

SPECTRE

Users Manual

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SPECTRE is a program for calculating spectroscopic and magnetic properties of rare-earth ions in crystals. The calculation employs intermediate-coupling basis states, and allows mixing of all terms within the f^n configuration. The various electrostatic and spin-orbit parameters in the free ion Hamiltonian are taken from Carnall *et al.* [1]. The program includes a facility for fitting crystal field parameters to sets of energy levels and transition intensities for one or more ions.

The core routines in SPECTRE are based on a program called SHELL, which was developed at Argonne National Laboratory by G. L. Goodman and colleagues. Further revisions were made by R. Osborn. SPECTRE uses numerical minimization and matrix diagonalisation subroutines from the NAG Fortran Library [2].

How to cite the program:

A. T. Boothroyd, SPECTRE — a program for calculating spectroscopic properties of rare earth ions in crystals (1990-2014).

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Disclaimer

SPECTRE is distributed in the hope that it will be useful, but without any guarantee that it is error-free. In no event will the author or his institution be liable to you for damages, including any general, special, incidental or consequential damages arising out of the use or inability to use the program. The author is not responsible for erroneous results obtained with the program.

Contents

1	Installation	3
2	Theoretical background	3
3	Getting started	5
4	Calculations	8
4.1	Eigenvalues, eigenvectors and transition matrix elements . . .	9
4.2	Scale CEF parameters to different rare-earth ion	13
4.3	Neutron cross-section	14
4.4	Fit to observed energies and intensities	15
4.5	Specific heat capacity	18
4.6	Magnetic susceptibility	18
4.7	Magnetisation	18
4.8	Magnetic moment	19
4.9	Matrix elements of magnetic moment operator	19
5	References	19

1 Installation

The current version was compiled under Windows 7 and works on Windows. For Mac OS you'll need to install a Windows emulator. The suite comprises a single executable file

`Spectre.exe`

compiled from fortran source code, together with a number of ascii files which contain single-ion parameters and input data. All files must be located in the same folder. The ascii files should under no circumstances be modified because if the formatting is changed then SPECTRE will not be able to read them.

To launch the program, double-click on the file `spectre.exe`.

2 Theoretical background

We assume the magnetism of the rare earth ion derives from n equivalent f electrons (i.e. we work within an f^n configuration). The effective single-ion Hamiltonian has the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{Z}}, \quad (1)$$

where \mathcal{H}_0 is the free-ion Hamiltonian and

$$\mathcal{H}_{\text{CF}} = \sum_{k=0}^{2l} \sum_{q=-k}^{+k} B_q^k C_q^{(k)} \quad (2)$$

$$\mathcal{H}_{\text{ex}} = 2 \mathbf{H}_{\text{ex}} \cdot \mathbf{S} \quad (3)$$

$$\mathcal{H}_{\text{Z}} = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (4)$$

Term (3) describes an interaction with an exchange field \mathbf{H}_{ex} , and term (4) is the Zeeman interaction between the magnetic moment $\boldsymbol{\mu} = -\mu_{\text{B}}(\mathbf{L} + 2\mathbf{S})$ and an external magnetic field of flux density \mathbf{B} .

Equation (2) defines the crystal field Hamiltonian. The B_q^k are crystal field parameters, and the $C_q^{(k)}$ are the *Wybourne tensor operators*, which are given by

$$C_q^{(k)}(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_{k,q}(\theta, \phi), \quad (5)$$

where $Y_{k,q}(\theta, \phi)$ are the spherical harmonic functions. There are several slightly different definitions in use for the spherical harmonics. We use the

Condon–Shortley phase convention,

$$Y_{k,q}(\theta, \phi) = (-1)^q \left[\frac{2k+1}{4\pi} \frac{(k-q)!}{(k+q)!} \right]^{\frac{1}{2}} P_k^q(\cos \theta) \exp(iq\phi) \quad (q \geq 0), \quad (6)$$

and

$$Y_{k,-q} = (-1)^q Y_{k,q}^* \quad (q \geq 0). \quad (7)$$

The $P_k^q(\cos \theta)$ are the *associated Legendre polynomials*.

