Effective methodology for calculation of magnetic properties of atomic systems in ordered state and around phase transition temperature

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Abstract: We present main algorithms of new software application developed to calculate magnetic, spectral and calorimetric properties of materials under Crystal Electric Field (CEF) and Mean Field Approximation paradigm. The novelty of our approach lies in the automatic construction of Hamiltonian matrices and computation of true 3-dimensional properties of the material in wide range of temperatures also around the phase transition temperature. User defined calculation rules as real or complex matrices and two calculation spaces ($|JJ_z>$ or $|LSL_zS_z>$) to define interactions, utilize single diagonalization procedure in all cases. Our software predicts thermal dependent properties of materials in isostructural series of compounds, such as: magnetic moment in ordered state, paramagnetic susceptibility, specific heat, entropy and absorption spectra. Calculated properties are closely related to local symmetry of crystal surrounding of paramagnetic ion. Obtained angular momentum coordinates of paramagnetic ions makes it possible to calculate anisotropy coefficients as a result of dynamic calculations using Mean Field Approximation scheme.

Key-Words: - Crystal Electric Field, Spin-Orbit coupling, Hamiltonian diagonalization, Mean Field Approximation, CEF, MFA, Atomic Matters

1 Introduction

Materials with special magnetic properties are of great importance to our civilization. To predict properties of some new material and to see if it satisfies given requirements we need to produce a sample (which may be expensive) or an efficient and accurate method of calculating its fine electronic structure and simulating properties we are interested in. In this paper we deal with this problem for solid compounds with localized electron states - our aim is to find and parameterize the most important interactions in atoms and ions in ligand environments and to perform fast calculations of magnetic properties that can produce reliable results. Our method is based on Crystal Electric Field (CEF) theory and makes it possible to easily transfer the influence of local charge surroundings between different ions (i.e. central ion substitution). Further details on Atomic Matters computation system are published in [1] and are available on the software web page [2], together with hundreds of examples - calculations of ions of selected materials from different areas of the periodic table. Single atomic properties calculated by Atomic Matters accurately describe properties of materials in defined temperature regions. We have calculated properties of materials in both paramagnetic and ordered states for over 100 real materials [2]. Although the static Atomic Matters calculations are surprisingly useful, they cannot provide accurate description of phase transitions. Therefore, we decided to develop software for phase-transition simulations according to the Mean Field Approximation model. In this paper we describe our model and its theoretical justification and give outlines of the algorithms used by the software.

2 Theoretical background

Our theoretical approach is based on methods dating back to [3] and further developed through the history of atomic and solid state physics; for some general introduction and references see for example [4-8].

Taking into consideration the individual population of energy levels of the fine electronic structure at different temperatures enables one to define the temperature dependencies of such properties as: free energy, magnetic entropy, magnetic susceptibility (calculated for different orientations of elementary cell in relation to the direction of magnetic field vector), p, d or f -electronic contribution to specific heat, structure of discrete electron levels and the probability of the INS (Inelastic Neutron Scattering) transitions, magnetic anisotropy, spin and orbital contribution to angular momentum of open electron subshell and many more. We use the following CEF+Spin-Orbit+Zeeman Hamiltonian:

$$\mathrm{H_J} = \mathrm{H_{CEF}} + \mathrm{H_{Zeeman}} = \sum_n \sum_m \mathrm{B}_n^m \,\hat{\mathbf{O}}_n^m(\mathrm{J},\mathrm{J_z}) + \mathrm{g_L}\,\mu_\mathrm{B}\,\mathbf{J}\cdot\mathbf{B}_\mathrm{ext} \qquad (1)$$

or

$$\mathrm{H_{LS}} = \mathrm{H_{CEF}} + \mathrm{H_{S\text{-}O}} + \mathrm{H_{Zeeman}} =$$

$$= \sum_n \sum_m \mathrm{B}_n^m \hat{\mathbf{O}}_n^m(\mathrm{L},\mathrm{L_z}) + \lambda\,\mathbf{L}\cdot\mathbf{S} + \mu_\mathrm{B}(\mathbf{L} + \mathrm{g_e}\,\mathbf{S})\cdot\mathbf{B}_\mathrm{ext} \qquad (2)$$

$\mathrm{B}^m{}_n$ denotes CEF parameters, $\mathbf{O}^m{}_n$ are Stevens operators, λ-is the spin–orbit constant, and $\mathrm{g_L}$ and $\mathrm{g_e} \approx 2.002319$ are the gyromagnetic factors, μ_B is the Bohr magneton and $\mathbf{B}_\mathrm{ext}$ is the external magnetic field.

