



SIMPRE
SINGLE ION MAGNET MAGNETIC PREDICTION

Installation and user manual

July 24, 2014

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1 License

The `..SIMPRE` software package is © 2013-2014 by Juan M. Clemente-Juan and José J. Baldoví. The present installation and user manual is ©2013-2014 by José J. Baldoví, Juan M. Clemente-Juan and Alejandro Gaita-Ariño.

The source code of `..SIMPRE` is freely available by request to the authors at juan.m.clemente@uv.es and will be uploaded to the website of the European Institute of Molecular Magnetism:

<http://www.eimm.eu/>

Cite when using `..SIMPRE` \implies Any published work that contains results obtained using `..SIMPRE` should cite: José J. Baldoví, Salvador Cardona-Serra, Juan M. Clemente-Juan, Eugenio Coronado, Alejandro Gaita-Ariño, Andrew Palií, *Journal of Computational Chemistry* 34 (22), 1961-1967, **2013**. When using improved or patched versions of this software, and until said versions get published as independent programs, the same reference should be cited.

Use `..SIMPRE` with REC \implies To model real systems with `..SIMPRE`, it is strongly advised to apply the Radial Effective Charge (REC) model, citing: José J. Baldoví, Juan J. Borrás Almenar, Salvador Cardona-Serra, Juan M. Clemente-Juan, Eugenio Coronado, Alejandro Gaita-Ariño, *Dalton Transactions Chemistry* 41, 13705, **2012**

BECAUSE THE PROGRAM IS LICENSED FREE OF CHARGE, THERE IS NO WARRANTY FOR THE PROGRAM, TO THE EXTENT PERMITTED BY APPLICABLE LAW. EXCEPT WHEN OTHERWISE STATED IN WRITING THE PROGRAM IS PROVIDED "AS IS" WITHOUT WARRANTY OF ANY KIND, EITHER EXPRESSED OR IMPLIED, INCLUDING, BUT NOT LIMITED TO, THE IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE.

2 Introduction

Molecular magnetism applies molecular techniques for designing and studying new classes of molecule-based magnetic materials, from the bulk to the nanoscale. Over the past ten years, the field has been revitalized by the discovery that mononuclear metal complexes may show a single-molecule magnetic (SMM) behavior, with a new set of unusual quantum physical phenomena as compared with polynuclear complexes.

In contrast with the classical polynuclear SMMs, whose properties are dominated by exchange interactions between the ions, in Single Ion Magnets there is a direct relationship between the electronic spectrum resulting from the crystal field splitting of the single ion and the magnetic properties of the molecule. For this reason, there is a need for general models that are capable to correlate the structural and electronic features of the metal complex with its SMM properties.

`..SIMPRE` is a fortran77 code based on an effective electrostatic model of point charges around a rare earth ion. Although the minimal Point Charge Electrostatic Model (PCEM) is a very rough approximation, it presents some interesting features that, together with its beautiful simplicity, makes it attractive for some purposes. For example, using ideal symmetries it can be used to reduce the number of adjustable parameters in a fitting procedure. Moreover, in the case of ionic homoleptic complexes it can be used to predict the sign of the crystal field parameters. It has been found remarkable that such a simple model produces good agreement between experimentally and theoretically determined crystal field parameter signs.¹

The program calculates the full set of crystal field parameters, energy levels and wave functions, as well as the magnetic properties such as magnetization and the temperature dependence of the magnetic susceptibility. It is designed for real systems that need not display ideal symmetry, and is able to automatically determine the orientation that results in the most compact description of the wavefunction; which usually -but not always- coincides with the calculated easy axis of magnetization.

This handbook includes three examples with full input and output files. When performing test runs in your own system, please note that technical details including the compiler version are known to affect the results. Changes in the order of 1% in the coefficients of the wavefunctions are routinely encountered and should not be taken as a sign of a problem.

The systematic application of `..SIMPRE` to different coordination environments allows magneto-structural studies. The package has already been successfully applied to several mononuclear systems with single-molecule magnetic behavior, and, thanks to the parameterization of common ligands as effective charges, it is possible to build upon these results to not only rationalize but also predict the properties of more complex systems.

Check out **4. A step beyond**
for ways of getting more out of
`..SIMPRE` !

2.1 Theoretical model

This section consists in a complete explanation to be used if a detailed *Methodology* section is required.

We have resolved a Crystal Field (CF) Hamiltonian where the CF parameters for the ground J -multiplet have been obtained by a corrected electrostatic point charge model. For a given J -multiplet, such Hamiltonian expressed in terms of the Extended Stevens Operators (ESOs)² takes the general form:

$$\widehat{H}_{cf}(J) = \sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q = \sum_{k=2,4,6} \sum_{q=-k}^k a_k (1 - \sigma_k) A_k^q \langle r^k \rangle O_k^q \quad (2.1)$$

where k (for f -elements, $k = 2, 4, 6$) is the order (also called rank or degree) and q is the operator range (that varies between k and $-k$), of the Stevens operator equivalents O_k^q , as defined by Ryabov in terms of the angular momentum operators J_{\pm} and J_z (where the components $O_k^q(c)$ and $O_k^q(s)$ correspond to the ESOs with $q \geq 0$ and $q < 0$ respectively).³ Note that all the Stevens CF parameters B_k^q are real, whereas the matrix elements of O_k^q ($q < 0$) are imaginary. a_k are the tabulated α , β and γ Stevens coefficients⁴ for $k = 2, 4, 6$, respectively, which are tabulated and depend on the number of f electrons. σ_k are the Sternheimer shielding parameters⁵ of the 4f electronic shell and $\langle r^k \rangle$ are the expectation values of the radius.⁵

In *SIMPREG* 1.1,6 the A_k^q parameters are determined by the following relations:

$$A_k^0 = \frac{4\pi}{2k+1} \sum_{i=1}^N \frac{Z_i e^2}{R_i^{k+1}} Z_{k0}(\theta_i, \phi_i) p_{kq} \quad (2.2)$$

$$A_k^q = \frac{4\pi}{2k+1} \sum_{i=1}^N \frac{Z_i e^2}{R_i^{k+1}} Z_{kq}^c(\theta_i, \phi_i) p_{kq}; (q > 0) \quad (2.3)$$

$$A_k^q = \frac{4\pi}{2k+1} \sum_{i=1}^N \frac{Z_i e^2}{R_i^{k+1}} Z_{k|q|}^s(\theta_i, \phi_i) p_{k|q|}; (q < 0) \quad (2.4)$$

where R_i, θ_i, ϕ_i , are the effective polar coordinates of the point charges with the lanthanoid at the origin; Z_i is the effective point charge, associated with the i -th donor atom; N is the number of effective charges; e is the electron charge; p_{kq} are the prefactors of the spherical harmonics and Z_{kq} are the tesseral harmonics expressed in terms of the polar coordinates for the i -th donor atom.

References

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3 User guide

3.1 System requirements

`..SIMPRE` is not distributed as operating-system-specific binary but as a portable `fortran77` code. Thus, its use requires a standard `fortran77` compiler (contact your local system administrator for help if needed). So far it has been tested with `gfortran`, `ifort` and `g77`, and it has been optimized for `gfortran`. Additionally, it requires the `lapack` library, which can be freely obtained from:

Remember, `..SIMPRE` will **not** compile without `lapack`!

<http://www.netlib.org/lapack/>

`..SIMPRE` is a lightweight program, which will run even on a linux netbook or an old desktop computer (1 GB RAM, 1.0 GHz processor). With the rotation option turned off (`irof=0`, see below), execution is very fast and in practice the limiting step is compilation, which takes a few seconds. Compiling is required for every change in the input files and/or when moving to a different environment, e.g. to a different computer or operative system. Execution with full rotation can take about an hour in a minimal system and just a few minutes on a more powerful workstation. As described in the next section, you will also need a plain text editor -such as `vi`, `TextEdit` or `Notepad`- to prepare the input files.

3.2 Input files and syntax

The input of `..SIMPRE` is divided into two files:

- `simpre.par`, which defines computational parameters and yes/no switches for the calculation and
- `simpre.dat`, which defines the actual data: the metal and the point charges, but also, if needed, the output options for the susceptibility and the magnetization.

3.2.1 `simpre.par`

As `simpre.par` is taken as an `include` by `simpre.f`, it is a file in standard `fortran77` format, i.e.: the text is case insensitive, you need to leave 6 blank characters at the beginning of each line containing a command such as `parameter`, every line beginning by `C` is a comment and the rest of the line after a `!` is also a comment. It defines nine parameters:

`..SIMPRE` will **not** compile if `simpre.par` is not valid `fortran77` !

