S_{1/2}$ in Sodium and the result was in perfect agreement with the Breit–Rabi formula [13]. Calculations were also done in the field free limit for the hyperfine levels of $1s 2p^3 P$ in Helium-like Beryllium for comparison with experiment [14] and other theoretical calculations [15], and a detailed agreement was found. Similar calculations were also made for the hyperfine levels derived from the same fine-structure levels as above for Helium-like Fluorine. Here the off-diagonal hyperfine interaction elements are large compared to the fine-structure

```

Number of relativistic eigenvalues
4
Lev    J  Parity      E
1      2.0  -      -2.133263484
1      1.0  -      -2.133263133
2      1.0  -      -2.123928445
1      0.0  -      -2.133258631
Zeeman interaction matrix
0.18385E+01 -0.35435E+00  0.65484E-04  0.00000E+00
0.45746E+00  0.10614E+01 -0.13145E-03  0.40917E+00
-0.84540E-04 -0.13145E-03  0.70710E+00 -0.13154E-03
0.00000E+00 -0.70870E+00  0.22784E-03  0.00000E+00
HFI-matrix for the magnetic dipole operator
0.94782E-01 -0.54202E-01  0.77020E-01  0.00000E+00
0.69975E-01  0.55198E-01  0.77232E-01  0.62251E-01
-0.99433E-01  0.77232E-01  0.35275E-03  0.44233E-01
0.00000E+00 -0.10782E+00 -0.76613E-01  0.00000E+00
HFI-matrix for the electric quadrupole operator
0.26114E-01  0.29610E-01 -0.66692E-05 -0.19739E-01
-0.38227E-01 -0.22070E-01  0.11955E-04  0.00000E+00
0.86099E-05  0.11955E-04  0.19441E-01  0.00000E+00
-0.44137E-01  0.00000E+00  0.00000E+00  0.00000E+00

```

Fig. 9. The hfszeeman output file 3Pn6.cgjhfs containing J quantum numbers and energies for the fine-structure levels of $1s2p^{1,3}P$ together with reduced electronic matrix elements of the hyperfine and magnetic interaction.

```

Nuclear spin          5.000000000000000D-01 au
Nuclear magnetic dipole moment 2.127497720000000D+00 n.m.
Nuclear electric quadrupole moment 0.000000000000000D+00 barns

Eigenenergies:

Level J Parity      Hartrees      Kaysers      eV
1  0  -  -2.13325863106008D+00 -4.68196150196834D+05 -5.80489458068455D+01
1  1  -  -2.13326313263103D+00 -4.68197138177454D+05 -5.80490683008760D+01
2  1  -  -2.12392844472579D+00 -4.66148410996939D+05 -5.77950584098832D+01
1  2  -  -2.13326348364110D+00 -4.68197215215261D+05 -5.80490778523503D+01

Energy of each level relative to immediately lower level:

Level J Parity      Hartrees      Kaysers      eV
1  1  -  -4.50157094356030D-06 -9.87980620317715D-01 -1.22494030467627D-04
2  1  -  9.33468790523939D-03  2.04872718051548D+03  2.54009890992817D-01
1  2  -  -9.33503891531640D-03 -2.04880421832249D+03 -2.54019442467093D-01

Energy of each level relative to lowest level:

Level J Parity      Hartrees      Kaysers      eV
1  1  -  -4.50157094356030D-06 -9.87980620317715D-01 -1.22494030467627D-04
2  1  -  9.33018633429583D-03  2.04773919989516D+03  2.53887396962350D-01
1  2  -  -4.85258102056463D-06 -1.06501842733320D+00 -1.32045504743184D-04

Interaction constants:

Level1 J Parity      A (MHz)      B (MHz)      g_J      delta g_J      total g_J
1  1  -  2.1713872786D+03  0.0000000000D+00  1.4999565728D+00  1.1599965276D-03  1.5011165693D+00
2  1  -  1.3876531139D+01  0.0000000000D+00  9.9999359428D-01  2.5473373189D-09  9.9999359682D-01
1  2  -  2.1526837767D+03  0.0000000000D+00  1.4999582945D+00  1.1599999886D-03  1.5011182945D+00