According to Mean Field Approximation (MFA) methodology, magnetic phase transitions of ionic/atomic systems according to dynamic calculations of the molecular field $\mathbf{B}_\mathrm{mol}$, is simply defined as:

$$\mathbf{B}_\mathrm{mol}(\mathrm{T}) = n_\mathrm{mol}\,\mathbf{m}(\mathrm{T}) \qquad (3)$$

Such self-consistent calculations can only be performed after establishing the molecular field factor n_mol that is closely related to the temperature of phase transitions, $\mathrm{T_C}$.

For calculating properties in temperatures in ordered state and around the magnetic phase transition point, a self-consistent methodology for molecular field calculation called Mean Field Approximations (MFA) is applied. The idea behind this method is to estimate the direction and value of the magnetic field (molecular field) generated by ions at a defined temperature, and to calculate the influence of this magnetic field for electronic state structures of ions. In a selected calculation space, according to equation (1) we define a molecular field as an expected value of the total moment of the electronic subshell multiplied by the molecular field, inter ionic exchange factor n_mol:

$$\mathbf{B}_\mathrm{mol} = -n_\mathrm{mol}\,\mathrm{g_L}\,\mu_B < \mathbf{J} > \qquad (4)$$

or

$$\mathbf{B}_\mathrm{mol} = -n_\mathrm{mol}\,\mu_B < \mathbf{L} + \mathrm{g_e}\mathbf{S} > \qquad (5)$$

The formal expression of the full Hamiltonian used by Atomic Matters MFA computation system, according to the chosen calculation space: $|\mathrm{JJ_z}>$ or $|\mathrm{LSL_zS_z}>$ respectively, has the form:

$$\mathrm{H_{J\,mol}} = \mathrm{H_J} + \mathrm{H_{mol}} = +\sum_n \sum_m \mathrm{B}_n^m \,\hat{\mathbf{O}}_n^m(\mathrm{J},\mathrm{J_z}) +$$

$$+ n_\mathrm{mol}\,\mathrm{g_L^2}\,\mu_B^2\left(-\mathbf{J} < \mathbf{J} > + \frac{1}{2} < \mathbf{J} >^2\right) + \mathrm{g_L}\,\mu_B\,\mathbf{J}\cdot\mathbf{B}_\mathrm{ext} \qquad (6)$$

or

$$\mathrm{H_{LS\,mol}} = \sum_n \sum_m \mathrm{B}_n^m \hat{\mathbf{O}}_n^m(\mathrm{L},\mathrm{L_z}) + \lambda\mathbf{L}\cdot\mathbf{S} +$$

$$+ n_\mathrm{mol}\,\mu_B^2\left(-(\mathbf{L} + \mathrm{g_e}\mathbf{S}) < \mathbf{L} + \mathrm{g_e}\mathbf{S} > + \frac{1}{2} < \mathbf{L} + \mathrm{g_e}\mathbf{S} >^2\right) +$$

$$+ \mu_B(\mathbf{L} + \mathrm{g_e}\mathbf{S})\cdot\mathbf{B}_\mathrm{ext} \qquad (7)$$

The eigenvectors of the Hamiltonian are described according to the selected base of calculations by the total momentum quantum numbers $|\mathrm{JJ_z}>$ or spin and orbit quantum numbers $|\mathrm{LSL_zS_z}>$. Calculated eigenvectors and expected values define spin and orbital magnetic moments of paramagnetic ions. Using the commutation relations of the angular momentum operators, we obtain information about expected values of the projections of magnetic momentum of all electronic states [4,5,7,9].

Taking into consideration the possibility of the thermal population of states we automatically obtain thermal evolution of the single ion properties of the compound. This technique is based on the equivalent operator theory [4] defined as the CEF widened by thermodynamic and analytical calculations defined as the supplement of the CEF theory by including thermodynamic and analytical calculations.

