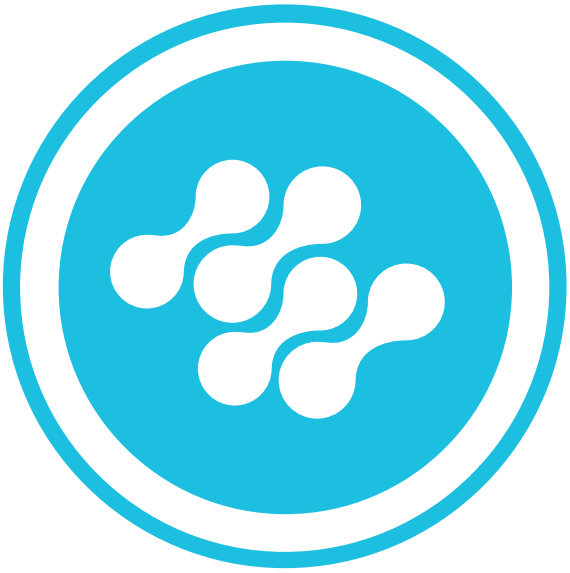

atomic matters

atomic properties and magnetism of solids

ATOMIC MATTERS is a computer application for the scientific calculation of localized electronic states and magnetic, spectroscopic and thermodynamic properties of material containing specified ions. The ATOMIC MATTERS Computation System is based on Atomic Physics and Solid State Physics.

ATOMIC MATTERS combines a package of unique tools that accurately describe the physical properties of atomic electron systems with an unclosed electron shell, under interaction with the electrostatic potential of definable symmetry and an external magnetic field. The effect of these interactions, as well as intra-atomic spin-orbit coupling, is the creation of discrete multi-electron eigenstates called Fine Electronic Structure. Taking into consideration the individual population of energy levels of the Fine Electronic Structure at different temperatures permits temperature dependencies to be defined of properties such as:

- structure of discrete electron levels E_i and the probability of transitions between them
- spin and orbital contribution to angular momentum of the electron subshell
- Helmholtz free energy F(T)
- internal energy U(T)
- magnetic entropy $S_{mag}(T)$
- magnetic susceptibility $\chi^{\alpha}(T)$
- localized-electronic contribution to specific heat $c_{Sch}(T)$
- magnetic anisotropy

ATOMIC MATTERS software, with its rich set of helpful calculation aids and result comparison tools, was designed to simplifies the prediction of properties of novel and technologically significant materials.

The application's interface is based on a system of hierarchical tabs that contain tools for managing input data and viewing results. The ability to view a variety of data from a single result in sub-grouped tabs makes comparison of the influence of different ions' charge environment on microscopic physical properties easy with just one mouse click. As well as fine electronic structure with absorption spectra simulations, sub-tabs contain easily comparable visualizations of macroscopic properties such as magnetic susceptibility $\chi^{\alpha}(T)$ (calculated for different orientations of elementary cell in relation to the direction of magnetic field vector), effective magnetic moment, localized electron specific heat $c_{Sch}(T)$, and magnetic entropy $S_{mag}(T)$.

Advanced visualization methods and comparison of results on 2D and 3D interactive plots make working with the application intuitive and productive.

MAIN ASSUMPTIONS

- Ions/atoms with an unclosed *2p, 3p, 3d, 4d, 5d, 4f,* or *5f* electronic shell have the structure of discrete electron states that affect the properties of the whole compound. Multi-electron systems $2p^n$, $3p^n$, $3d^n$, $4d^n$, $5d^n$, $4f^n$, and $5f^n$ are strongly correlated systems.
- In a solid, an atom/ion interacts with the charge environment (Stark effect). This interaction leads to the removal of the degeneracy of states and is referred to as the Crystal Electric Field (CEF). The symmetry of the local surrounding is reflected in the symmetry of the crystal-field (CEF) Hamiltonian.
- Through modifications of the fine structure of electron states of the atom, the CEF determines the properties of an atom in a solid and corresponds to the properties of the whole crystal.
- Magnetic interactions, both internal-intra ionic and with an external field, lead to further reduction in the degeneracy of states (Zeeman effect).
- A correct description of such multi-electron systems is based on atomic physics, with atomic numbers S, L, of the entire shell. This results in a space of $n=(2S+1)(2L+1)$ states.
- Spin-orbit coupling makes an important contribution to the structure of states and must be taken into account in calculations.