```

Fig. 10. The hfszeeman output file 3Pn6.ch with nuclear data, J quantum numbers, energies and Landé g_J factors for the fine-structure levels of $1s2p^{1,3}P$.

```

> plothfszeeman
Name of the file
> 3Pn6
Are the calculations based on a relativistic CI calculation? (Y/N)
> y
Nuclear spin I
> 0.5
Nuclear magnetic dipole moment
> -2.12749772
Nuclear electric quadrupole moment
> 0
B-field in Tesla (0) or Gauss (1) ?
> 1
Give the upper limit for the B-field.
> 2000
Energies in a.u. (0), cm-1 (1) or MHz (2) ?
> 2

level    E_hfs (a.u.)  FS-LEV  J      F
-----
1        -2.133263809  1       2     5/2
2        -2.133263537  2       1     3/2
3        -2.133262757  1       2     3/2
4        -2.123928446  3       1     3/2
5        -2.133262854  2       1     1/2
6        -2.133258583  4       0     1/2
7        -2.123928443  3       1     1/2

Would you like a plot? (Y/N)
> y
Give an index vector of the levels for which the zeeman patterns should be plotted
> [1 2 3 5]
Energies and the F-value printed in the plot ? (Y/N)
> y
More plots ? (Y/N)
> n

PLOTTHFSZEEMAN finished

```

Fig. 11. Session log for the `plothfszeeman` program. Magnetic sublevels are plotted for the hyperfine levels $1s2p^3P_2$, $F = 5/2, 3/2$ and $1s2p^3P_1$, $F = 3/2, 1/2$ in ^3He . FS-LEV is used to identify which hyperfine levels that are derived from the same fine-structure level.

Fig. 12. Magnetic sublevels of the hyperfine levels of $1s2p^3P_{1,2}$ as functions of the magnetic field. The displayed energy levels are relative to the weighted average energy at zero field.

B =	2000.00000000 Gauss		N_EIGVEC =		7		
Eigenv.	J-val	F-val	HFS-energy				
1	2.0	2.5	-2.133263809				
2	2.0	1.5	-2.133262757				
3	1.0	1.5	-2.133263537				
4	1.0	0.5	-2.133262854				
5	1.0	1.5	-2.123928446				
6	1.0	0.5	-2.123928443				
7	0.0	0.5	-2.133258583				
2*M =	5	NUMBER =	1				
1	-2.133262532						
1.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	
2*M =	3	NUMBER =	4				
1	-2.133263138						
0.94367336	-0.12393920	0.30678928	0.00000000	0.00001432	0.00000000	0.00000000	
3	-2.133262709						
-0.24758034	0.35062589	0.90319735	0.00000000	0.00000299	0.00000000	0.00000000	
2	-2.133261701						
0.21950982	0.92827828	-0.30019141	0.00000000	-0.00005821	0.00000000	0.00000000	
5	-2.123928021						
0.00000001	0.00005476	-0.00002456	0.00000000	1.00000000	0.00000000	0.00000000	
2*M =	1	NUMBER =	7				
1	-2.133263696						
0.92685088	-0.19693530	0.30313722	-0.10063495	0.00001822	0.00000536	-0.01201538	
3	-2.133263277						
-0.19799410	0.45986011	0.85003001	-0.15775530	-0.00000430	0.00000924	-0.04346575	
4	-2.133262657						
0.26147416	0.63499405	-0.15258503	0.70993261	-0.00003851	-0.00003371	-0.03357561	
4	-2.133262038						
-0.18265302	-0.58858213	0.39692437	0.67511239	0.00004198	-0.00003029	-0.08296539	
7	-2.133258593						
-0.00386367	-0.00993976	0.06874346	0.07214449	0.00000224	-0.00003784	0.99496522	
5	-2.123928445						
0.00000001	0.00004482	-0.00002010	-0.00002822	0.81849587	-0.57451241	-0.00001981	
6	-2.123928018						
0.00000000	0.00003146	-0.00001411	0.00004019	0.57451241	0.81849587	0.00002821	
.....							
2*M =	-3	NUMBER =	4				
1	-2.133264695						
0.88936071	-0.45457033	-0.04902396	0.00000000	0.00002368	0.00000000	0.00000000	
3	-2.133264476						
0.36619399	0.64401572	0.67167382	0.00000000	-0.00001878	0.00000000	0.00000000	
3	-2.133263486						
-0.27375079	-0.61531258	0.73922320	0.00000000	0.00005184	0.00000000	0.00000000	
5	-2.123928871						
0.00000001	0.00005475	-0.00002455	0.00000000	1.00000000	0.00000000	0.00000000	
2*M =	-5	NUMBER =	1				
1	-2.133265086						
1.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	0.00000000	