If the multi-electron basis states can be restricted to either a single L term with weak spin–orbit coupling, or a single J level, then \mathcal{H}_{CF} can be expressed in an alternative form which is often simpler to use in practice:

$$\mathcal{H}_{\text{CF}} = \sum_{k=0}^{2l} \sum_{q=-k}^{+k} B_k^q O_k^q, \quad (8)$$

where l is the orbital quantum number of the one-electron orbital ($l = 3$ for f electrons), and the O_k^q are known as *Stevens operator equivalents* and are functions of angular momentum operators: $O_k^q = O_k^q(\mathbf{J})$ in the $SLJM_J$ basis, or $O_k^q = O_k^q(\mathbf{L})$ in the $SLM_S M_L$ basis. Note that the crystal field parameters B_q^k in (2) and B_k^q in (8) are not the same. The indices are interchanged.

It is often convenient to group the spherical operators into real combinations. From (6) and (7) it can be seen that a suitable basis of real functions is

$$\left. \begin{aligned} Z_{k,q}^c &= \frac{1}{\sqrt{2}} \{Y_{k,-q} + (-1)^q Y_{k,q}\} \propto \cos q\phi \\ Z_{k,q}^s &= \frac{i}{\sqrt{2}} \{Y_{k,-q} - (-1)^q Y_{k,q}\} \propto \sin q\phi \end{aligned} \right\} q > 0, \quad (9)$$

$$Z_{k,0} = Y_{k,0}.$$

The $Z_{k,q}$ are known as *Tesseral harmonics*.

Similar real and imaginary combinations of the Wybourne tensors (but without the $1/\sqrt{2}$ pre-factor) are defined:

$$\begin{aligned} \mathcal{H}_{\text{CF}} &= \sum_{k=0}^{2l} B_0^k C_0^{(k)} + \sum_{k=2}^{2l} \sum_{q=1}^k \left[B_q^k(c) \{C_{-q}^{(k)} + (-1)^q C_q^{(k)}\} + i B_q^k(s) \{C_{-q}^{(k)} - (-1)^q C_q^{(k)}\} \right] \\ &= \sum_{k=0}^{2l} B_0^k C_0^{(k)} + \sum_{k=2}^{2l} \sum_{q=1}^k B_q^k(c) C_q^{(k)}(c) + B_q^k(s) C_q^{(k)}(s). \end{aligned} \quad (10)$$

The operators associated with $B_q^k(c)$ and $B_q^k(s)$ parameters have $\cos \phi$ and $\sin \phi$ angular dependence, respectively, as can be seen from (9). Likewise, in

Table 1: Multiplicative factors λ_{kq} in the relation $B_k^q(c, s) = \lambda_{kq}\theta_k B_q^k(c, s)$ between the Stevens crystal field parameters in (11) and the corresponding Wybourne parameters in (10). The θ_k are numerical coefficients which have been tabulated for the ground states of the trivalent $4f$ ions — see Tables VI & VII of M.T. Hutchings, Solid State Physics **16** (1964) 227.

	q						
	0	1	2	3	4	5	6
	$\frac{1}{2}$	$\sqrt{6}$	$\frac{1}{2}\sqrt{6}$				
k	$\frac{1}{8}$	$\frac{1}{2}\sqrt{5}$	$\frac{1}{4}\sqrt{10}$	$\frac{1}{2}\sqrt{35}$	$\frac{1}{8}\sqrt{70}$		
	$\frac{1}{16}$	$\frac{1}{8}\sqrt{42}$	$\frac{1}{16}\sqrt{105}$	$\frac{1}{8}\sqrt{105}$	$\frac{3}{16}\sqrt{14}$	$\frac{3}{8}\sqrt{77}$	$\frac{1}{16}\sqrt{231}$

terms of Stevens operators,

$$\mathcal{H}_{\text{CF}} = \sum_{k=0}^{2l} B_k^0 O_k^0 + \sum_{k=2}^{2l} \sum_{q=1}^k B_k^q(c) O_k^q(c) + B_k^q(s) O_k^q(s). \quad (11)$$

Note that in the $LSJM_J$ basis the matrix elements of the “sine” operators in (10) and (11) are imaginary.

The crystal field parameters that appear in (10) are not the same as those in (11) — it is unfortunate that B is used for both the Wybourne and Stevens parameters in the literature, but note that the positions of the k and q indices are reversed. Within the reduced basis of states on which the Stevens operators act, the Stevens and Wybourne parameters are related by $B_k^q(c, s) = \lambda_{kq}\theta_k B_q^k(c, s)$. The λ_{kq} coefficients are given in Table 1.

The parameterisation of the crystal field Hamiltonian in SPECTRE is that given in eqn (10).