At a temperature of T = 0 K, only the ground state is occupied. In this situation, the magnetic moment of the ion is exactly equal to the momentum of the ground state. At extremely low temperatures, it is possible to excite the system e.g. by magnetic interaction with low-energy neutrons (which is used in Inelastic Neutron Scattering Spectroscopy, INS). It should be remembered, however, that the observed transitions are excitations from the ground state.

When the temperature rises, the probability of occupying higher states increases according to the Boltzmann statistics. The number of ions with the energy E_i within a system at temperature T, is:

$$\mathrm{N}_i(\mathrm{T}) = \mathrm{N}_0\beta_i(T), \text{ where } \beta_i(T) = \frac{\exp\left(-\dfrac{\mathrm{E}_i(\mathrm{T})}{\mathrm{k_B T}}\right)}{\mathrm{Z(T)}} \qquad (8)$$

$$Z(T) = \sum_i \exp\left(-\frac{E_i(T)}{k_B T}\right) \qquad (9)$$

In the above expression, N denotes the total number of particles, and Z is the statistical sum of states (partition function). Knowing the statistical sum of the states, we can determine the Helmholtz free energy F(T):

$$F(T) = -k_B T \ln Z(T) \qquad (10)$$

The fine structure of states (E_i, Γ_i) allows determining the thermodynamic functions for the statistical group of N ions. The most sensible value for is $N_0 \approx 6.022.1023\ \mathrm{mol}^{-1}$ (Avogadro constant).

In our methodology, calculating the magnetization amounts to summing the identically behaving magnetic moments of individual ions with an unclosed electron shell. Due to the fact that the open subshell ions are in the self-aligned molecular field, their magnetic moment changes with temperature. Bearing in mind that each eigenstate of the CEF Hamiltonian is related to its magnetic moment, the total moment of a strongly correlated electron system at a given temperature is the resultant moment of occupied states calculated with the inclusion of the Boltzmann weight:

$$m_J^{\alpha}(T) = \frac{g_L \mu_B}{Z(T)} \sum_i < J_{\alpha}^{i} > \exp\left(-\frac{E_i(T)}{k_B T}\right) \qquad (11)$$

$$m_{LS}^{\alpha}(T) = \frac{\mu_B}{Z(T)} \sum_i < L_{\alpha}^{i} + g_e S_{\alpha}^{i} > \exp\left(-\frac{E_i(T)}{k_B T}\right) \qquad (12)$$

Where: α indexes directional components, *i* numbers the Hamiltonian eigenstates, while Γ_i represents the expected value of the total angular momentum along the α-axis in the *i*-th state. This approach provides a clear way to determine the components of the total magnetic moment of paramagnetic ions. The total magnetic moment of the ion consists of the orbital and spin parts: $\mathbf{m}=\mathbf{m}_L+\mathbf{m}_S$.

According to thermodynamic principles, the contribution of localized electrons to the total specific heat of materials can be calculated by numerical derivation of Helmholtz free energy:

$$c_{mol}(T) = -T\left(\frac{\partial^2 F(T)}{\partial T^2}\right) \qquad (13)$$

This makes it possible to calculate entropy according to the well-known definition:

$$S(T) = S(0) + \int_0^T \frac{c(T)}{T} dT \qquad (14)$$

The value of electronic entropy for a defined temperature is difficult to compare, but the isothermal change of the entropy of the system at a given temperature is a very important material parameter that describes its thermomagnetic properties. Isothermal Entropy change $-\Delta S(T, B_{ext})$, captured for different temperatures under the influence of different magnetic fields, is one the most important properties of a material that describes its usefulness as a magnetocaloric material. The value $\Delta S(T, B_{ext})$, extracted from experimental specific heat measurements, is often presented as a basic description of the Magnetocaloric Effect (MCE) of a material [10].

