

BonnMag 1.4

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Manual (29.03.19) Windows 64-bit Version

Introduction

'BonnMag' (A. Bronova, T. Bredow, R. Glaum, M. J. Riley and W. Urland, *J. Comp. Chem.* **2018**, *39*,176) is a ligand field computer program which calculates symmetry assigned energy levels, g-values, electric dipole intensities and magnetic susceptibilities of all f^n ions (lanthanides and actinides). This program is based on the program 'SURGEV' written by W. Urland (W. Urland, *Habilitation thesis*, University of Gießen, **1980**).

File structure: Input and Output

The program requires two input files, 'setup' and 'run' (small letters). In 'setup' all parameters which are not dependent on particular parameter values are provided (coordinates of all considered atoms, cell parameters). The second data file 'run' contains all parameters used for the ligand-field calculation (interelectron repulsion and ligand field perturbations as Condon-Shortley-parameters, spin-orbit coupling etc.)

The program produces data files called $f_*.out$ where an asterisk * indicates the number of f electrons. The files $f_*.out$ contains the various reduced matrix elements which have been taken from "*Spectroscopic Coefficients for the p^n , d^n and f^n Configurations*", C. W. Nielson and G. F. Koster, MIT Press, **1963**. These files are automatically generated by BonnMag during the calculation.

After the calculation the data file 'OUTPUT' is generated, where all parameters and calculated values are located.

Note: The input data files can be called 'setup' and 'run' and will be automatically read by BonnMag. In this case the output data file is called 'OUTPUT'. If the input data files have other names, the user will be asked for the names of these files (max. 72 letters). The output file gets the name $*.out$ where * is the name of the 'setup' part.

Example: 'setup' is called 'PrZnPO'

'run' is called 'PrZnPO-run' (**Attention!** Use different names)

output data file gets the name 'PrZnPO.out'

The input commands:

In the input files for BonnMag each line is called a command. These commands control the extent of the calculations performed by the program. The first four characters (except command TITLE) in each line identify the command, while columns 5-72 are used to convey numerical data. The data can be separated by spaces. All numbers should be given with one or more decimal places even if they are zero.

The commands in the file RUN can be given in any order unless stated otherwise. In SETUP the commands should be in the specified order (see appendix).

*** An asterisk indicates that the command is compulsory.**

SETUP:

Allowed commands (in alphabetic order):

CELL CONF END LGND MULT PRTL TITLE XREF

"atomic coordinates"

* 'CELL' a b c alpha beta gamma

Unit cell dimensions in Angstroms and degrees.

* 'CONF' m

m = number of electrons, $1 \leq m \leq 14$ for f electrons.

* 'END'

This must be the last command.

* 'LGND' m n1 n2 n3

'm' is the ligands number

Defines a local cartesian system for a ligand in terms of the atoms n1, n2, n3 in the atom list. n1, n2, and n3 refer to the atom number in the listing in the input file! The Z axis is parallel to the vector $n1 \rightarrow n2$. The Y axis is perpendicular to the plane defined by the 3 atoms n1, n2 and n3. The X axis will form a right-handed coordinate system with Z and Y.

Note: There must be at least 2 'LGND' commands.

An error will occur if n1, n2, n3 are collinear.

* 'MULT' n

n = 1 if there is no centre of inversion.

n = 2 if there is a centre of inversion, in which case only symmetry-independent ligands should be given in the LGND commands.

Note: It is not a problem to describe a centrosymmetric chromophore with MULT 1.

'PRTL' n

Print level, content of the output file is controlled by this command, which is not compulsory.

n = 0 (Default value, used if no PRTL keyword is given in SETUP).

Output contains: coordinates of all atoms and distances from each ligand to the metal atom, Slater-Condon-Shortley, spin-orbit and angular overlap, parameters, energies with intensities and J projections, eigenvectors, magnetic susceptibilities, crystal susceptibilities and g-tensor.

n = 1 additionally: direction cosines for all atoms, crystal field parameters (Wybourne)

n = 2 additionally: Nielson/Koster coefficients, basis set, electrostatic matrices.