3 Getting started

After launching the program you get the following screen, which is the point to which the program returns after completion of any task:

```

CEF Parameters (meV):
1 B(2,0) = 0.533E+01 2 B(4,0) = -0.157E+03 3 B(6,0) = 0.000E+00
4 B(2,1)c = 0.000E+00 16 B(2,1)s = 0.000E+00
5 B(2,2)c = 0.000E+00 17 B(2,2)s = 0.000E+00
6 B(4,1)c = 0.000E+00 18 B(4,1)s = 0.000E+00
7 B(4,2)c = 0.000E+00 19 B(4,2)s = 0.000E+00

```

```

8 B(4,3)c = 0.000E+00 20 B(4,3)s = 0.000E+00
9 B(4,4)c = 0.000E+00 21 B(4,4)s = 0.000E+00
10 B(6,1)c = 0.000E+00 22 B(6,1)s = 0.000E+00
11 B(6,2)c = 0.000E+00 23 B(6,2)s = 0.000E+00
12 B(6,3)c = 0.000E+00 24 B(6,3)s = 0.000E+00
13 B(6,4)c = 0.000E+00 25 B(6,4)s = 0.000E+00
14 B(6,5)c = 0.000E+00 26 B(6,5)s = 0.000E+00
15 B(6,6)c = 0.000E+00 27 B(6,6)s = 0.000E+00

```

Exchange field (He) and applied field (B):

```

28 Hex = 0.000E+00 29 Hey = 0.000E+00 30 Hez = 0.192E+02 meV
31 Bx = 0.000E+00 32 By = 0.000E+00 33 Bz = 0.000E+00 Tesla

```

34 No. f electrons = 5. (select 34 to check free-ion levels also)

number ... new value (<CR> to end) :

The $B(\mathbf{k}, \mathbf{q})$ (1...27) are crystal field parameters defined in eqn (10). Parameter numbers 28...30 are the three orthogonal components of the internal exchange (or molecular) field \mathbf{H}_{ex} defined in eqn (3), and 31...33 are the equivalent components of an externally applied magnetic field \mathbf{B} .

To change the value of a parameter, enter the parameter number followed by a space then the new value:

```

number ... new value (<CR> to end) : 1 530.5 <CR>

```

Typing the ENTER or Carriage Return key (here denoted by <CR>) allows you to change another parameter. Typing <CR> without any new data brings up the revised list of all the parameters.

Parameter number 34 gives you the following menu:

Free ion and submatrix information

Sm3+

```

1 Truncate free ion basis set ? (0=No, 1=Yes) : 1
2 Number of CF submatrices (if unsure use 1) : 1
3 q min for CF submatrices (if unsure use 1) : 1
4 No. submatrices per mu (if unsure use 1) : 1
5 Orbital reduction factor (if unsure use 1) : 1.000

```

number ... new value (<CR> to end) :

The first option allows you to reduce the number of basis states from that in the complete f^n basis. This is necessary if the number of basis states exceeds 300, which is the maximum size of the arrays in the routine that diagonalises the Hamiltonian. Truncation means restricting the number of $^{2S+1}L_J$ terms in the basis. Reducing the number of basis states speeds up the calculations.

If the truncation flag is 1 then when you hit <CR> you get the following:

Use intermediate coupling basis states (N or <CR>)?

Normally you will want to use intermediate coupling free-ion basis states, in which case hit <CR>. However, if you want to ‘switch off’ intermediate coupling and use pure LSJ basis states then answer N. Whichever answer you give you see the next output:

	J	no. J multiplets to keep and skip	
0	0.5	1	0
1	1.5	1	0
2	2.5	2	0
3	3.5	2	0
4	4.5	2	0
5	5.5	2	0
6	6.5	1	0
7	7.5	1	0
8	8.5	0	0
9	9.5	0	0
10	10.5	0	0
11	11.5	0	0
12	12.5	0	0

number ... N(keep), (N(skip), (N(keep) ...)) <CR> to end :

This table makes sense if you look at the energy level scheme of Sm^{3+} [3]. In the energy range up to 1.3 eV there are 2 terms, 6F and 6H , containing a total of 12 J multiplets. The table contains a list of the 12 J values. Whenever a J value exists in both the 6F and the 6H terms the number of kept J multiplets in the table is given as 2. If the J value occurs only once then the entry is 1.