Atomic Matters MFA also provides single-ionic magnetocrystalline anisotropy prediction including full calculations (without Brillouin functions approximation) of magnetocrystalline constants $K_i(T)$ for defined range of temperature according to relations given in [11]:

$$\begin{aligned}
K_1(T) &= \frac{3}{2} B_2^0 \left(\langle \hat{\mathbf{O}}_2^0 \rangle_T - \langle \hat{\mathbf{O}}_2^2 \rangle_T\right) - 5 B_4^0 \left(\langle \hat{\mathbf{O}}_4^0 \rangle_T - 3\langle \hat{\mathbf{O}}_4^2 \rangle_T\right) - \\
&\quad - \frac{21}{2} B_6^0 \left(\langle \hat{\mathbf{O}}_6^0 \rangle_T - 5\langle \hat{\mathbf{O}}_6^2 \rangle_T\right), \\
K_2(T) &= \frac{35}{8} B_4^0 \left(\langle \hat{\mathbf{O}}_4^0 \rangle_T - 4\langle \hat{\mathbf{O}}_4^2 \rangle_T + \langle \hat{\mathbf{O}}_4^4 \rangle_T\right) + \\
&\quad + \frac{63}{8} B_6^0 \left(\langle \hat{\mathbf{O}}_6^0 \rangle_T - 20\langle \hat{\mathbf{O}}_6^2 \rangle_T + 5\langle \hat{\mathbf{O}}_6^4 \rangle_T\right), \\
K_2^*(T) &= \frac{1}{8} \left(B_4^0 \langle \hat{\mathbf{O}}_4^0 \rangle_T + 5 B_6^4 \langle \hat{\mathbf{O}}_6^4 \rangle_T\right), \\
K_3(T) &= -\frac{231}{16} B_6^0 \langle \hat{\mathbf{O}}_6^0 \rangle_T, \quad K_3^*(T) = -\frac{11}{16} B_6^4 \langle \hat{\mathbf{O}}_6^4 \rangle_T. \qquad (15)
\end{aligned}$$

where: $\langle \hat{\mathbf{O}}_n^m \rangle_T$ denotes of thermal expected values of Stevens operators.

More details about calculation methods of our theoretical approach are available on Atomic Matters website [2].

3 Algorithms

Following the approach presented in previous chapter, we conclude that it is possible calculate magnetic properties of a material, provided that simulation software is capable of doing the following:

- define crystal-electric field of the ion (CEF parameters) and all considered interactions (spin-orbit coupling, magnetic field)
- generate and diagonalize the resulting Hamiltonian matrix
- calculate properties of the material

The first task is widely covered in [1] so now we present a general outline of our algorithm for Hamiltonian matrix generation and diagonalization.

Main algorithm.

Input: ion (eg. Sm^{3+}), calculation base ($|LSL_zS_z>$ or $|JJ_z>$), calculation field (real or complex), crystal-field parameters A^m_n, magnetic field B, spin-orbit coefficient λ (only for the $|LSL_zS_z>$ base)

Output: eigenvalues and eigenvectors of the Hamiltonian matrix given by (1) or (2)

Algorithm:

1. obtain the electronic configuration and ionic radii of the ion
2. calculate Stevens factors θ_n for the electronic configuration
3. construct (real part of) Stevens (O^m_n) and magnetic field (**(L+g$_e$S)·B** or **J·B**) operators matrices
4. if calculation base is $|LSL_zS_z>$ construct the spin-orbit (**L·S**) interaction matrix
5. if calculation field is complex, construct imaginary part of the Stevens and magnetic field operators matrices
6. if calculation field is complex, transform real matrices constructed in steps 3-5 to complex matrices
7. multiply constructed matrices with appropriate coefficients (θ_n , $<r^n>$, A^m_n , λ) and add them together to form the Hamiltonian matrix
8. diagonalize the Hamiltonian matrix using Jacobi method to determine its eigenvalues and eigenvectors
9. if calculation field is complex, transform 2n eigenvalues and 2n eigenvectors obtained in step 8 to n real eigenvalues and n (possibly complex) eigenvectors

We now summarize specific methods used to perform calculations in Main algorithm and justify them according to our theoretical model.

Stevens factors calculation (step 2 in Main algorithm).