* 'TITLE' Title

Title of the calculation (up to 72 characters).

* 'XREF' n1 n2 n3

Defines a cartesian reference frame in terms of the atoms n1, n2, n3. The Z axis will be in the n2→n1 direction. The Y axis will be perpendicular to the plane defined by the 3 atoms n1, n2 and n3. The X axis will form a right hand coordinate system with Z and Y.

Note: If symmetry analysis should be done, the Z axis has to be parallel to the general rotation axis of the given point group! If there is no atom in the chromophor which fulfills this requirement a dummy atom has to be introduced. Otherwise the obtained eigenvalues would be wrong!

* 'Atom coordinates' x/a y/b z/c

Each atom command starts with up to 4 characters to identify the atom, then the three fractional coordinates with respect to *a*, *b*, *c* of the cell command. There must be at least 3 'atom commands'.

Note: different numbering of the atoms like O1 and O2 means, that these two atoms belong to the different ligand types (for example "oxide" oxygen atom and oxygen atom from phosphate) and could have independent e_{σ} and e_{π} . Atoms of the same ligand type must have the same identification character ('element' symbol).

Dummy atoms or atoms from a second coordination sphere have to be defined by the character 'X'. The atoms defined by 'X' are not included into the moment of inertia calculation. It is not necessary to give e_{σ} or e_{π} values for the dummy atoms in "run".

RUN:

Allowed commands (bold face) and parameters:

EORF **EPIX** **EPIY** **ESIG** **GTEN** **JOPS** **KVAL** **LATT** **MAGN** **MOLS**
NVEC **REFR** **SCSZ** **SYML** **TEMP** **VLEC**

* 'EORF' n

n = 0 the Condon-Shortley Parameter in RUN are given as E_1 , E_2 , E_3 .

n = 1 the Condon-Shortley Parameter in RUN are given as F_2 , F_4 , F_6 .

$e_{\sigma, \max}$ only for the shortest d(M-L) for each ligand type
 * 'ESIG' } (ligand types are determined from the atom list by BonnMag
 * 'EPIX' } by analysing the "element" symbols)
 * 'EPIY' } $e_{\sigma}(\text{M-L})$ for the atoms of the same ligand types are calculated using the relation

$$e_{\sigma} \sim d(\text{M-L})^{-7}$$

Angular overlap parameters or interaction energies. ESIG = e_{σ} , EPIX = $e_{\pi, x}$, EPIY = $e_{\pi, y}$. If isotropic π -interaction is assumed the values for EPIX and EPIY should be equal, for anisotropic different. If π -interaction is zero then it should be given as 0.0.

* 'GTEN' n

n = 0 g-values will not be calculated in appropriate crystal planes.

n = 1 g-values will be calculated in appropriate crystal planes.

Note: Calculation of g-values can be done just for ions with an odd number of f-electrons ("Kramers ions")! For ions with an even number of f-electrons ("non-Kramer ions") the calculation result is zero and is wrong! (M. Kaupp, M. Bühl, V. G. Malkin, *Calculation of NMR and EPR Parameters: Theory and Applications*, Wiley-VCH Verlag, 2014).

'JOPS' $\Omega_2 \Omega_4 \Omega_6$.

Judd-Ofelt-Parameters in m^2 for calculation of relative intensities of electric dipole transitions.

This command is not compulsory. If no Judd-Ofelt parameters are given in 'RUN' **default** values for rare-earth ions in LaF_3 will be used (R.P. Leavitt and C. A. Morrison, *J. Chem. Phys.* **1980**, 73, 749).

Table 1. Calculated Judd-Ofelt parameters for rare-earth ions in LaF₃.