One can now change the number of kept J multiplets in the table. For example, if you want to perform the calculations in the intermediate coupling ground state multiplet $^6H_{5/2}$ then you will set the $J = 2.5$ ‘keep’ flag to 1

(enter: 2 1<CR>) and set all the other ‘keep’ flags to 0 (0 0<CR>, 1 0<CR>, etc). Note, however, that when there are two or more terms with the same J they are not always indexed in order of energy. There are two situations when this occurs. One is when there is no truncation of the free-ion basis, i.e. the `truncate free ion basis set` flag is set to 0, and the other is when there is truncation (the ‘truncate’ flag is set to 1) but the user chooses not to use intermediate coupling basis states. In these two cases the pure LS -coupling basis states are indexed in order of increasing L starting with those of largest S . For example, the $4f^2$ configuration (Pr^{3+}) has three terms that include $J = 4$ and these are indexed in the order (1) 3F , (2) 3H and (3) 1G . The 3H is the ground state term, so if you want to do the calculations in 3H then you can select this by setting the $J = 4$ ‘keep’ flag to 2 and the ‘skip’ flag to 1. If the ‘truncate’ flag is set to 1 and intermediate coupling basis states are chosen then the intermediate coupling states are indexed in order of increasing energy. In the case of $4f^2$, the intermediate coupling term which derives predominantly from 3H would then be first.

One application of the keep/skip functionality is to perform a calculation that is identical to the Stevens’ operator method. Taking $4f^2$ (Pr^{3+}) as an example, you would set the ‘truncate’ flag is set to 1 and answer N to the question `Use intermediate coupling basis states (N or <CR>)?`. You would then set the ‘keep’ flags for all $J \neq 4$ to 0. For $J = 4$ you would set the ‘keep’ flag to 2 and the ‘skip’ flag to 1.

Options 2 to 4 in the `Free ion and submatrix information` menu allow the user to take advantage of symmetry to transform the crystal field matrix into block diagonal form and hence to diagonalise 2 or more sub-matrices rather than the entire matrix. For example, time reversal symmetry causes the crystal field matrix of all Kramers’ ions to have two blocks. Changing the number of CF sub-matrices to 2 means that sub-matrices corresponding to each block are diagonalised separately. This is faster than diagonalising the complete CF matrix. Note: make sure you know what you are doing if you decide to take advantage of this facility!

Option 5 in the `Free ion and submatrix information` menu makes it possible to take into account covalency effects which effectively reduce the orbital quantum number relative to that of the free ion. For example, the magnetic moment is calculated from $-\mu_B(x\mathbf{L} + 2\mathbf{S})$, where $0 < x < 1$ is the orbital reduction factor.

4 Calculations

When you have finished changing parameters, hit <CR>. You get the menu:

Calculations:

- 1 Eigenvalues, eigenvectors and transition matrix elements
 - 2 Scale CEF parameters to different RE ion.
 - 3 Neutron cross-section.
 - 4 Fit to observed energies and intensities
 - 5 Specific heat.
 - 6 Susceptibility.
 - 7 Magnetisation.
 - 8 Magnetic moment.
 - 9 Matrix elements of mu.
- 99 Quit.

Option number (default = 1) :

You can choose between 9 different calculations, or exit the program by typing:

Option number (default = 1) : 99 <CR>

4.1 Eigenvalues, eigenvectors and transition matrix elements

If you chose 1 or hit <CR>, you will see the following series of outputs — here corresponding to the crystal field splitting of Pr^{3+} in $\text{Pr}_2\text{Sn}_2\text{O}_7$, A. J. Princep *et al.*, Phys. Rev. B **88**, 104421 (2013):

1	1936.900	EAVE
2	8536.400	F2
3	6239.800	F4
4	4077.600	F6
5	2011.500	1000ALPHA
6	-70.220	BETA
7	169.900	GAMMA
8	93.160	ZETA
9	0.258	M0
10	0.144	M2
11	0.080	M4
12	-11.000	P2
13	-5.490	P4
14	-1.100	P6

```

    1    2
    2    1
    3    3
    4    1
    5    3
    6    1
    7    2
  1  1  2
  2  3  5
  3  5 20
  4  7 27
  5  9 54
  6 11 65
  7 13 91

```

MATRIX 1 HAS 9152 COEFFICIENTS

```

SUB  MTX  COEFS  COEFS
MTX  DIM  READ  WRITTEN
  1    91  9152    0
0 COEFFICIENTS READ

```

```

VECTORS CALCULATED (REAL PART)
  1    638.27    53  0.87363733
  2    638.27    50  0.87363733
  3    656.29    29  0.95890379
  :
  etc

```

LOWEST LEVEL MADE 0.0 BY SUBTRACTING 638.