- `idtot` is the dimension of the full energy matrix, which is calculated as $idtot = 2J + 1$. For f elements it is safe to leave it as the maximum possible value $17 = 2 \cdot 8 + 1$.
- `iuni` defines the energy (or energy equivalent) units for the output: 1 for equivalent temperature in K, 2 for energy in meV, 3 for wavenumber in cm^{-1}

- `icoo` is the type of coordinates in `simpre.dat`: 1 for spherical (radius r in Å, polar angle θ and azimuthal angle ϕ in °), 2 for cartesian (x, y, z in Å)
- `ishi`, a yes/no (1/0) switch, controls the use of Sternheimer shielding parameters
- `irod` (1/0) switch controls whether a rotation of the coordinates searching for the most compact description of the wavefunction has to be performed or not
- the `isus` (1/0) switch controls whether the magnetic susceptibility will be calculated
- the `imag` (1/0) switch controls whether the magnetization will be calculated
- `ieig` decides whether the eigenvalues are going to be included in the output (1) or not (0), or if not only the eigenvalues but also the eigenvectors will be included (2)
- `EPS` is a numerical parameter to deal with underflow problems, it is safe to leave it as 10^{-12} (1.D-12) and not change it unless dealing with technical problems in a particular computer
- `ICHAR` is the number of charges to be accepted as input in `simpre.dat`; this is needed for forward-compatibility reasons, as future versions of `SIMPRE` may deal with polynuclear complexes. If a high number of charges needs to be used for any reason, `ICHAR` should be changed accordingly.

Remember to adjust the number of charges as needed!

3.2.2 `simpre.dat`

`simpre.dat` needs to define the metal with the following code, which is included as first line of the input as a reminder:

1	2	3	4	5	6	7	8	9	10	11	12
Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	user-defined

Thus, after the reminder and a blank line, the third line starts with an integer code (length 3) from 1 to 12 that defines the metal ion. If the user chooses the code 12, the lower part of the file defines the metal, as we will see below.

In the fourth line, the user defines the number of effective charges, again as a length 3 integer. This is followed by a list containing, in five columns, the ordinal of each charge (length 3 integer), the coordinates (cartesian or spherical, as specified in `simpre.par`) and the magnitude of each charge. Both the coordinates and the charge are length 13, with the decimal point in position 6. Note that the charge in the input is a **positive** number which is understood as the fraction of a (negative) electron charge. The coordinates are in Å and °.

Do not use negative numbers for the charge.

Immediately after the charge list, two extra lines detail the desired output for the magnetization and susceptibility. If `simpre.par` indicates that mag-

These lines should not be deleted.

netization and/or susceptibility need to be calculated, they will be read. Otherwise, they will be ignored. Nevertheless, the lines themselves need to be there. For the susceptibility, the input indicates the minimum and maximum temperatures (in K, length 9 with the decimal point in position 6), the number of points (length 6 integer) and the applied magnetic field (in mT, length 9 with the decimal point in position 7). For the magnetization, the input indicates the temperature (in K, length 9 with the decimal point in position 6), the maximum field (mT, length 9 integer), the field increment (mT, length 6 integer) and a number defining the angular integration (length 9 integer). Large numbers (100 would be large in this context) for angular integration mean longer calculations but produce more precise values for average magnetization and average χT products, specially in very anisotropic environments. After this two lines comes a mandatory blank line, meaning **at least three lines need to be present after the coordinate list**.

You only need to care about the last part of the input if there is a user-defined metal. The first line indicates the symbol for the metal, its angular momentum as $2J$ and the value of g_J . The second line indicates the Stevens parameters α, β, γ . The third line indicates the shielding parameters $\sigma_2, \sigma_4, \sigma_6$. The last line defines the expectation values of the radius powers $\langle r^2 \rangle, \langle r^4 \rangle, \langle r^6 \rangle$. This is also a way of changing the default choice for $\langle r^k \rangle^1$ (and/or for the shielding parameters).

3.3 Output files and interpretation

3.3.1 `simpre.out`

At the very top of `simpre.out` one can see a standard message including the version number and the program name in ASCII art.

The first real information is a repetition of some of the input data. We can read the name of the ion, the number of charges, the value of the Landé g factor for said ion and the energy units, followed by a small table for the Stevens parameters α, β, γ , the radius expectation values $\langle r^2 \rangle, \langle r^4 \rangle, \langle r^6 \rangle$ and the shielding parameters σ^2, σ^4 and σ^6 (including the contribution from the 4f perturbation), if `ishi=1`.

Check out **4. A step beyond** for ways of getting more out of `..SIMPRE` !

Next come the input coordinates, which are given both as cartesian and as spherical, with distances in Å and angles in radians. If the rotation option was activated, this is followed by the applied Euler angles and the spherical coordinates after rotation that produce the most compact description of the wavefunction, i.e. the orientation that allows grouping the highest weight onto a single M_J component in the ground state. This does not always coincide with the easy axis of magnetization, and indeed in some complexes it can be precisely the hard axis of magnetization. In any case, it is always possible to obtain the easy axis by rotating the input coordinates manually and calculating the parallel magnetization until reaching the maximum. Improved versions of `..SIMPRE` exist that can automatize this procedure.

These coordinates define the reference frame for the A_k^q Stevens parameters, which are given as a table in the form $A_k^q \langle r^k \rangle$ and B_k^q .

¹ Compare Freeman and Watson, *Phys. Rev.* 127, 2058 (1962) with Freeman and Desclaux, *J. Magn. Magn. Mater.* 12, 11 (1979)

Finally, if requested, the list of eigenvalues and eigenvectors are included, using all M_J from the ground J multiplet as basis set. First the coefficients are written as complex numbers (first line: real part, second line: imaginary part), and later as the squares of the moduli (i.e.: normalized to unity) to facilitate the comparison of the different contributions. Note that energies are given with a precision up to the millionth of the unit to allow for testing, but for most purposes it makes more sense to round to the nearest unit.

3.3.2 sus.out

At the very top of `simplre.out` one can see a standard message including the version number and the program name in ASCII art.

Then the relevant input data are repeated: minimum and maximum temperature, number of points and value of the magnetic field.

Finally, the result is given in five columns: temperature in K, and χT product in emu·K/mol for the different orientations and the average: $\chi_z T$, $\chi_x T$, $\chi_y T$, $\chi_{av} T$.

3.3.3 mag.out

At the very top of `simplre.out` one can see a standard message including the version number and the program name in ASCII art.

Then the relevant input data are repeated: temperature, maximum field and field step and integration angle. The integration angle is given indirectly in the input as number of points.

Finally, the result is given in five columns: field in T and magnetization in Bohr Magnetons for the different orientations and the average: M_z , M_x , M_y , M_{av} .

3.4 Example 1: Ideal cube (DyX_8)

This is an idealized example that can serve as a test run, or it could also be part of a magnetostructural study. The center ion is Dy^{3+} and the environment consists in 8 unity charges in the corners of a cube, each at a distance of 2.5\AA from the center. There are three mandatory lines (blank, in this case) after the charge list.

simpre.par

```

PARAMETER (idtot= 17)! dimension of full energy matrix
c
PARAMETER (iuni=3) ! units (1=K, 2=meV, 3=cm-1)
c
PARAMETER (icoo=1) ! spherical coordinates=1, cartesian coordinates=2
c
PARAMETER (ishi=1) ! use of Sternheimer shielding parameters [1(yes)/0(no)]
c
PARAMETER (irot=0) ! rotation for a compact ground-state wave function [1(yes)/0(no)]
c
PARAMETER (isus=0) ! magnetic susceptibility calculation [1(yes)/0(no)]
c
PARAMETER (imag=0) ! magnetization calculation [1(yes)/0(no)]
c
PARAMETER (ieig=2) ! write eigenvalues
c
                        [no(0)/yes(1)/yes+eigenvectors(2)]
c
-----
c* The following parameter is defined to minimize underflow problems
PARAMETER (EPS      = 1.D-12)
c
PARAMETER (ICHAR = 12)! number of charges

```

simpre.dat

```

1=Ce3+, 2=Pr3+, 3=Nd3+, 4=Pm3+, 5=Sm3+, 6=Tb3+, 7=Dy3+, 8=Ho3+, 9=Er3+, 10=Tm3+, 11=Yb3+, 12=user

7  !ion code (from 1 to 12, see above)
8  !number of effective charges
1  2.5000000  54.7356103  0.0000000  1.0000000
2  2.5000000  54.7356103  90.0000000  1.0000000
3  2.5000000  54.7356103  180.0000000  1.0000000
4  2.5000000  54.7356103  270.0000000  1.0000000
5  2.5000000  125.2643897  0.0000000  1.0000000
6  2.5000000  125.2643897  90.0000000  1.0000000
7  2.5000000  125.2643897  180.0000000  1.0000000
8  2.5000000  125.2643897  270.0000000  1.0000000