As seen from our general formula for the Hamiltonian (1) or (2), we use the A^m_n Stevens parameters to express the crystal-field interaction - as they are the most general and ion-independent and thus allow for easy transfer of crystalline structure between different ions. But to make the transfer possible and to actually construct the Hamiltonian matrix, we also need to calculate the Stevens factors θ_n and the values of $<r^n>$ for n=2,4,6. The averages of shell radii powers $<r^n>$ can be found in the literature (unfortunately, mainly for the 3d transition metal ions and the trivalent ions of the 4f group) – they are generally calculated using the Hartree-Fock methodology and we include a list of known values with references taken from [7,12] in our software. New values can be easily entered by the user and are automatically applied in future calculations. As for the values of Stevens factors however, we do not rely on the lists given in the literature, as they contain numerous errors (see for ex. [9]). On the contrary, following the methods outlined in [7], we were able to develop analytic formulas for these factors using integrals of spherical harmonics, given below:

$$\theta_n(l) = \frac{\int_{-\pi}^{\pi}\int_{0}^{\pi}\left|\Psi^l_l(\theta,\varphi)\right|^2 \sin\theta\, P^0_n(\cos\theta)\, d\theta\, d\varphi}{O^0_n(l,l)} \qquad (16)$$

$$\theta_n(J) = \frac{\theta_n(l)\ \sum_{Jz=l-N+1}^{l} O^0_n(J,Jz)}{O^0_n(J,J)} \qquad (17)$$

$$\theta_n(L) = \frac{\theta_n(l)\ \sum_{Lz=l-N+1}^{l} O^0_n(L,Lz)}{O^0_n(L,L)} \qquad (18)$$

Where O^0_n denote Stevens operator equivalents [4], P^0_n Legendre polynomials and Ψ^m_n standard spherical harmonics. Moreover *l* numbers atomic orbitals (s, p, d, f,…) and J (resp. L) is the total (resp. orbital) angular momentum quantum number of the ground J-multiplet (ground atomic LS-term) established by Hund's rules.

This way we can tabulate exact values of θ_n for all possible configurations (all possible ions) and use them in our calculations and parameter transfers. It is worth noting that using the formulas for θ_n also enables Atomic Matters to perform automatic recalculation of parameters between various CEF conventions.

Hamiltonian matrix transformations and diagonalization (steps 6, 8, 9 in Main algorithm).

To provide full 3-dimensional information associated with the considered ion, we have to deal with complex-valued operators (eg. J_y, L_y, S_y) and matrices with complex entries. This is rarely considered in literature, fortunately recent results of [13] allowed us to build efficient diagonalization method that can be applied to both real and complex symmetric matrices. For real matrices (when selected calculation field is real and calculations are limited to 2-dimensional space given by the x- and z-axis) we use standard Jacobi diagonalization procedure based on rotations (see for example [14]).

For complex matrices we need some simple preparatory steps that are based on the following paradigm: each complex entry z=a+b*i* in the complex matrix is represented by a 2x2 real (sub)matrix of the form:

a	b

-b	a

This way we obtain real (and symmetric) matrix of dimension 2nx2n as a representation of complex matrix of dimension nxn. Of course in Step 6 the real-valued parts of the Stevens, magnetic field and spin-orbit operators of Steps 3 and 4 will be transformed to entries of the form:

a	0
0	a

while imaginary parts of Step 5 will be transformed to:

0	b
-b	0

in the final 2nx2n matrix. This way we can apply modifications to the Jacobi method presented in [13,15] and obtain an algorithm performing operations on real numbers only. Main advantage of this approach is the possibility to use the same diagonalization procedure for real and complex matrices and to perform Step 9 in the algorithm by simply taking the first n of total 2n eigenvalues and their corresponding eigenvectors. This fact is of great importance as we often have to deal with eigenvalues (i.e. energy levels) of multiplicity 2 or more and we can be sure that the correct eigenvectors are selected.

We now proceed to the second algorithm - used by our Mean Field Approximation scheme found in Atomic Matters MFA software. Detailed flow chart of the whole procedure is given in Appendix 1 but here we concentrate on the part called "computation loop" in which the self-consistent mean-field calculation takes place.

MFA calculation algorithm.

Input: as in the Main algorithm; molecular field factor n_{mol}, temperature T_{max} and temperature step dT

Output: time dependency of energy levels, magnetic susceptibility, anisotropy, etc.