Eigenvalues relative to ground state:
 0.0 0.0 18.0 57.6 57.6 82.3 100.2 100.2 114.9

```

I 2J 2M                               Eigenvectors (real part):
.
:
1  8  0  0.000 0.000-0.040 0.000 0.000 0.015 0.000 0.000 0.000
2  8  0  0.000 0.000 0.959 0.000 0.000 0.200 0.000 0.000 0.000

```

```

3 8 0 0.000 0.000 0.165 0.000 0.000 0.024 0.000 0.000 0.000
1 8 -2 0.001 0.015 0.000-0.034 0.007 0.000 0.001-0.009 0.000
2 8 -2 -0.038-0.409 0.000 0.851-0.174 0.000-0.006 0.089 0.000
3 8 -2 -0.006-0.069 0.000 0.147-0.030 0.000-0.001 0.021 0.000
1 8 2 -0.015 0.001 0.000-0.007-0.034 0.000 0.009 0.001 0.000
2 8 2 0.409-0.038 0.000 0.174 0.851 0.000-0.089-0.006 0.000
3 8 2 0.069-0.006 0.000 0.030 0.147 0.000-0.021-0.001 0.000
1 8 -4 -0.017 0.002 0.000 0.003 0.013 0.000-0.044-0.003 0.000
2 8 -4 -0.141 0.013 0.000 0.031 0.151 0.000 0.932 0.059 0.000
3 8 -4 -0.015 0.001 0.000 0.003 0.016 0.000 0.164 0.010 0.000
1 8 4 -0.002-0.017 0.000-0.013 0.003 0.000 0.003-0.044 0.000
2 8 4 -0.013-0.141 0.000-0.151 0.031 0.000-0.059 0.932 0.000
3 8 4 -0.001-0.015 0.000-0.016 0.003 0.000-0.010 0.164 0.000
1 8 -6 0.000 0.000 0.011 0.000 0.000 0.029 0.000 0.000-0.029
2 8 -6 0.000 0.000-0.142 0.000 0.000 0.683 0.000 0.000 0.679
3 8 -6 0.000 0.000-0.027 0.000 0.000 0.093 0.000 0.000 0.115
1 8 6 0.000 0.000-0.011 0.000 0.000-0.029 0.000 0.000-0.029
2 8 6 0.000 0.000 0.142 0.000 0.000-0.683 0.000 0.000 0.679
3 8 6 0.000 0.000 0.027 0.000 0.000-0.093 0.000 0.000 0.115
1 8 -8 -0.003-0.031 0.000-0.020 0.004 0.000 0.001-0.023 0.000
2 8 -8 0.082 0.874 0.000 0.366-0.075 0.000-0.011 0.179 0.000
3 8 -8 0.014 0.147 0.000 0.065-0.013 0.000-0.003 0.043 0.000
1 8 8 -0.031 0.003 0.000 0.004 0.020 0.000-0.023-0.001 0.000
2 8 8 0.874-0.082 0.000-0.075-0.366 0.000 0.179 0.011 0.000
3 8 8 0.147-0.014 0.000-0.013-0.065 0.000 0.043 0.003 0.000
:
etc

```

M	N	Eigenvalue(N)	Lgst EVec. comp.			2nd Lgst EVec. comp.		
			ST	I	J 2M	ST	I	J 2M
1	1	0.000	53 (0.874)	2	8 8	35 (0.409)	2	8 2
1	2	0.000	50 (0.874)	2	8 -8	32 (-0.409)	2	8 -2
1	3	18.014	29 (0.959)	2	8 0	30 (0.165)	3	8 0
:								
etc								

$|\langle n/M_{\text{uperp}}/m \rangle|^2$:

```

0.0 0.0 18.0 57.6 57.6 82.3 100.2 100.2 114.9
0.0 4.3101 0.1528 1.1440 0.0900 0.3022 0.7153 0.3580 0.3820 0.4718

```

```

0.0  0.1528 4.3101 1.1440 0.3022 0.0900 0.7153 0.3820 0.3580 0.4718
18.0 1.1440 1.1440 0.0000 2.5667 2.5667 0.0000 0.1354 0.1354 0.1094
57.6 0.0900 0.3022 2.5667 0.7837 0.1437 0.8107 3.1798 0.4620 0.0619
57.6 0.3022 0.0900 2.5667 0.1437 0.7837 0.8107 0.4620 3.1798 0.0619
82.3 0.7153 0.7153 0.0000 0.8107 0.8107 0.0000 0.7621 0.7621 3.2197
100.2 0.3580 0.3820 0.1354 3.1798 0.4620 0.7621 1.4283 0.0227 2.1629
100.2 0.3820 0.3580 0.1354 0.4620 3.1798 0.7621 0.0227 1.4283 2.1629
114.9 0.4718 0.4718 0.1094 0.0619 0.0619 3.2197 2.1629 2.1629 0.0000
:
etc