```

simplre.out

```
*****  
** output file generated by SIMPRE version 1.1 **  
*****
```

```
-----  
.#####.#####.#####.#####.#####  
##...##.###.###...##.#####.#####.#####  
##.....##.###.###...##.#####.#####.#####  
#####.###.###.###.###.#####.#####.#####  
.....##.###.###...##.#####.#####.#####  
##...##.###.###...##.#####.#####.#####  
#####.#####.#####.#####.#####
```

```
*****
```

```
ion:      Dy(III)  
number of charges: 8  
g:        1.333  
units:    cm-1
```

```
stv       2         4         6  
-0.00634921 -0.00005920 0.00000103
```

```
<r>k      2         4         6  
0.84900000 1.97700000 10.44000000
```

```
shi       2         4         6  
0.52700000 -0.01990000 -0.03160000
```

input coordinates

cartesian (A)

x	y	z	Z
2.0412415	0.0000000	1.4433757	1.0000000
0.0000000	2.0412415	1.4433757	1.0000000
-2.0412415	0.0000000	1.4433757	1.0000000
-0.0000000	-2.0412415	1.4433757	1.0000000
2.0412415	0.0000000	-1.4433757	1.0000000
0.0000000	2.0412415	-1.4433757	1.0000000
-2.0412415	0.0000000	-1.4433757	1.0000000
-0.0000000	-2.0412415	-1.4433757	1.0000000

spherical (rad)

r	theta	phi	Z
2.5000000	0.9553166	0.0000000	1.0000000
2.5000000	0.9553166	1.5707963	1.0000000
2.5000000	0.9553166	3.1415927	1.0000000
2.5000000	0.9553166	4.7123890	1.0000000
2.5000000	2.1862760	0.0000000	1.0000000
2.5000000	2.1862760	1.5707963	1.0000000
2.5000000	2.1862760	3.1415927	1.0000000
2.5000000	2.1862760	4.7123890	1.0000000

```
*****
```

Stevens Crystal Field Parameters (cm-1)

```
*****
```

k	q	Akq <rk>	Bkq
2	0	0.00000142	-0.00000001
4	0	-73.12735068	0.00432914
4	4	365.63675289	-0.02164572
4	-4	0.00000000	0.00000000
6	0	5.00013438	0.00000517
6	4	105.00282221	0.00010867
6	-4	0.00000000	0.00000000

Eigenvalues (cm⁻¹) and eigenvectors

	-7.50	-6.50	-5.50	-4.50	-3.50	-2.50	-1.50	-0.50	0.50	1.50	2.50	3.50	4.50	5.50	6.50	7.50
0.000000	0.000000	0.000000	0.941752	-0.000000	-0.000000	0.000000	0.271189	-0.000000	-0.000000	0.000000	0.197992	-0.000000	-0.000000	0.000000	0.018963	0.000000
	-0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.018963	-0.000000	-0.000000	-0.000000	0.197992	-0.000000	-0.000000	-0.000000	0.271189	-0.000000	-0.000000	-0.000000	0.941752	-0.000000	0.000000
	0.000000	0.000000	-0.000000	-0.000000	-0.000000	0.000000	-0.000000	-0.000000	-0.000000	0.000000	-0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000
0.000002	-0.000000	0.000000	-0.000000	0.798851	-0.000000	0.000000	-0.000000	0.419831	-0.000000	0.000000	0.000000	0.430642	-0.000000	0.000000	-0.000000	-0.011195
	-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000002	-0.011195	0.000000	0.000000	0.000000	0.430642	0.000000	0.000000	0.000000	0.419831	0.000000	0.000000	0.000000	0.798851	0.000000	0.000000	-0.000000
	0.000000	-0.000000	0.000000	0.000000	-0.000001	0.000000	0.000000	0.000000	-0.000001	-0.000000	0.000000	0.000000	-0.000001	-0.000000	0.000000	0.000000
30.943069	0.000000	0.773482	-0.000000	0.000000	-0.000000	0.485988	0.000000	-0.000000	-0.000000	0.344246	0.000000	-0.000000	0.000000	-0.216878	0.000001	0.000000
	0.000000	0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	-0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000
30.943069	0.000000	-0.000001	-0.216878	-0.000000	-0.000000	-0.000000	0.344246	0.000000	-0.000000	-0.000000	0.485988	0.000000	0.000000	0.000000	0.773482	-0.000000
	0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000
30.943070	0.026523	-0.000000	0.000000	-0.000000	-0.795615	-0.000000	-0.000000	0.000000	-0.240210	-0.000000	-0.000000	0.000000	0.555510	0.000000	-0.000000	-0.000000
	-0.000000	0.000000	-0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000	0.000000
30.943070	0.000000	-0.000000	-0.000000	0.555510	-0.000000	-0.000000	0.000000	-0.240210	-0.000000	-0.000000	0.000000	-0.795615	0.000000	0.000000	0.000000	0.026523
	0.000000	-0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000	-0.000000	-0.000000	0.000000	0.000000
35.821651	0.000000	-0.633278	-0.000000	-0.000000	-0.000000	0.581843	0.000001	0.000000	-0.000000	0.450694	0.000001	0.000000	0.000000	-0.239357	-0.000001	-0.000000
	0.000000	-0.000000	-0.000000	-0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	-0.000000	-0.000000	-0.000000
35.821651	-0.000000	-0.000001	0.239357	0.000000	0.000000	0.000001	-0.450694	0.000000	0.000000	0.000001	-0.581843	0.000000	-0.000000	-0.000000	0.633278	-0.000000
	-0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000	0.000000
138.450427	-0.549062	0.000000	0.000000	0.000000	0.312086	0.000000	0.000000	-0.000000	-0.677614	0.000000	-0.000000	-0.000000	0.180183	-0.000000	0.000000	0.000000
	-0.192542	0.000000	0.000000	0.000000	0.109441	0.000000	-0.000000	-0.000000	-0.237622	0.000000	0.000000	-0.000000	0.063186	0.000000	0.000000	0.000000
138.450427	0.000000	0.000000	0.000000	-0.190941	0.000000	-0.000000	-0.000000	0.718070	-0.000000	0.000000	0.000000	-0.330719	0.000000	-0.000000	-0.000000	0.581844
	0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000
141.734248	-0.812791	-0.000000	-0.000000	-0.000000	-0.268642	0.000000	0.000000	-0.000000	0.500416	-0.000000	-0.000000	-0.000000	-0.129562	0.000000	0.000000	-0.000000
	-0.000017	-0.000000	0.000000	-0.000000	-0.000006	0.000000	-0.000000	0.000000	0.000010	-0.000000	0.000000	-0.000000	-0.000003	0.000000	-0.000000	0.000000
141.734248	-0.000000	-0.000000	-0.000000	0.129562	-0.000000	0.000000	0.000000	-0.500416	0.000000	-0.000000	-0.000000	0.268642	-0.000000	0.000000	0.000000	0.812791
	-0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000
141.734252	0.000000	-0.018007	0.000019	0.000000	0.000000	0.621348	-0.000161	0.000000	-0.000000	-0.777706	0.000128	-0.000000	0.000000	0.093682	-0.000004	0.000000
	-0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	0.000000	0.000000	-0.000000	-0.000000	-0.000000	-0.000000	0.000000	0.000000	0.000000
141.734252	0.000000	-0.000004	-0.093682	-0.000000	0.000000	0.000128	0.777706	-0.000000	-0.000000	-0.000161	-0.621348	-0.000000	0.000000	0.000019	0.018007	0.000000
	0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	-0.000000	0.000000

Eigenvalues (cm⁻¹) and eigenvectors (modulus square)

	-7.50	-6.50	-5.50	-4.50	-3.50	-2.50	-1.50	-0.50	0.50	1.50	2.50	3.50	4.50	5.50	6.50	7.50
0.000000	0.000000	0.000000	0.886896	0.000000	0.000000	0.000000	0.073544	0.000000	0.000000	0.000000	0.039201	0.000000	0.000000	0.000000	0.000360	0.000000
0.000000	0.000000	0.000360	0.000000	0.000000	0.000000	0.039201	0.000000	0.000000	0.000000	0.073544	0.000000	0.000000	0.000000	0.886896	0.000000	0.000000
0.000002	0.000000	0.000000	0.000000	0.638163	0.000000	0.000000	0.000000	0.176258	0.000000	0.000000	0.000000	0.185453	0.000000	0.000000	0.000000	0.000125
0.000002	0.000125	0.000000	0.000000	0.000000	0.185453	0.000000	0.000000	0.000000	0.176258	0.000000	0.000000	0.000000	0.638163	0.000000	0.000000	0.000000
30.943069	0.000000	0.598275	0.000000	0.000000	0.000000	0.236184	0.000000	0.000000	0.000000	0.118505	0.000000	0.000000	0.000000	0.047036	0.000000	0.000000
30.943069	0.000000	0.000000	0.047036	0.000000	0.000000	0.000000	0.118505	0.000000	0.000000	0.000000	0.236184	0.000000	0.000000	0.000000	0.598275	0.000000
30.943070	0.000703	0.000000	0.000000	0.000000	0.633004	0.000000	0.000000	0.000000	0.057701	0.000000	0.000000	0.000000	0.308592	0.000000	0.000000	0.000000
30.943070	0.000000	0.000000	0.000000	0.308592	0.000000	0.000000	0.000000	0.000000	0.057701	0.000000	0.000000	0.000000	0.633004	0.000000	0.000000	0.000703
35.821651	0.000000	0.401042	0.000000	0.000000	0.000000	0.338542	0.000000	0.000000	0.000000	0.203125	0.000000	0.000000	0.000000	0.057292	0.000000	0.000000
35.821651	0.000000	0.000000	0.057292	0.000000	0.000000	0.000000	0.203125	0.000000	0.000000	0.000000	0.338542	0.000000	0.000000	0.000000	0.401042	0.000000
138.450427	0.338542	0.000000	0.000000	0.000000	0.109375	0.000000	0.000000	0.000000	0.515625	0.000000	0.000000	0.000000	0.036458	0.000000	0.000000	0.000000
138.450427	0.000000	0.000000	0.000000	0.036458	0.000000	0.000000	0.000000	0.515625	0.000000	0.000000	0.000000	0.109375	0.000000	0.000000	0.000000	0.338542
141.734248	0.660629	0.000000	0.000000	0.000000	0.072168	0.000000	0.000000	0.000000	0.250416	0.000000	0.000000	0.000000	0.016786	0.000000	0.000000	0.000000
141.734248	0.000000	0.000000	0.000000	0.016786	0.000000	0.000000	0.000000	0.250416	0.000000	0.000000	0.000000	0.072168	0.000000	0.000000	0.000000	0.660629
141.734252	0.000000	0.000324	0.000000	0.000000	0.000000	0.386073	0.000000	0.000000	0.000000	0.604826	0.000000	0.000000	0.000000	0.008776	0.000000	0.000000
141.734252	0.000000	0.000000	0.008776	0.000000	0.000000	0.000000	0.604826	0.000000	0.000000	0.000000	0.386073	0.000000	0.000000	0.000000	0.000324	0.000000