Fig. 13. The file 3Pn6.zm with energies and mixing coefficients of the magnetic sublevels of the hyperfine levels of $1s2p^3P_{0,1,2}$ and $1s2p^1P_1$ in ^3He at a magnetic field of 2000 Gauss.

splittings and have a large impact on the energies. No experimental values are available, but again there is an excellent agreement with [15]. As a further test, the programs were applied to the $4s4d^3D_2 - 4s4f^3F_{2,3}$ transitions in Ga II, where the off-diagonal hyperfine interaction is necessary to explain the features of recent Fourier transform spectra [16].

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Appendix A. Test run output

The first test run is for the two fine-structure levels $4s^2 4f^2 F_{5/2,7/2}$ in Ge II. The test run generates Landé g_J factors for each of the two levels together with energies and mixing coefficients of the magnetic sublevels for the largest value of the given magnetic field. In addition the energies of the magnetic sublevels of $4s^2 4f^2 F_{5/2,7/2}$ are plotted as functions of the magnetic field. Some preparatory calculations using the programs of grasp2K have to be done in order to perform the test run. First, lists of configuration state functions (CSFs) are generated using `jjgen`. Then the radial wave functions are estimated using `erwf`, and by using `mcp2` and `rscf2` multiconfiguration Dirac–Hartree–Fock calculations are done. In our test case the Breit interaction and leading QED effects are included in subsequent relativistic configuration interaction calculations using `rci2`. The calculations account for correlation between the three outer electrons and includes orbitals with principal quantum numbers up to $n = 5$. The largest configuration expansion consists of 1850 CSFs and is in the file named `2Fn5.c`. The radial wave functions are in `2Fn5.w` and the mixing coefficients from `rci2` are saved in `2Fn5.c`. These files reside in the `grasp2K/src/appl/v2/hfszeeman/data_Ge` directory. We can now run the `hfszeeman` program, and the session log is displayed in Fig. 2. `hfszeeman` produces two output files; `2Fn5.cgjhfs` (see Fig. 3) which gives the reduced electronic hyperfine and magnetic interaction matrices and `2Fn5.ch` (see Fig. 4) which displays the Landé g_J factors. Using `2Fn5.cgjhfs` we can run `plothfszeeman`, see Fig. 5, to produce the plot in Fig. 6 and the mixing file `2Fn5.czm`, see Fig. 7.

The next test run is for the hyperfine levels of $1s2p^3 P$ in neutral ^3He . This isotope has a nuclear spin of $1/2$, a nuclear dipole moment of -2.12749772 n.m. The test run produces Landé g_J factors for the fine-structure levels, A_J and B_J hyperfine interaction constants and mixing coefficients for the magnetic hyperfine sublevels at the magnetic field 2000 Gauss. In addition a plot of the energies of the magnetic sublevels of $1s2p^3 P_{1,2}$ as functions of the magnetic field is produced. The plot is compared with a similar plot by Wu and Drake [11].

The preparatory work follows the steps outlined above and we add a large number of correlation orbitals in an accurate calculation. The generated configuration list `3Pn6.c`, the radial wave functions `3Pn6.w` and the mixing file `3Pn6.cm` can be found in `grasp2K/src/appl/v2/hfszeeman/data_He`. We run `hfszeeman` and the session log is depicted in Fig. 8. The program produces two files; `3Pn6.cgjhfs` which contains the reduced electronic hyperfine and magnetic interaction matrices (see Fig. 9) and `3Pn6.ch`, see Fig. 10, which shows the Landé g_J factor and the hyperfine interaction constants A_J and B_J for each of the fine-structure levels. Using `3Pn6.cgjhfs` we run `plothfszeeman`, see Fig. 11, to produce a plot of the energies of the $1s2p^3 P_{1,2}$ hyperfine levels as functions of the magnetic field, Fig. 12, and a file `3Pn6.czm` with the magnetic hyperfine sublevels and mixing coefficients at the magnetic field of 2000 Tesla, Fig. 13.

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