```

CEF Parameters (meV):

```

1 B(2,0) = 0.579E+02  2 B(4,0) = 0.433E+03  3 B(6,0) = 0.145E+03
4 B(2,1)c = 0.000E+00 16 B(2,1)s = 0.000E+00
5 B(2,2)c = 0.000E+00 17 B(2,2)s = 0.000E+00
6 B(4,1)c = 0.000E+00 18 B(4,1)s = 0.000E+00
7 B(4,2)c = 0.000E+00 19 B(4,2)s = 0.000E+00
8 B(4,3)c = 0.161E+03 20 B(4,3)s = 0.000E+00
9 B(4,4)c = 0.000E+00 21 B(4,4)s = 0.000E+00
10 B(6,1)c = 0.000E+00 22 B(6,1)s = 0.000E+00
11 B(6,2)c = 0.000E+00 23 B(6,2)s = 0.000E+00
12 B(6,3)c = -0.108E+03 24 B(6,3)s = 0.000E+00
13 B(6,4)c = 0.000E+00 25 B(6,4)s = 0.000E+00
14 B(6,5)c = 0.000E+00 26 B(6,5)s = 0.000E+00
15 B(6,6)c = 0.192E+03 27 B(6,6)s = 0.000E+00

```

Exchange field (He) and applied field (B):

```

28 Hex = 0.000E+00 29 Hey = 0.000E+00 30 Hez = 0.000E+00 meV
31 Bx = 0.000E+00 32 By = 0.000E+00 33 Bz = 0.000E+00 Tesla

```

```

34 No. f electrons = 2. (select 34 to check free-ion levels also)

```

number ... new value (<CR> to end) :

The printout contains the following information (in the order it appears):

- List of 14 parameters of the atomic Hamiltonian; Pr³⁺ has 13 *J* levels

- Diagnostics relating to the Hamiltonian matrix, which for Pr^{3+} has dimension 91
- List of eigenvalues of the Hamiltonian, in order of increasing energy
- Horizontal list of the first $2J + 1$ eigenvalues, with $E = 0$ as the lowest level
- Eigenvectors of the first $2J + 1$ eigenvalues, in the $|IJM_J\rangle$ basis, where I is an index that labels the three $J = 4$ levels of the $4f^2$ configuration of Pr^{3+} . Note that $I = 2$ corresponds to the $J = 4$ level which is lowest in energy.
- List of energy levels in order of increasing energy, giving the largest two eigenvector components
- Table of the squared dipole matrix elements of $\boldsymbol{\mu}_\perp$ — these give the transition probabilities for neutron scattering from a powder sample
- Finally the program returns to the list of crystal field and exchange and magnetic field parameters.

During the calculation, the program writes the eigenvectors, eigenvalues and dipole matrix elements to the file `CF_Levels.dat` in the same format as the screen output. Note that the file `CF_Levels.dat` must already exist in the folder, and is overwritten each time the calculation is performed. So remember to copy the results from `CF_Levels.dat` to a separate text file if you want to save them.

The program also write some diagnostic data to files called `fort.8`, `fort.16` and `fort.21`. These files contain lists of intermediate coefficients and can be deleted.

4.2 Scale CEF parameters to different rare-earth ion

This option transforms the crystal field parameters from one trivalent rare earth ion to another, assuming the crystal field parameters can be expressed in the form

$$B_q^k = \langle r^k \rangle A_q^k, \quad (12)$$

where $\langle r^k \rangle$ is the k^{th} radial moment of the $4f$ electron distribution, and A_q^k are intrinsic crystal-field parameters independent of the lanthanide ion.

4.3 Neutron cross-section

This option calculates the neutron spectrum in the dipole approximation. The transition intensities are given in absolute units of cross section. The program asks for the temperature, then diagonalises the Hamiltonian and outputs a list of transition energies and their cross sections for neutron scattering:

Neutron cross-section:

double diff. X-section = $k_f/k_i \cdot |F(Q)|^2 \cdot \exp(-2W) \cdot S(Q,w)$

from	to	w /meV	S(Q,w) /mb(sr ion) ⁻¹
2	1	0.00	5.53
2	2	0.00	156.03
1	1	0.00	156.03
1	2	0.00	5.53
2	3	18.01	41.41
1	3	18.01	41.41
2	4	57.56	10.94
2	5	57.56	3.26
1	4	57.56	3.26
1	5	57.56	10.94
2	6	82.30	25.89
1	6	82.30	25.89
2	7	100.21	13.83
1	7	100.21	12.96
2	8	100.21	12.96
1	8	100.21	13.83
2	9	114.89	17.08
1	9	114.89	17.08
:			
etc			