3.5 Example 2: $\text{LiHo}_x\text{Y}_{(1-x)}\text{F}_4$

This is a well-known solid-state example. In this case, we simplified the input by taking average radiuses. As susceptibility and magnetization are requested in `simpre.par`, the corresponding details are introduced in `simpre.dat`. There is a mandatory (blank) line after the details for the magnetization.

`simpre.par`

```

PARAMETER (idtot= 17)! dimension of full energy matrix
c
PARAMETER (iuni=3) ! units (1=K, 2=meV, 3=cm-1)
c
PARAMETER (icoo=1) ! spherical coordinates=1, cartesian coordinates=2
c
PARAMETER (ishi=1) ! use of Sternheimer shielding parameters [1(yes)/0(no)]
c
PARAMETER (irot=1) ! rotation for a compact ground-state wave function [1(yes)/0(no)]
c
PARAMETER (isus=1) ! magnetic susceptibility calculation [1(yes)/0(no)]
c
PARAMETER (imag=1) ! magnetization calculation [1(yes)/0(no)]
c
PARAMETER (ieig=2) ! write eigenvalues
c
                        [no(0)/yes(1)/yes+eigenvectors(2)]
c
-----
c* The following parameter is defined to minimize underflow problems
PARAMETER (EPS      = 1.D-12)
c
PARAMETER (ICHAR = 12)! number of charges

```

`simpre.dat`

```

1=Ce3+, 2=Pr3+, 3=Nd3+, 4=Pm3+, 5=Sm3+, 6=Tb3+, 7=Dy3+, 8=Ho3+, 9=Er3+, 10=Tm3+, 11=Yb3+, 12=user

8 !ion code (from 1 to 12, see above)
8 !number of centers coordinated to the lanthanoid
1 1.4893000 67.0800000 0.0000000 0.2003000
2 1.4893000 112.9200000 90.0000000 0.2003000
3 1.4893000 67.0800000 180.0000000 0.2003000
4 1.4893000 112.9200000 270.0000000 0.2003000
5 1.4893000 142.0500000 3.9800000 0.2003000
6 1.4893000 37.9500000 93.9800000 0.2003000
7 1.4893000 142.0500000 183.9800000 0.2003000
8 1.4893000 37.9500000 273.9800000 0.2003000
2.000 300.000 25 100.00 !SUSCEPTIBILITY: Tmin(K),Tmax(K),# of points,H(mT)
2.000 5000 250 61 !MAGNETIZATION: T(K),Hmax(mT),H increment (mT),# of angles

```

simplere.out

```
*****
**  output file generated by SIMPRE version 1.1  **
*****
```

```
-----
.#####.###.##...#.#####.#####.#####
##...##.##.###...###.##...#.##...#.##...
##...###.###.###.###...#.##...#.##...
.#####.##.##.###.##.#####.#####.#####
...##.##.##...#.##...#.##...#.##...
##...##.##.##...#.##...#.##...#.##...
.#####.###.##...#.##...#.##...#####
```

```
*****
```

```

          ion:      Ho(III)
number of charges:      8
          g:        1.250
          units:      cm-1

stv      2      4      6
-0.00222222 -0.00003330 -0.00000129

<r>k      2      4      6
0.81000000 1.81600000 9.34500000

shi      2      4      6
0.53400000 -0.03060000 -0.03130000
```

input coordinates

cartesian (A)

x	y	z	Z
1.3717190	0.0000000	0.5800012	0.2003000
0.0000000	1.3717190	-0.5800012	0.2003000
-1.3717190	0.0000000	0.5800012	0.2003000
-0.0000000	-1.3717190	-0.5800012	0.2003000
0.9136713	0.0635696	-1.1743841	0.2003000
-0.0635696	0.9136713	1.1743841	0.2003000
-0.9136713	-0.0635696	-1.1743841	0.2003000
0.0635696	-0.9136713	1.1743841	0.2003000

spherical (rad)

r	theta	phi	Z
1.4893000	1.1707669	0.0000000	0.2003000
1.4893000	1.9708258	1.5707963	0.2003000
1.4893000	1.1707669	3.1415927	0.2003000
1.4893000	1.9708258	4.7123890	0.2003000
1.4893000	2.4792402	0.0694641	0.2003000
1.4893000	0.6623525	1.6402604	0.2003000
1.4893000	2.4792402	3.2110568	0.2003000
1.4893000	0.6623525	4.7818531	0.2003000

ROTATION

```

-----
alpha = 2.0 degrees
beta = 0.0 degrees
gamma = 8.0 degrees

```

```

*****
COORDINATES AFTER ROTATION
*****

```

Spherical coordinates

```

-----
#      r      theta    phi      charge
#      [A]     [rad]    [rad]     [e]

1  1.48930  1.17077  0.17453  0.20030
2  1.48930  1.97083  1.74533  0.20030
3  1.48930  1.17077 -2.96706  0.20030
4  1.48930  1.97083 -1.39626  0.20030
5  1.48930  2.47924  0.24400  0.20030
6  1.48930  0.66235  1.81479  0.20030
7  1.48930  2.47924 -2.89760  0.20030
8  1.48930  0.66235 -1.32680  0.20030

```

```

*****
Stevens Crystal Field Parameters (cm-1)
*****

```

```

k  q      Akq <rk>      Bkq
-----
2  0      238.51771524    -0.53003937
4  0      -83.48560350         0.00278007
4  4      643.64874438     -0.02143352
4 -4      592.28941789         0.01972326
6  0      -7.01279402          0.00000907
6  4      249.45424878     -0.00032272
6 -4      298.50706758         0.00038618