Ion	$\Omega_2 (10^{-24} \text{ m}^2)$	$\Omega_4 (10^{-24} \text{ m}^2)$	$\Omega_6 (10^{-24} \text{ m}^2)$
Ce ³⁺	1.868	3.996	10.61
Pr ³⁺	1.078	2.014	4.529
Nd ³⁺	0.944	1.322	2.486
Pm ³⁺	0.632	1.012	1.910
Sm ³⁺	0.561	0.867	1.580
Eu ³⁺	0.444	0.651	1.119
Gd ³⁺	0.346	0.480	0.774
Tb ³⁺	0.660	1.020	1.865
Dy ³⁺	0.477	0.686	1.159
Ho ³⁺	0.387	0.530	0.846
Er ³⁺	0.375	0.506	0.798
Tm ³⁺	0.368	0.493	0.771
Yb ³⁺	0.309	0.397	0.587

* 'KVAL' k1 k2 k3 etc.

Stevens-orbital reduction factor k ($k \leq 1.0$) reduces the value of Bohr magneton numbers and g -tensors. Its value should be similar to the nephelauxetic ratio β for the reduction of the Slater-Condon-Shortley parameters. It can be varied inside the subroutines which calculate g -values and magnetic susceptibilities. This makes the calculation very fast for a series of calculations where k values are varied. The number of given k values corresponds to the number of performed calculations (K. W. H. Stevens, *Proc. Roy. Soc.* **1954**, *A219*, 542; M. Gerloch, *Magnetism and Ligand Field Theory*, Cambridge Univ. Press, **1983**).

*** EQUATIONS***

* 'LATT' n

Defines the crystal system.

n = 0 crystal susceptibilities will not be calculated.

n = 1 Monoclinic.

n = 2 Orthorhombic.

n = 3 Tetragonal or hexagonal.

Compulsory for GTEN command.

* 'MAGN' n

n = 0 magnetic susceptibilities will not be calculated.

n = 1 magnetic susceptibilities will be calculated (necessary in case of g-tensor calculation)

* 'MOLS' n

n = 1 Cubic.

n = 2 Axial.

n = 3 Rhombic

n = 4 Lower symmetry.

Indicates nature of molecular symmetry. If higher symmetry is given, the calculation of magnetic susceptibilities would be proceed just for unequal directions. Equal directions would get the same results. (For example, if molecular symmetry is cubic the calculation of magnetic susceptibilities would be made only for one direction).

* 'NVEC' n

n = 0 No eigenvectors are listed.

n = 1 All eigenvectors are listed.

n = N Lowest N of eigenvectors are listed.

'REFR' n

n = Refraction index used for the Judd-Ofelt analysis (intensity calculations).

If no refraction index is given in RUN and intensities will be calculated, the default value of n = 1.8 is used (L. Zundu, C. Xueyuan, Z. Tingjie, *Opt. Commun.*, **1997**, 134, 415).

* 'SCSZ' F₂(E₁) F₄(E₂) F₆(E₃) Zeta

Input of Slater-Condon-Shortley electron repulsion parameters F_2, F_4, F_6 in cm^{-1} and spin-orbit coupling constant ζ . SCSZ are *not* reduced by k (Stevens-orbital-reduction factor). These parameters must be explicitly reduced in the input.

The parameters can be taken from the following table (A. Bronova, T. Bredow, R. Glaum, M. J. Riley and W. Urland, *J. Comp. Chem.* **2018**, 39,176)

Table 1. Free ion SCS and spin-orbit coupling parameters obtained from NEV-PT2 (F_2, F_4, F_6) and CASSCF (ζ) calculations in cm^{-1} .