The program also gives you the option to simulate the spectrum and write it to a file. The transition lines are modelled by Gaussian peaks, all with the same width. You are asked to enter the energy range for the simulation (E_{\min} and E_{\max}), the number of points (≤ 501), and the full width at half maximum (FWHM) of the Gaussian line shape. You are also asked for a file name. Note: there must not already exist a file with the name you choose.

4.4 Fit to observed energies and intensities

This option allows you to fit a CF model to a set of experimental transition energies and relative intensities. If you select this option the first thing you will be asked is

Fit with existing data ? (N):

If you haven't entered any experimental observables then answer no (N or <CR>). If you have entered the experimental observables then answering yes (Y) saves you from entering the observables again and proceeds directly to the fit. This allows you to vary the starting parameters and fit to the same set of observables.

Next, you will have the following options for fitting:

Enter option (E,C,R,V,G,M,S,X,Q,H(elp),<CR> to fit):

Each letter has a different function. If you select H you get a basic statement of what they mean:

```
E - to input transition energies
C - to combine peak intensities
R - to input peak intensity ratios
V - to vary one of the B coefficients
G - to fix the ratio of 2 parameters
    (1st determined by 2nd; both .TRUE. in V)
M - to fit to magnetic moment
S - to include data from >= 2 lanthanide ions
X - to change the B coefficient normalising factor
Q - to quit the fitting program
H - Help; this menu
<CR> to fit
```

- E — this allows you to enter a set of observed transition energies. The energy levels are are number in order of ascending energy, starting with 1 (the ground state). For example, suppose experiments have established that the ground state is a doublet, the first excited state is a singlet at 18 ± 0.5 meV, the second excited state is a doublet at 58 ± 1 meV, etc., you would enter E <CR> then

```
Level 1, level 2, energy, uncertainty: 1 2 0.0 0.5
Level 1, level 2, energy, uncertainty: 1 3 18 0.5
Level 1, level 2, energy, uncertainty: 1 4 58 1
Level 1, level 2, energy, uncertainty: 1 5 58 1
Level 1, level 2, energy, uncertainty: <CR>
```

This input implies that you can number the transitions in order of energy, which is not always the case. For example, if you suspected another singlet between the 18 and 58 meV levels then the above numbering would be incorrect. There is no simple way round this problem. You would have to try fitting again with the 58 meV doublet numbered as levels 5 and 6.

- C — if there are overlapping peaks in the experimental spectrum then you can combine their intensities. For example, if you suspect unresolved transitions from the ground state (level 1) to singlet levels at 18 and 19 meV (levels 3 and 4) then you can combine their intensities as follows:

```
Enter option (E,C,R,V,G,M,S,X,Q,H(elp),<CR> to fit): C
Type in transitions which are to be grouped together (<CR> to finish)
Level 1, level 2: 1 3
Level 1, level 2: 1 4
Level 1, level 2: <CR>
```

- R — This allows you to enter experimentally-determined ratios of transition intensities. For example, suppose the intensity of the 18 meV transition (from the ground state doublet to level 3) is 4 ± 1 times larger than the transition from the ground state to the 58 meV doublet (levels 4 and 5), both transitions measured at a temperature of 5 K. First you would select option C and combine the intensities of transitions 1 to 3 and 2 to 3, and levels 1 to 4, 1 to 5, 2 to 4 and 2 to 5. Then

```
Enter option (E,C,R,V,G,M,S,X,Q,H(elp),<CR> to fit): R
1st peak: Temp., level 1, level 2 : 5 1 3
2nd peak: Temp., level 1, level 2 : 5 1 4
Ratio, uncertainty : 4 1
1st peak: Temp., level 1, level 2 : <CR>
```

- V — This is how you enter which parameters you want to vary in the fitting procedure. If you don't specify that a parameter is to be varied then it will remain fixed at its initial value. Suppose you want to fit the parameters B_0^4 , B_0^6 , B_3^4 and B_3^6 . Do the following:

```
Enter option (E,C,R,V,G,M,S,X,Q,H(elp),<CR> to fit): V
Vary which B coeff. ? : 2
```


Vary which B coeff. ? : 3
 Vary which B coeff. ? : 8
 Vary which B coeff. ? : 12
 Vary which B coeff. ? : <CR>

You can fit the exchange and magnetic field components, as well as the crystal field parameters.