```

Eigenvalues (cm⁻¹) and eigenvectors

	-8.00	-7.00	-6.00	-5.00	-4.00	-3.00	-2.00	-1.00	0.00	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
0.000000	0.000000	0.786464	0.000000	0.000000	-0.000000	0.482960	0.000000	0.000000	0.000000	0.031978	0.000000	0.000000	-0.000000	0.013237	0.000000	0.000000	0.000000
	-0.000000	-0.260893	0.000000	-0.000000	-0.000000	0.280411	0.000000	0.000000	-0.000000	0.004359	-0.000000	-0.000000	0.000000	0.017632	0.000000	0.000000	0.000000
0.000000	0.000000	-0.000000	0.000000	0.005587	0.000000	-0.000000	-0.000000	0.027956	-0.000000	-0.000000	-0.000000	0.341071	-0.000000	-0.000000	-0.000000	0.826723	-0.000000
	-0.000000	0.000000	-0.000000	-0.021328	0.000000	0.000000	-0.000000	-0.016127	0.000000	0.000000	0.000000	-0.442213	0.000000	-0.000000	-0.000000	-0.055861	-0.000000
11.255613	0.000000	0.000000	-0.552390	-0.000000	0.000000	0.000000	-0.344962	0.000000	0.000000	0.000000	-0.176053	-0.000000	-0.000000	0.000000	-0.573263	-0.000000	-0.000000
	0.000000	-0.000000	0.218205	-0.000000	0.000000	-0.000000	-0.168085	0.000000	0.000000	-0.000000	0.340964	0.000000	0.000000	0.000000	0.155300	0.000000	0.000000
19.197764	-0.000000	0.000000	-0.570016	-0.000000	-0.000000	0.000000	-0.318614	0.000000	-0.000000	-0.000000	0.165501	0.000000	0.000000	-0.000000	0.591019	0.000000	0.000000
	-0.000000	-0.000000	0.220359	0.000000	-0.000000	-0.000000	-0.158142	-0.000000	-0.000000	0.000000	-0.314854	-0.000000	-0.000000	0.000000	-0.155477	-0.000000	0.000000
60.705255	-0.446141	-0.000000	0.000000	0.000000	-0.298101	-0.000000	0.000000	0.000000	0.012653	0.000000	-0.000000	0.000000	0.339785	0.000000	-0.000000	0.000000	0.448485
	-0.045791	0.000000	-0.000000	-0.000000	-0.423514	-0.000000	0.000000	-0.000000	-0.247196	0.000000	0.000000	-0.000000	-0.390864	0.000000	0.000000	0.000000	0.000000
71.349065	-0.485555	-0.000000	0.000000	0.000000	-0.294481	-0.000000	0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.335659	0.000000	-0.000000	0.000000	-0.488106
	-0.049837	0.000000	-0.000000	-0.000000	-0.418371	-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.386117	0.000000	0.000000	0.000000	0.000000
77.076016	-0.000000	-0.000000	-0.000000	0.678938	-0.000000	0.000000	-0.000000	0.054157	-0.000000	0.000000	0.000000	-0.001802	0.000000	-0.000000	-0.000000	0.013560	0.000000
	0.000000	-0.000000	-0.000000	0.538337	0.000000	-0.000000	-0.000000	0.494669	0.000000	0.000000	0.000000	-0.003302	0.000000	0.000000	0.000000	-0.037527	0.000000
77.076016	0.000000	-0.036588	0.000000	-0.000000	0.000000	-0.003410	0.000000	-0.000000	-0.000000	0.497114	0.000000	0.000000	0.000000	0.580478	0.000000	0.000000	0.000000
	0.000000	0.015922	0.000000	0.000000	0.000000	-0.001588	-0.000000	0.000000	0.000000	0.022548	-0.000000	-0.000000	-0.000000	0.643280	0.000000	0.000000	0.000000
214.949594	-0.397396	0.000000	-0.000000	0.000000	0.089754	-0.000000	0.000000	-0.000000	-0.040644	-0.000000	0.000000	-0.000000	-0.102305	-0.000000	0.000000	0.000000	0.399484
	-0.040788	-0.000000	0.000000	-0.000000	0.127515	-0.000000	0.000000	0.000000	0.794067	0.000000	-0.000000	0.000000	0.117684	-0.000000	-0.000000	0.000000	0.000000
271.221415	-0.508944	0.000000	-0.000000	0.000000	0.280947	-0.000000	0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.000000	0.320233	0.000000	-0.000000	0.000000	-0.511618
	-0.052238	-0.000000	0.000000	-0.000000	0.399144	-0.000000	0.000000	-0.000000	-0.000000	0.000000	-0.000000	0.000000	-0.368372	0.000000	0.000000	0.000000	0.000000
274.041991	0.000000	-0.000003	-0.000000	0.429408	-0.000000	0.000005	0.000000	-0.670210	0.000000	0.000010	-0.000000	-0.376148	-0.000000	-0.000005	-0.000000	0.158068	0.000000
	0.000000	0.000002	0.000000	-0.130300	-0.000000	0.000001	0.000000	-0.363300	-0.000000	-0.000002	-0.000000	-0.040088	0.000000	-0.000003	0.000000	0.222221	0.000000
274.041991	-0.000000	-0.216334	0.000000	-0.000006	0.000000	0.371345	-0.000000	0.000009	-0.000000	0.747327	-0.000000	0.000005	0.000000	-0.372245	0.000000	-0.000002	-0.000000
	-0.000000	0.166034	-0.000000	0.000001	0.000000	0.072090	-0.000000	0.000005	0.000000	-0.150568	0.000000	0.000001	-0.000000	-0.250606	0.000000	-0.000003	0.000000
283.277708	-0.000000	-0.000000	0.367018	0.000000	0.000000	-0.000000	-0.511431	0.000000	-0.000000	-0.000000	-0.313771	-0.000000	0.000000	0.000000	0.377214	0.000000	-0.000000
	0.000000	-0.000000	-0.112023	0.000000	0.000000	0.000000	-0.301972	-0.000000	0.000000	-0.000000	0.504279	-0.000000	-0.000000	0.000000	-0.070433	0.000000	0.000000
291.044315	0.000000	0.380134	-0.000000	0.000001	-0.000000	-0.727559	-0.000000	-0.000002	-0.000000	0.402545	0.000000	0.000004	0.000000	-0.183122	-0.000000	-0.000002	-0.000000
	-0.000000	-0.304873	-0.000000	-0.000000	-0.000000	-0.125173	0.000000	-0.000001	0.000000	-0.090094	0.000000	-0.000000	-0.000000	-0.117676	-0.000000	-0.000002	0.000000
291.044315	-0.000000	0.000002	-0.000000	-0.182568	0.000000	-0.000001	0.000000	0.083406	0.000000	0.000001	0.000000	-0.413279	-0.000000	-0.000000	-0.000000	-0.121590	0.000000
	0.000000	0.000001	-0.000000	-0.118534	0.000000	-0.000003	0.000000	0.403984	-0.000000	0.000001	-0.000000	-0.611727	0.000000	-0.000001	-0.000000	0.471874	0.000000
297.817674	0.371244	-0.000000	-0.000000	-0.000000	-0.262164	0.000000	0.000000	-0.000000	-0.028302	-0.000000	-0.000000	-0.000000	0.298823	0.000000	0.000000	-0.000000	-0.373195
	0.038104	0.000000	0.000000	-0.000000	-0.372459	0.000000	0.000000	0.000000	0.552937	0.000000	0.000000	-0.000000	-0.343745	0.000000	-0.000000	0.000000	0.000000
304.397378	-0.000000	0.000000	-0.342690	0.000000	0.000000	-0.000000	0.518335	0.000000	0.000000	0.000000	-0.335689	0.000000	-0.000000	0.000000	0.351177	-0.000000	0.000000
	0.000000	-0.000000	0.095329	0.000000	0.000000	-0.000000	0.323736	-0.000000	-0.000000	0.000000	0.510675	0.000000	0.000000	-0.000000	-0.056553	-0.000000	0.000000

Eigenvalues (cm⁻¹) and eigenvectors (modulus square)

	-8.00	-7.00	-6.00	-5.00	-4.00	-3.00	-2.00	-1.00	0.00	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
0.000000	0.000000	0.686591	0.000000	0.000000	0.000000	0.311881	0.000000	0.000000	0.000000	0.001042	0.000000	0.000000	0.000000	0.000486	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000486	0.000000	0.000000	0.000000	0.001042	0.000000	0.000000	0.000000	0.311881	0.000000	0.000000	0.000000	0.686591	0.000000
11.255613	0.000000	0.000000	0.352749	0.000000	0.000000	0.000000	0.147251	0.000000	0.000000	0.000000	0.147251	0.000000	0.000000	0.000000	0.352749	0.000000	0.000000
19.197764	0.000000	0.000000	0.373476	0.000000	0.000000	0.000000	0.126524	0.000000	0.000000	0.000000	0.126524	0.000000	0.000000	0.000000	0.373476	0.000000	0.000000
60.705255	0.201139	0.000000	0.000000	0.000000	0.268229	0.000000	0.000000	0.000000	0.061266	0.000000	0.000000	0.000000	0.268229	0.000000	0.000000	0.000000	0.201139
71.349065	0.238247	0.000000	0.000000	0.000000	0.261753	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.261753	0.000000	0.000000	0.000000	0.238247
77.076016	0.000000	0.000000	0.000000	0.750763	0.000000	0.000000	0.000000	0.247631	0.000000	0.000000	0.000000	0.000014	0.000000	0.000000	0.000000	0.001592	0.000000
77.076016	0.000000	0.001592	0.000000	0.000000	0.000000	0.000014	0.000000	0.000000	0.000000	0.247631	0.000000	0.000000	0.000000	0.750763	0.000000	0.000000	0.000000
214.949594	0.159587	0.000000	0.000000	0.000000	0.024316	0.000000	0.000000	0.000000	0.632194	0.000000	0.000000	0.000000	0.024316	0.000000	0.000000	0.000000	0.159587
271.221415	0.261753	0.000000	0.000000	0.000000	0.238247	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.238247	0.000000	0.000000	0.000000	0.261753
274.041991	0.000000	0.000000	0.000000	0.201370	0.000000	0.000000	0.000000	0.581169	0.000000	0.000000	0.000000	0.143094	0.000000	0.000000	0.000000	0.074368	0.000000
274.041991	0.000000	0.074368	0.000000	0.000000	0.000000	0.143094	0.000000	0.000000	0.000000	0.581169	0.000000	0.000000	0.000000	0.201370	0.000000	0.000000	0.000000
283.277708	0.000000	0.000000	0.147251	0.000000	0.000000	0.000000	0.352749	0.000000	0.000000	0.000000	0.352749	0.000000	0.000000	0.000000	0.147251	0.000000	0.000000
291.044315	0.000000	0.237449	0.000000	0.000000	0.000000	0.545010	0.000000	0.000000	0.000000	0.170159	0.000000	0.000000	0.000000	0.047381	0.000000	0.000000	0.000000
291.044315	0.000000	0.000000	0.000000	0.047381	0.000000	0.000000	0.000000	0.170159	0.000000	0.000000	0.000000	0.545010	0.000000	0.000000	0.000000	0.237449	0.000000
297.817674	0.139274	0.000000	0.000000	0.000000	0.207456	0.000000	0.000000	0.000000	0.306540	0.000000	0.000000	0.000000	0.207456	0.000000	0.000000	0.000000	0.139274
304.397378	0.000000	0.000000	0.126524	0.000000	0.000000	0.000000	0.373476	0.000000	0.000000	0.000000	0.373476	0.000000	0.000000	0.000000	0.126524	0.000000	0.000000

sus.out

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** output file generated by SIMPRE version 1.1 **
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Magnetic susceptibility from 2.000 K to 300.000 K , number of points: 25,
at a magnetic field equal to 0.100 T