ATOMIC MATTERS HAMILTONIAN

Hamiltonian has the form:

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

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

or (depends on user's choice):

$$H_J = H_{CEF} + H_{Zeeman} =$$

$$= \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J, J_z) + g_L \mu_B \mathbf{J}\cdot\mathbf{B}_{ext}$$

where $\mathbf{B}^m_n$ are CEF parameters, $\mathbf{O}^m_n$ are Stevens operators, λ is the spin-orbit constant, g_L, g_e are the gyromagnetic electron factors for whole subshell and single electron respectively, μ_B is the Bohr magneton and $\mathbf{B}_{ext}$ is the external magnetic field.

Solution of Hamiltonian eigenproblem provides a structure of energy eigenstates together with related eigenfunctions expressed in the chosen base (|L,S,Lz,Sz> or |J,Jz>). Using the commutation relations of the angular momentum operators, information about expected values of the projections of magnetic momentum and its components of all electronic eigenstates are obtained. Fine electron structure is observed in a number of spectroscopic methods (Inelastic Neutron Scattering INS, EPR, ESR, IR spectroscopy, Raman scattering, etc.), so naturally ATOMIC MATTERS provides a set of tools for spectra simulations based on calculated Fine Electronic Structure.

THERMODYNAMICS

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 by, for example, magnetic interaction with low-energy neutrons (which are used in Inelastic Neutron Scattering Spectroscopy, INS). As the temperature rises, the probability of occupying higher states increases according to Boltzmann statistics.

The number of ions with the energy E_i within a system at temperature T is:

$$N_i = N_0 \frac{\exp\left(-\frac{E_i(T)}{k_B T}\right)}{Z(T)}$$

$$Z(T) = Tr\left(\exp\left(-\frac{\hat{\mathbf{H}}}{k_B T}\right)\right) = \sum_i \exp\left(-\frac{E_i(T)}{k_B T}\right)$$

In the above expression, N_0 denotes the total number of particles, and Z is the statistical sum of states. Knowing the statistical sum of the states, we can determine the Helmholtz free energy F(T):

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

where: k_B – Boltzmann constant,

which makes it possible to estimate the internal energy of the electronic system:

$$U(T) = F(T) - T\left(\frac{\partial F(T)}{\partial T}\right) = -k_B T \frac{\partial}{\partial T}\left(\frac{F(T)}{k_B T}\right)$$

According to thermodynamic principles, the localized electrons' contribution to total specific heat of a material has the Schottky formula:

$$c_{mol}(T) = \left(\frac{\partial U(T)}{\partial T}\right)_{E_i}$$

The fine structure of states (E_i, Γ_i) allows the thermodynamic functions for the statistical group of $N_0 = 6.022.1023$ mol^{-1} (Avogadro constant) ions to be determined. Taking into account the relationship between the thermodynamic functions, within the limit of low external fields, magnetic susceptibility is defined as the product of:

$$\chi^{\alpha}(T) = \frac{\partial M_{\alpha}(T)}{\partial B_{\alpha}} = \frac{k_B T}{B_{\alpha}}\left(\frac{\partial \ln Z}{\partial B_{\alpha}}\right)$$

Where a-index denotes Cartesian coordinates related to axes in the crystal lattice.

Collecting the most fundamental interactions in one Hamiltonian matrix (without perturbation methodology) allows unification of calculation methods for ions/atoms from all groups of the Periodic Table in one scientific work space. Now, applying special treatment for Strong Field, Intermediate Field and Weak Crystal Field ions can be achieved according to traditional classification. The value of the spin-orbit coupling parameter in relation to CEF parameters defines the types of interactions fully and correctly.

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