- G — This allows you to fix the ratio of two parameters. This function is needed if the symmetry of the crystal field constrains two parameters to be in a fixed ratio. For example, in cubic symmetry $B_4^4/B_0^4 = \pm\sqrt{70}/14 = \pm 0.5976$ and $B_4^6/B_0^6 = \mp\sqrt{14}/2 = \mp 1.871$. You would first use the V option to specify that the variable parameters are B_0^4 , B_4^4 , B_0^6 and B_4^6 , then

```
Enter option (E,C,R,V,G,M,S,X,Q,H(elp),<CR> to fit): G
Coeff.1, coeff.2, Ratio 1:2 : 9 2 0.5976
Coeff.1, coeff.2, Ratio 1:2 : 13 3 -1.871
Coeff.1, coeff.2, Ratio 1:2 : <CR>
```

- M — This allows you to fit to the magnitude of a magnetic moment induced by an exchange or external magnetic field at a given temperature.
- S — With this option you can fit observables from two or more rare earth ions simultaneously. After specifying the second ion and giving the single-ion levels to include in the basis, you enter the observables for the second ion. You can repeat for a third ion, and so on.
- X — The minimisation routine works most efficiently if the variables are kept in the range $[-1, +1]$. This is achieved with a normalisation factor, which by default is set to 200 meV. If a larger or small factor would be better then it can be changed via this option.
- Q — Quits without performing the fit.
- H — Prints out the list of fitting options described above.

Be aware that you can only fit as many parameters as you have observables. Once you have input all the information for the fit and hit <CR> you will see an iterative improvement in the parameters step by step until the final set of parameters is reached. The quality of the fit is gauged by the usual χ^2 function, and on completion the routine writes out the converged

values of the fitting parameters and χ^2 . There is also a parameter called `IFAIL`. If the fit reaches a global minimum in χ^2 then `IFAIL=0`. If not, then `IFAIL=1...5` and you might want to change the starting parameters and re-run the fit.

The results of the fit are written into a file called `RESULTS.DAT`. A file with this name must exist already before performing the fit. If you perform another fit then the contents of `RESULTS.DAT` will be overwritten with the results of the new fit. So if you want to keep the results, copy them into another file.

At the end of the fit you will see the following on the screen:

```
Details of fit written to file RESULT.DAT
```

```
Save these best-fit parameters ? (N) :
```

If you answer `Y` then the program will replace the parameters in the starting menu by those calculated here. Otherwise, the original parameters are kept as they were.

4.5 Specific heat capacity

With this option you can calculate (but not fit) the specific heat capacity as a function of temperature. The calculation makes use of the eigenvalues but not the eigenfunctions. You need to specify the temperature interval for the calculation $[T_{\min}, T_{\max}]$ and the number of points. You are asked whether you wish to save the results to a file.

4.6 Magnetic susceptibility

This option calculates the magnetic susceptibility as a function of temperature over the interval $[0, T_{\max}]$, where T_{\max} is user-specified. The calculation is performed at 100 temperature values (not changeable). The susceptibility is given in units of $\text{cm}^3 \text{mol}^{-1}$. The program calculates the susceptibility in the directions parallel and perpendicular to the crystal field axis, χ_z and $(\chi_x + \chi_y)/2$, respectively, and the powder-averaged susceptibility χ_{powder} . You are asked whether you wish to save the results to a file.

4.7 Magnetisation

This option calculates the magnetisation (in μ_B) as a function of applied field at a specified temperature. The direction of the applied field is specified by values B_x, B_y, B_z along the crystal field axes. The magnetisation is

calculated at 21 field values from 0 to B_{\max} , where $B_{\max} = \sqrt{B_x^2 + B_y^2 + B_z^2}$. You are asked whether you wish to save the results to a file.

4.8 Magnetic moment

This option calculates the value of the magnetic moment (in μ_B) at a given temperature.

4.9 Matrix elements of magnetic moment operator

This function writes out a list of certain matrix elements used by the program. The type of matrix element is chosen from a menu. The function is mainly for diagnostic purposes, but the default option (option 1: matrix elements of μ) is useful for calculating the scattering cross-section from single crystals.

5 References

References

- [1] W. T. Carnall, G. L. Goodman, K. Rajnak and R. S. Rana, J. Chem Phys. **90**, 3443 (1989)
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