T (K)	XzT (emuK/mol)	XxT (emuK/mol)	XyT (emuK/mol)	XavT (emuK/mol)
2.00	18.955733	1.316741	1.316741	7.196405
2.46	19.076473	1.620717	1.620717	7.439302
3.04	19.144374	1.990367	1.990367	7.708369
3.74	19.161943	2.432303	2.432303	8.008849
4.61	19.128331	2.946601	2.946601	8.340511
5.68	19.045000	3.523915	3.523915	8.697610
7.00	18.918390	4.145715	4.145715	9.069940
8.62	18.759376	4.789199	4.789199	9.445925
10.63	18.581103	5.435347	5.435347	9.817266
13.09	18.396426	6.075424	6.075424	10.182424
16.13	18.215369	6.711116	6.711116	10.545867
19.88	18.043345	7.347429	7.347430	10.912735
24.49	17.881396	7.982776	7.982776	11.282316
30.18	17.729112	8.603590	8.603590	11.645430
37.19	17.588419	9.188248	9.188248	11.988305
45.82	17.464479	9.717944	9.717944	12.300122
56.46	17.361256	10.186590	10.186590	12.578146
69.57	17.274018	10.603268	10.603268	12.826851
85.72	17.185100	10.986455	10.986455	13.052670
105.63	17.068476	11.353900	11.353900	13.258759
130.15	16.902061	11.713934	11.713934	13.443310
160.37	16.679318	12.063114	12.063114	13.601848
197.60	16.411622	12.390705	12.390705	13.731011
243.47	16.121081	12.685677	12.685677	13.830811
300.00	15.830666	12.941380	12.941380	13.904476

mag.out

```
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** output file generated by SIMPRE version 1.1 **
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```
*****
```

Magnetization at 2.000 K until 5.000 T with a step of: 0.250 T,
with an integration angle of 1.4754

H (T)	Mz (bm)	Mx (bm)	My (bm)	Mav(bm)
0.0000	0.008648	0.000590	0.000590	0.002986
0.2500	3.874290	0.294986	0.294986	1.413101
0.5000	6.001448	0.587175	0.587175	2.465570
0.7500	6.811746	0.875030	0.875030	3.157458
1.0000	7.077595	1.156548	1.156548	3.623112
1.2500	7.162470	1.430015	1.430015	3.963514
1.5000	7.191563	1.693611	1.693611	4.233418
1.7500	7.203675	1.946278	1.946278	4.460310
2.0000	7.210334	2.186941	2.186941	4.658530
2.2500	7.215649	2.415005	2.415005	4.835540
2.5000	7.220477	2.629926	2.629926	4.995930
2.7500	7.226344	2.832038	2.832038	5.142631
3.0000	7.230727	3.021478	3.021478	5.277348
3.2500	7.233305	3.198434	3.198434	5.401804
3.5000	7.237836	3.363568	3.363568	5.516760
3.7500	7.242344	3.518224	3.518224	5.623717
4.0000	7.248820	3.661059	3.661059	5.723251
4.2500	7.253710	3.795067	3.795067	5.816167
4.5000	7.255739	3.920576	3.920576	5.902834
4.7500	7.260164	4.037972	4.037972	5.984287
5.0000	7.266569	4.146565	4.146565	6.060429

3.6 Example 3: Diphenylbis(pyrazolborate) complex of a user-defined atom

This example illustrates the use of the *user-defined* ion. Notice the three mandatory lines after the coordinate list.

simpre.par

```

PARAMETER (idtot= 17)! dimension of full energy matrix
c
PARAMETER (iuni=1) ! units (1=K, 2=meV, 3=cm-1)
c
PARAMETER (icoo=2) ! spherical coordinates=1, cartesian coordinates=2
c
PARAMETER (ishi=1) ! use of Sternheimer shielding parameters [1(yes)/0(no)]
c
PARAMETER (irot=0) ! rotation for a compact ground-state wave function [1(yes)/0(no)]
c
PARAMETER (isus=0) ! magnetic susceptibility calculation [1(yes)/0(no)]
c
PARAMETER (imag=0) ! magnetization calculation [1(yes)/0(no)]
c
PARAMETER (ieig=2) ! write eigenvalues
c
                        [no(0)/yes(1)/yes+eigenvectors(2)]
c
-----
c* The following parameter is defined to minimize underflow problems
PARAMETER (EPS = 1.D-12)
c
PARAMETER (ICHAR = 12)! number of charges

```

simpre.dat

1=Ce3+, 2=Pr3+, 3=Nd3+, 4=Pm3+, 5=Sm3+, 6=Tb3+, 7=Dy3+, 8=Ho3+, 9=Er3+, 10=Tm3+, 11=Yb3+, 12=user

```

12 !ion code (from 1 to 12, see above)
6 !number of effective charges
1 -0.8379900 0.5157900 -0.7168800 0.0246667
2 -0.8881000 0.4130100 0.7456400 0.0246667
3 0.8931500 0.4530000 0.6378900 0.0246667
4 0.8289000 0.4798100 -0.8321300 0.0246667
5 -0.0011300 -0.9885800 -0.6730100 0.0246667
6 -0.0022500 -0.9781800 0.7919800 0.0246667

X(III) 9 0.71757575758 !SYMBOL, 2*J, GJ
-0.00642791551 -0.00029110772 -0.00003798795 !2nd,4th and 6th order Stevens parameters
0.8300 0.0026 -0.0390 !2nd,4th and 6th order shielding parameters
2.3460 10.9060 90.5440 !2nd,4th and 6th order expected values of radius

```

simpre.out

** output file generated by SIMPRE version 1.1 **

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##...##.##.##...##.##...##.##...##.##...##.##...##
#####.#####.#####.#####.#####.#####

ion: X(III)
number of charges: 6
g: 0.718
units: K

stv 2 4 6
-0.00642792 -0.00029111 -0.00003799

<r>k 2 4 6
2.34600000 10.90600000 90.54400000

shi 2 4 6
0.83000000 0.00260000 -0.03900000

input coordinates
cartesian (A)
x y z Z
-0.8379900 0.5157900 -0.7168800 0.0246667
-0.8881000 0.4130100 0.7456400 0.0246667
0.8931500 0.4530000 0.6378900 0.0246667
0.8289000 0.4798100 -0.8321300 0.0246667
-0.0011300 -0.9885800 -0.6730100 0.0246667
-0.0022500 -0.9781800 0.7919800 0.0246667

spherical (rad)
r theta phi Z
1.2174496 2.2004162 2.5898478 0.0246667
1.2309662 0.9201064 2.7062947 0.0246667
1.1873624 1.0036436 0.4693859 0.0246667
1.2687526 2.2861238 0.5247240 0.0246667
1.1959240 2.1685090 -1.5719394 0.0246667
1.2585998 0.8902023 -1.5730965 0.0246667

Stevens Crystal Field Parameters (K)

Table with 4 columns: k, q, Akq <rk>, Bkq. It lists Stevens Crystal Field Parameters for various k and q values, including numerical values for Akq and Bkq.