Ln^{3+}	F_2	F_4	F_6	ζ	Ln^{3+}	F_2	F_4	F_6	ζ
Ce	0.0	0.0	0.00	685.4	Tb	414.2	59.4	6.69	1761.7
Pr	324.2	52.1	5.25	802.2	Dy	427.6	61.5	6.93	1964.3
Nd	342.7	49.9	5.60	936.2	Ho	440.8	64.1	7.08	2182.5
Pm	356.6	52.1	5.83	1075.9	Er	454.2	65.7	7.37	2417.5
Sm	371.8	53.9	6.07	1231.3	Tm	467.4	69.9	7.60	2671.3
Eu	386.1	55.6	6.26	1395.4	Yb	0.0	0.0	0.00	2935.6
Gd	399.1	58.4	6.52	1576.0					

'SYML' n

The calculation of symmetry labels (irreducible representation = irrep) in the point group 'n' ($0 < n \leq 32$). 'n' corresponds to the numbering in the tables of Koster et al. (G. F. Koster, J. O. Dimmock, R. G. Wheeler and H. Statz, "*Properties of the 32 point groups*", MIT Press, **1963**).

1 C_1 (1)	9 C_4 (4)	17 C_{3i} / S_6 ($\bar{3}$)	25 C_{6v} (6mm)
2 C_i ($\bar{1}$)	10 S_4 ($\bar{4}$)	18 D_3 (32)	26 D_{3h} ($\bar{6}m2$)
3 C_2 (2)	11 C_{4h} (4/m)	19 C_{3v} (3m)	27 D_{6h} (6/m2/m2/m)
4 C_2 (m)	12 D_4 (422)	20 D_{3d} ($\bar{3}2/m$)	28 T (23)
5 C_{2h} (2/m)	13 C_{4v} (4mm)	21 C_6 (6)	29 T_h (2/m $\bar{3}$)
6 D_2 (222)	14 D_{2d} ($\bar{4}2m$)	22 C_{3h} ($\bar{6}$)	30 O (432)
7 C_{2v} (mm2)	15 D_{4h} (4/mmm)	23 C_{6h} (6/m)	31 T_d ($\bar{4}3m$)
8 D_{2h} (2/m2/m2/m)	16 C_3 (3)	24 D_6 (622)	32 O_h (4/m $\bar{3}2/m$)

In the output data file the Bethe notation (H. Bethe, *Ann. Physik* **1929**, 3, 133.) is used for irreducible representations. This command is not compulsory. If SYML is not given in the input file 'RUN' no symmetry analysis will be done.

* 'TEMP' a b c

Limits for temperature range (in K).

a: Lowest temperature.

b: Highest temperature.

c: Number of temperature values in the given range which will be considered for the calculation of magnetic susceptibilities.

* 'VLEC' a b c

Energy limits (in cm^{-1}) for the susceptibility calculations.

a: Cutoff for levels in the 2nd order Zeeman summation.

b: Cutoff for levels in the 1st order Zeeman summation.

c: Energy cutoff for levels to be considered degenerate.

Note: The limit given by "c" also determines if 2 or more levels are considered degenerate when the energy levels are printed.

For calculations up to 300 K the following limits can be used $a = 12000 \text{ cm}^{-1}$ and $b = 3000 \text{ cm}^{-1}$. For higher temperatures the limit for the 1st Zeeman summation has to be increased till the values for magnetic susceptibilities do not change.

Parametrization 1.0

The program `parameterization_all` (SCSZ and AOM parameters) and `parameterization_szs` (only SCSZ parameters) is a least-square fitting program for the fit parameters for obtaining a better match between calculated and observed energies. It is based on the root-mean-squares deviation reduction. The fitting procedure ends up, if the RMS of the new step is nearly equal to the RMS of the step before (limit is $\Delta(\text{RMS}_{\text{new}} - \text{RMS}_{\text{old}}) = 0.001$). Each step of the parameterization steps include a complete `BonnMag` calculation. From that reason it is recommended to keep the calculation as simple as possible (without calculations of the magnetic properties and g tensors).

The program requires an input data file "experiment.dat" (**must have this name!**), where the experimental transition energies, the corresponding multiplicity or degeneracy of each level ($M = 2J+1$) and the weighted factors are given (S. Appendix). The list of the energy levels has to start from the ground state (!) and going on till the energy level, that should be considered by this fitting procedure. The number of the listed energies belong to the same J **must(!)** be $2J+1$ (degeneracy). In this case the energy levels, which are not observed, should be weighted by 0.0. Thus the on-going list is complete, but the fitting procedure consider only the observed ("real" existing) energies.