Algorithm:

```
1.   choose initial vector $\mathbf{B}_{mol}$ and set temperature to T=0
2.   while $T<T_{max}$ do
     2.1. run Main algorithm with $\mathbf{B}=\mathbf{B}_{ext}+\mathbf{B}_{mol}$ to calculate magnetic moment $\mathbf{m}$
     2.2. if $|\mathbf{B}_{mol} + n_{mol}\cdot\mathbf{m}| > \varepsilon$ then set $\mathbf{B}_{mol} = -n_{mol}\cdot\mathbf{m}$
          and repeat Step 2.1 else proceed to Step 2.3
     2.3. calculate energy levels, mag. susceptibility, anisotropy, etc. at temperature T
     2.4. set T=T+dT
3.   end
```

The algorithm is fairly simple and relies on running Main algorithm with input modified on every step; it is clear that magnetic field contribution is the only part of the Hamiltonian that changes in subsequent steps and this can be used to speed up calculations. Also, to avoid infinite loop in Steps 3-4 we need to set some maximum number of iterations (100 is sufficient in most cases) and some threshold value ε (we used 0.001) – both values can be adjusted in the software. The algorithm provides a self-consistent calculation method for magnetic properties of the ion in question. Properties we can calculate in Step 5 include for example: magnetic susceptibility and its inverse, (x, y and z-) directional components of magnetic moment, magnetocrystalline anisotropy coefficients, specific heat and entropy. Most properties are straightforward to calculate from their equations, for example (11), (12), (13), (14) using standard methods for numerical differentiation and integration from [14]. We present method of calculation anisotropy coefficients as it is rarely found in the literature.

Magnetocrystalline anisotropy coefficients K_i calculation.

Using formulas (15) we can simulate temperature dependence of the anisotropy coefficients K_i, provided we are able to calculate thermal expected values of Stevens operators. Following [11], these expected values are calculated as the "double" Boltzmann sum:

$$\left\langle \hat{\mathbf{O}}_n^m \right\rangle_{\mathrm{T}} = \left\langle \sum_i \beta_i(\mathrm{T})\Gamma_i(\mathrm{T}) \middle| \hat{\mathbf{O}}_n^m \middle| \sum_i \beta_i(\mathrm{T})\Gamma_i(\mathrm{T}) \right\rangle \qquad (19)$$

where $\Gamma_i(T)$ denotes the eigenfunction associated with eigenenergy $E_i(T)$ of the Hamiltonian (1) or (2) at temperature T and $\beta_i(T)$ are the Boltzmann coefficients of equation (8). Note that the values obtained this way are given in energy units (per formula unit) and need to be scaled with material-dependent factor to obtain commonly used units (like J/m^3), but relations between the $K_i(T)$ for selected ion are preserved and can be conveniently analyzed on the graph produced by our software.

4 Conclusions and future work

We presented unified approach to the simulation of magnetic properties of materials using two software tools: Atomic Matters (for calculations with ions in paramagnetic state) and Atomic Matters MFA (for dynamic time-dependent calculations in ordered/paramagnetic state that is able to simulate phase transitions). Our methods allow several previous approximations to be treated in one framework and also provide generalization that gives full 3-dimensional information for the considered material. Validity of our approach is confirmed by several experimental results [16-19] and seems unlikely that similar predictions can be easily obtained with some other methodology.

We plan developing procedures to calculate some approximate values of ionic radii $<r^n>$ or spin-orbit coefficient λ for large groups of ions (when exact values are not known). This is the only obstacle that prohibits the user from transferring crystal-field parameters (i.e. crystal structure) between materials differing only with central ion. We will try to incorporate additional parameters that apply to CEF recalculation, for example Sternheimer shielding factors [20,21]. We also consider modifying our algorithms to support compounds with two-lattice structure and two sets of crystal-field parameters, though it will require great amount of computations. The extension of our mean field approach to include changes of the crystal structure (lattice parameters) magnetostriction is also considered.

Our ultimate goal is to automate the process of finding crystal-field parameters and build (maybe using some methods of artificial intelligence) software that would be able to automatically predict the structure and parameters of materials with interesting properties needed in various applications (for example permanent magnets, materials with large magnetocrystalline anisotropy or magnetocaloric effect).

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APENDIX 1. Flow chart of Atomic Matters MFA computation.