Eigenvalues (K) and eigenvectors

	-4.50	-3.50	-2.50	-1.50	-0.50	0.50	1.50	2.50	3.50	4.50
0.000000	-0.022218	0.077861	-0.400821	-0.065981	-0.003519	0.014811	0.053240	-0.045523	0.196565	0.014089
	-0.033810	-0.018635	-0.795638	0.061204	0.001481	-0.021880	0.115633	0.008663	0.363670	-0.000000
0.000000	-0.007738	0.411870	0.017760	0.125874	0.010152	-0.000695	-0.014913	-0.885041	-0.027186	-0.040457
	-0.011774	-0.035449	0.042801	-0.019010	-0.024394	-0.003754	0.088753	0.101978	-0.075303	0.000000
279.145959	0.196216	0.175393	-0.087109	-0.558219	0.030353	0.090522	-0.275267	0.055419	-0.056453	0.249567
	-0.363215	-0.023435	0.200441	-0.007118	-0.006526	0.058910	0.524343	0.003256	0.083364	0.000000
279.145959	0.118619	0.100178	0.023476	0.592164	-0.008806	-0.020169	-0.259059	0.217756	0.103983	-0.412827
	-0.219575	-0.010046	-0.050307	0.007034	-0.107644	0.023603	0.494518	0.018629	-0.143176	0.000000
582.517724	-0.183831	-0.188890	-0.034632	0.048243	-0.063245	0.422689	-0.065625	-0.090902	0.003939	-0.024206
	-0.685349	0.249931	-0.063749	-0.041454	-0.158023	0.144996	-0.349640	0.131904	-0.087000	0.000000
582.517724	0.006271	-0.083009	-0.103850	-0.354704	-0.249553	-0.169013	0.027540	-0.070544	-0.192462	-0.709576
	0.023379	0.026343	0.121971	0.027198	-0.370693	-0.020147	-0.057336	-0.016934	0.247191	0.000000
858.416889	0.047289	0.653795	0.028543	-0.032383	-0.038308	0.276854	0.008060	0.265042	-0.000872	-0.110868
	-0.041785	-0.462127	-0.008626	0.023283	-0.050885	0.159595	-0.344055	-0.212647	-0.012469	0.000000
858.416889	-0.083081	-0.007603	0.339419	-0.233856	0.101791	-0.004987	-0.039683	-0.027101	0.795933	-0.063105
	0.073411	-0.009921	-0.016146	-0.252488	-0.302915	-0.063497	0.003995	0.012436	-0.086605	0.000000
1114.397935	-0.292810	0.083644	0.016138	-0.067247	0.166577	-0.748419	-0.153497	0.023531	0.022763	-0.041277
	-0.397060	-0.142917	-0.055444	-0.024945	0.233183	0.097817	-0.184369	-0.046268	-0.080085	0.000000
1114.397935	0.024498	-0.050945	0.023272	-0.239488	0.365471	0.286537	0.059989	-0.035045	0.065379	-0.493350
	0.033220	0.065852	-0.046399	-0.014112	0.660402	-0.004332	0.039317	0.045895	-0.152142	0.000000

Eigenvalues (K) and eigenvectors (modulus square)

	-4.50	-3.50	-2.50	-1.50	-0.50	0.50	1.50	2.50	3.50	4.50
0.000000	0.001637	0.006410	0.793697	0.008099	0.000015	0.000698	0.016206	0.002147	0.170894	0.000199
0.000000	0.000199	0.170894	0.002147	0.016206	0.000698	0.000015	0.008099	0.793697	0.006410	0.001637
279.145959	0.170426	0.031312	0.047765	0.311659	0.000964	0.011665	0.350707	0.003082	0.010137	0.062284
279.145959	0.062284	0.010137	0.003082	0.350707	0.011665	0.000964	0.311659	0.047765	0.031312	0.170426
582.517724	0.503497	0.098145	0.005263	0.004046	0.028971	0.199690	0.126555	0.025662	0.007585	0.000586
582.517724	0.000586	0.007585	0.025662	0.126555	0.199690	0.028971	0.004046	0.005263	0.098145	0.503497
858.416889	0.003982	0.641009	0.000889	0.001591	0.004057	0.102119	0.118439	0.115466	0.000156	0.012292
858.416889	0.012292	0.000156	0.115466	0.118439	0.102119	0.004057	0.001591	0.000889	0.641009	0.003982
1114.397935	0.243394	0.027422	0.003335	0.005144	0.082122	0.569699	0.057553	0.002694	0.006932	0.001704
1114.397935	0.001704	0.006932	0.002694	0.057553	0.569699	0.082122	0.005144	0.003335	0.027422	0.243394

4 A step beyond

4.1 Different electrostatic models

In the past century, many electrostatic models have been proposed to deal with the problem of estimating the Crystal Field parameters of lanthanoid ions, briefly reviewed by P. Porcher.¹ Being fundamentally similar, most of them are compatible with `SIMPFE`, either in its standard state or after small modifications(see below). We discuss here the differences between the most important of these models.

- the Point Charge Electrostatic Model (PCEM)² is the simplest possibility: substitute each atom in the first coordination sphere for point charges by values determined by the valence of each atom. It is a rough approximation for ionic systems such as Ln:LiYF₄ but fails in cases of less ionic bonding. To implement the classical PCEM in `SIMPFE`, the user just needs to set the control variable `ishi=0` to cancel Sternheimer's shielding parameters, while `ishi=1` includes this shielding which decreases the second order CF parameters, which generally constitutes an improvement in the quality of the results.
- The Effective Charge Model (ECM)³ allows reproducing the covalent effects by changing both the position and the magnitude of the charges, thus being similar to the REC model (see below). It also includes as effective charges all atoms in a 100 Å radius sphere. It is able to reproduce the CF parameters in many cases, being a more limited approximation in systems with a higher covalent character. ECM can be implemented by means of the user-defined atom, where the $\langle r^k \rangle$ and σ_k should be substituted accordingly to include the antishielding effect, see Table 17 in ref.⁴.
- The Simple Overlap Model (SOM)⁵ is more versatile than ECM and as a major advantage, does only need to consider the first coordination sphere. The effective charges are very similar to those in ECM, but SOM does not include free parameters. SOM can be implemented in `SIMPFE` with `ishi=0` and calculating charge and distance according to the following formulas (for details see ref. [6]): the input distance r_i is related to the crystallographic distance R_i by $r_i = R_i(1 \pm \rho_i)/2$ with $\rho_i = 0.05 \cdot (R_0/R_\mu)^{3.5}$. The input charge Z_i is related to a tabulated charge g_i by $Z_i = |g_i| \cdot \rho_i$
- The Angular Overlap Model (AOM)⁶ includes specific parameters to discriminate the angular part of the crystal field effect. Like SOM (and REC and LPEC), it allows to classify the ligands in terms of their relative covalence, and allows an interpretation of the CF parameters in terms of a connection with the nature of the ligands and their coordinates. Note that in all previous to AOM the ration between the CF parameters found by the PCEM does not change. In this AOM

is similar to the LPEC model (see below). Implementing AOM in ~~SIMCFE~~ would require more elaborate changes.

- The Radial Effective Charge (REC) model the Lone Pair Effective Charge (LPEC) model are our basic tools and thus are explained with more detail beyond.

All these models are relatively easy to apply, as they only require the crystallographic positions. They are also oversimplified when compared with the whole list of interactions that one could take into account. However, they produce a reasonable order of magnitude of the CF parameters. This is of crucial importance, if we keep in mind the great number of phenomenological parameters that have to be varied for the simulation of a $4f_N$ configuration energy level scheme. Thus, these starting values are as essential for the spectroscopic simulation as atomic positions are for structure determinations.

References

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- [2] H. Bethe, *Ann. Phys.* 1929, **3**, 133
- [3] see e.g. B. R. Judd, *Operators Techniques in Atomic Spectroscopy*, McGraw-Hill, 1963
- [4] C. A. Morrison, *Lectures on Crystal Field Theory*, HDL-SR-82-2, Harry Diamond Laboratories Report, 1982
- [5] O. L. Malta, *Chem. Phys. Lett.*, 1982, **82**, 27; 1982, **88**, 353
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4.2 Effective Charge Models: REC and LPEC

The rationalizing and predictive capacity of ~~SIMCFE~~ is strongly enhanced by a wise use of effective charges that are displaced from the crystallographic position of the nuclei. Indeed, extensive testing has demonstrated that naïve use of formal charges and crystallographic coordinates rarely results in an accurate prediction of the magnetic properties due to the intrinsic limitations of the Point Charge Electrostatic Model (PCEM). If, instead, the value and displacements of the charges are allowed to be fitted as free parameters to some property, the description of the system is often realistic enough to predict other properties which have not been used in the fit. Likewise, the description of the ligands can be such that the properties of analogous compounds can be predicted. It is thus strongly recommended to use either the Radial Effective Charge (REC) or, when needed, the Lone Pair Effective Charge (LPEC) models, for a more realistic description of the interaction between the lanthanoid and the donor atoms. When high-quality spectroscopic information is available, the obtained crystal field parameters can be used as a starting point for fitting purposes.

The use of **REC** is very simple: for a complex that is coordinated by a given ligand, such as fluorine or a pyrazol-kind nitrogen (see examples 2 and 3), a set of calculations is launched with two free parameters: the effective charge

and a reduction in the effective radius. The preparation of the input and the comparison of the outputs with the experimental data can be easily done by hand, or with the aid of an external program, or an improved version of `...SIMPRE` with extra loops. As usually different solutions are possible, it is best to do either a collective fit to several isostructural complexes of different lanthanoids, or use spectroscopic data instead of a χT curve, or both.

Of course, this strategy is time-consuming and can even be impractical when dealing with heteroleptic complexes, where the number of free parameters is higher. Fortunately, there is a growing body of parameterized ligands, with the final goal of building a **general library**, as explained below. In simple cases (homoleptic or with abundance of experimental information), reusing published parameters can serve to check their validity, and in complex cases (heteroleptic and/or limited experimental information) it is arguably the best way to reduce or eliminate the overparameterization problem.

The use of **LPEC** is very similar to the use of **REC**, but additionally it requires the determination of a unit vector pointing in the direction of the lone pair, usually using chemical arguments and simple geometry. In the case of the phthalocyaninato nitrogens, this can be done by taking into account the planarity of the ligand and the sp^2 character of the lone pair, which displays angles close to 120° with the other two sp^2 orbitals that form the N-C bonds. In a way, it is reminiscent of the Angular Overlap Model -a more chemical approach- which discriminates the angular part of the crystal field (see section 4.1).