Example: for the Pr^{3+} the ground state is $^3\text{H}_4$ with $J = 4$ and $M = 9$. The list of the energies must be as followed in case if only the ground state (level at 0.0 cm^{-1}) is known:

0.0	9	1.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0
0.0	9	0.0

After these energies, 11 levels for $^3\text{H}_5$ has to be listed etc.

Which values are given, if the energy is weighted by 0.0 is not important (not considered by the program, is only for the correct number of the levels).

APENDIX

SETUP	RUN
TITLE Pr3+ in alpha-PrZnPO PRTL 1 (optional) CONF 2 CELL 3.993 3.993 8.772 90.0 90.0 90.0 MULT 1 Pr 0.25 0.25 0.13641 O -0.25 0.25 0.0 O 0.25 -0.25 0.0 O 0.25 0.75 0.0 O 0.75 0.25 0.0 P 0.75 0.75 0.3310 P 0.75 -0.25 0.3310 P -0.25 0.75 0.3310 P -0.25 -0.25 0.3310 XREF 2 1 3 LGND 1 2 1 3 LGND 2 3 1 4 LGND 3 4 1 5 LGND 4 5 1 4 LGND 5 6 1 7 LGND 6 7 1 8 LGND 7 8 1 9 LGND 8 9 1 8 END	NVEC 9 EORF 1 MAGN 1 GTEN 0 MOLS 4 SYML 13 (optional) JOPS 1.078 2.014 4.529 (optional) REFR 2.0 (optional) SCSZ 296.2 50.3 5.21 707.6 ESIG 559.4 77.3 EPIX 399.6 29.7 EPIY 399.6 29.7 VLEC 12000. 3000. 0.5 TEMP 1.74 300. 100 KVAL 1.0 LATT 0 ESIG: $e_{\sigma, \max}(\text{Pr-O})$ and $e_{\sigma, \max}(\text{Pr-P})$
experiment.dat	
0.0 9 1.0 0.0 9 0.0 14.0 9 0.0 124.0 9 0.0 273.0 9 0.0 273.0 9 0.0 399.0 9 0.0 511.0 9 0.0 703.0 9 0.0 2110.0 11 0.0 2119.0 11 0.0 2119.0 11 0.0 2330.0 11 0.0 2341.0 11 0.0 2346.0 11 0.0 2346.0 11 0.0 2654.0 11 0.0 2372.0 11 0.0 2600.0 11 0.0 2600.0 11 0.0	

4447.0	13	0.0
4242.0	13	1.0
4242.0	13	1.0
4447.0	13	0.0
4448.0	13	0.0
4477.0	13	1.0
4477.0	13	0.0
4505.0	13	1.0
4562.0	13	1.0
4604.0	13	1.0
4604.0	13	1.0
4890.0	13	1.0
5000.0	13	0.0
5204.0	5	0.0
4972.0	5	1.0
5022.0	5	1.0
5022.0	5	1.0
5113.0	5	1.0
6311.0	7	1.0
6311.0	7	1.0
6358.0	7	1.0
6396.0	7	1.0
6396.0	7	1.0
6422.0	7	1.0
6480.0	7	1.0
6770.0	9	1.0
6801.0	9	1.0
6801.0	9	1.0
6826.0	9	1.0
6839.0	9	1.0
6863.0	9	1.0
6922.0	9	1.0
6922.0	9	0.0
6969.0	9	1.0
9786.0	9	0.0
9786.0	9	0.0
9898.0	9	0.0
9898.0	9	0.0
9768.0	9	1.0
9899.0	9	0.0
9899.0	9	0.0
9900.0	9	0.0
10039.0	9	1.0
16295.0	5	1.0
16652.0	5	1.0
16758.0	5	1.0
16848.0	5	1.0
16848.0	5	1.0

**This is the last energy level,
that should be considered by
the fitting procedure!!!**