4.2.1 Library of ligands

The effective point charge model used by `...SIMPRE` can be seen as part of a rediscovery, in a new context, of the Crystal Field Theory of the 1960s by the molecular magnetism community. However, what made tools like the Angular Overlap Model powerful was the availability of consistent parameters describing the influence of a given ligand on the electronic structure of the central ion. This was achieved by measuring the optical properties of large series of complexes, and distilling optimal parameter values from the observed level splittings. Thus, we need a similar work to be done with `...SIMPRE`, so that a **general library of ligands** can be established which parameterizes the most common ligands in terms of the Radial Effective Charge (REC) or Lone Pair Effective Charge (LPEC) models. This work has already started, and the results are very encouraging for a simple and inexpensive estimate of the magnetic properties and ground state wave-function. Of course, the availability of sophisticated experimental information is needed a proper understanding of the full set of energy levels and wavefunctions.

At the time of this writing, the provisional parameterization of following ligands has been published (D_h, D_r in \AA , Z in electron charges, note that the influence of the different Coordination Index (CI) has not yet been established):

Save time and improve your results building upon previous knowledge!

- fluoride, CI = 6: $D_r \simeq 1.03$, $Z \simeq 0.20$
- chloride, CI = 6: $D_r \simeq 1.00$, $Z \simeq 0.26$

- bromide, CI = 6: $D_r \simeq 0.90$, $Z \simeq 0.45$
- pyrazolyl nitrogens, CI = 6-9: $1.3 \leq D_r \leq 1.5$, $0.015 \leq Z \leq 0.03$

Moreover, the following ligands are currently under study and their provisional parameters might be available by request:

- aromatic carbon ring
- vacant polyoxotungstate
- amine oxide
- (dialkylphosphito-P)cobaltate

4.3 Community

Sign up for the email list: be up-to-date and increase the visibility of your latest results!

The ambitious goal of the general library of ligands can only be achieved by means of a community work, where different groups extract these parameters from the highest quality data available and then check their validity in analogous compounds. An email list is maintained by the authors to facilitate the communication within the user community. This allows users to share their (published) results and be updated on both experimental data and theoretical advances. These progressively build up a general library of ligands, thus making *SIMPRE* an increasingly powerful tool. This email list is also used to keep the community up-to-date on new versions and patches of the program as soon as they are available.

4.4 Extensions and patches

As the source code of *SIMPRE* is distributed, it is possible for users to adapt it to their own needs. Additionally, the authors are still working on their own improvements and will distribute extended or patched codes by request, as soon as they are usable. Among the problems that may be solved with extra subroutines or small modifications that are currently work-in-progress are:

- automatic determination of the easy axis of magnetization
- obtaining the angular dependence of the magnetic susceptibility
- considering the hyperfine coupling to the nuclear spin
- automatic fitting of the REC or LPEC parameters to available χT vs T or spectroscopic data
- plotting the magnetic field dependence of the energy levels

4.5 Bibliography

The following works rely on `..SIMPRE` and contain results that can be useful for the `..SIMPRE` community:

Reference	Summary
J. Comput. Chem. 2013, 34, 1961	Program is presented.
Inorg. Chem. 2012, 51, 12565	Theoretical background is given. <code>..SIMPRE</code> is applied for magnetostructural studies.
Dalton Trans., 2012, 41, 13705	REC and LPEC models are introduced. Parameterization of fluoride, chloride, bromide, phthalocyaninato ligands.
Chem. Sci., 2013, 4, 938	Uranium is introduced as user-defined metal. Limitations for actinides are discussed. Parameterization of pyrazole ligands.
Polyhedron, 2013, 66, 39	Library of ligands successfully applied, pyrazole ligand parameters confirmed.

5 Appendix: Operators

Explicit list of the extended Stevens operators $O_k^q(J)$ used in the *SIMPRE* code.

$$X = J \cdot (J + 1)$$

O_2^0	$= [3J_z^2 - X]$
$O_2^1 \equiv O_2^1(c)$	$= 1/4 [J_z (J_+ + J_-) + (J_+ + J_-) J_z]$
$O_2^{-1} \equiv O_2^1(s)$	$= -i/4 [J_z (J_+ - J_-) + (J_+ - J_-) J_z]$
$O_2^2 \equiv O_2^2(c)$	$= 1/2 [(J_+^2 + J_-^2)]$
$O_2^{-2} \equiv O_2^2(s)$	$= -i/2 [(J_+^2 - J_-^2)]$
O_4^0	$= [35J_z^4 - (30X - 25) J_z^2 + 3X^2 - 6X]$
$O_4^1 \equiv O_4^1(c)$	$= 1/4 [(J_+ + J_-) (7J_z^3 - (3X + 1)J_z) + (7J_z^3 - (3X + 1)J_z) (J_+ + J_-)]$
$O_4^{-1} \equiv O_4^1(s)$	$= -i/4 [(J_+ - J_-) (7J_z^3 - (3X + 1)J_z) + (7J_z^3 - (3X + 1)J_z) (J_+ - J_-)]$
$O_4^2 \equiv O_4^2(c)$	$= 1/4 [(J_+^2 + J_-^2) (7J_z^2 - X - 5) + (7J_z^2 - X - 5) (J_+^2 + J_-^2)]$
$O_4^{-2} \equiv O_4^2(s)$	$= -i/4 [(J_+^2 - J_-^2) (7J_z^2 - X - 5) + (7J_z^2 - X - 5) (J_+^2 - J_-^2)]$
$O_4^3 \equiv O_4^3(c)$	$= 1/4 [(J_+^3 + J_-^3) J_z + J_z (J_+^3 + J_-^3)]$
$O_4^{-3} \equiv O_4^3(s)$	$= -i/4 [(J_+^3 - J_-^3) J_z + J_z (J_+^3 - J_-^3)]$
$O_4^4 \equiv O_4^4(c)$	$= 1/2 [(J_+^4 + J_-^4) + (J_+^4 + J_-^4)]$
$O_4^{-4} \equiv O_4^4(s)$	$= -i/2 [(J_+^4 - J_-^4) + (J_+^4 - J_-^4)]$

$$X = J \cdot (J + 1)$$

O_6^0	$= [231J_z^6 - (315X - 735)J_z^4 + (105X^2 - 525X + 294)J_z^2 - 5X^3 + 40X^2 - 60X]$
$O_6^1 \equiv O_6^1(c)$	$= 1/4 [(J_+ + J_-) (33J_z^5 - (30X - 15)J_z^3 + (5X^2 - 10X + 12)J_z) + (33J_z^5 - (30X - 15)J_z^3 + (5X^2 - 10X + 12)J_z) (J_+ + J_-)]$
$O_6^{-1} \equiv O_6^1(s)$	$= -i/4 [(J_+ - J_-) (33J_z^5 - (30X - 15)J_z^3 + (5X^2 - 10X + 12)J_z) + (33J_z^5 - (30X - 15)J_z^3 + (5X^2 - 10X + 12)J_z) (J_+ + J_-)]$
$O_6^2 \equiv O_6^2(c)$	$= 1/4 [(J_+^2 + J_-^2) (33J_z^4 - (18X + 123)J_z^2 + X^2 + 10X + 102) + (33J_z^4 - (18X + 123)J_z^2 + X^2 + 10X + 102) (J_+^2 + J_-^2)]$
$O_6^{-2} \equiv O_6^2(s)$	$= -i/4 [(J_+^2 - J_-^2) (33J_z^4 - (18X + 123)J_z^2 + X^2 + 10X + 102) + (33J_z^4 - (18X + 123)J_z^2 + X^2 + 10X + 102) (J_+^2 - J_-^2)]$
$O_6^3 \equiv O_6^3(c)$	$= 1/4 [(J_+^3 + J_-^3) (11J_z^3 - (3X + 59)J_z) + (11J_z^3 - (3X + 59)J_z) (J_+^3 + J_-^3)]$
$O_6^{-3} \equiv O_6^3(s)$	$= -i/4 [(J_+^3 - J_-^3) (11J_z^3 - (3X + 59)J_z) + (11J_z^3 - (3X + 59)J_z) (J_+^3 - J_-^3)]$
$O_6^4 \equiv O_6^4(c)$	$= 1/4 [(J_+^4 + J_-^4) (11J_z^2 - X - 38) + (11J_z^2 - X - 38) (J_+^4 + J_-^4)]$
$O_6^{-4} \equiv O_6^4(s)$	$= -i/4 [(J_+^4 - J_-^4) (11J_z^2 - X - 38) + (11J_z^2 - X - 38) (J_+^4 - J_-^4)]$
$O_6^5 \equiv O_6^5(c)$	$= 1/4 [(J_+^5 + J_-^5) J_z + J_z (J_+^5 + J_-^5)]$
$O_6^{-5} \equiv O_6^5(s)$	$= -i/4 [(J_+^5 - J_-^5) J_z + J_z (J_+^5 - J_-^5)]$
$O_6^6 \equiv O_6^6(c)$	$= 1/2 [(J_+^6 + J_-^6)]$
$O_6^{-6} \equiv O_6^6(s)$	$= -i/2 [(J_+^6 - J_-^6)]$