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J2suscep: Calculation of magnetic exchange coupling and temperature dependence of magnetic susceptibility

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Statement of need

The field of molecular magnetism has attracted significant interest owing to the rising need to miniaturize magnets. Advances in this field require a deep understanding of the electronic structure of magnets, and computational approaches have played a key role in pushing the limits further (Neese, 2009). A deep understanding of the magnetic properties not only helps in making magnets smaller, but has also been instrumental for reasoning about the structure of systems that are difficult to crystallise, and about intermediate states during catalytic processes (Krewald et al., 2016).

In molecular complexes, the magnetic interaction between paramagnetic centres, called the isotropic exchange interaction, has a strong influence on the magnetic properties. Within the framework of density functional theory (DFT), using what is known as the broken symmetry approach, this interaction can be quantified; the coupling strength is called the *J-value* or coupling constant (Noodleman & Case, 2009; Ruiz et al., 1999). The broken symmetry approach requires the modelling of multiple spin states using DFT but the final solution obtained can be dependent on the states modelled (Cremades, Cano, et al., 2009; Cremades, Cauchy, et al., 2009; Rajeshkumar et al., 2015; Tandon, Venkatesan, et al., 2020; Vignesh et al., 2015). To remove this dependency, more states can be modelled but this procedure results in a large number of solutions, which have to be averaged in some sensible way. Additionally, the problem of singular solutions also arises, which must be identified and removed. Until now, however, there has been no convenient way to do so.

The purpose of this package is to provide a means to accomplish this arduous task. Additionally, this package can also calculate the temperature dependence of magnetic susceptibility, thereby enabling the comparison of computational data with experiment. Although other codes like MAGPACK (Ramos et al., 2010) and PHI (Chilton et al., 2013) are available for the calculation of the magnetic susceptibility, this package provides a one-stop solution for the calculation of coupling constants and the determination of the magnetic susceptibility using these coupling constants.

J2suscep

This package essentially contains two standalone codes written in FORTRAN 2008 – `ej_calc` and `suscep`. Both codes rely only on the LAPACK library (Anderson et al., 1999). The code `ej_calc` uses the data obtained from the DFT calculations and determines the isotropic exchange coupling between paramagnetic centres. With a completely programmable Hamiltonian, this code allows the calculation of any number of J-values and is only limited by the number of states modelled. It employs the spin density approach (Paul & Misra, 2012), and spin densities obtained from any approach can be used for the calculation of J-values.

The code calculates all possible solutions based on the Hamiltonian and the states modelled, removes any singular solutions and calculates an average set of coupling constants and the standard deviations. Additionally, it also calculates the energy of the different spin states relative to each other using the coupling constants, for comparison to the original DFT data.

The `suscep` code calculates the temperature dependence of magnetic susceptibility using the coupling constants. Similar to `ej_calc`, the Hamiltonian is flexible and any number of coupling constants can be provided for the calculation of the magnetic susceptibility.

To illustrate the use of this package, we present the example of the Mn_6 complex shown in Figure 1 (a) (Tandon, Venkatesan, et al., 2020). The Mn atoms are arranged in an octahedron, resulting in each Mn being cis to 4 other Mn atoms and trans to 1 Mn atom with the Mn atoms interacting via Cl^- and phosphonate bridges. One requires 2 J-values to account for these cis- and trans- interactions between Mn centres. Modelling of 6 states for the calculation of the 2 J-values results in 60 possible solutions; using `ej_calc`, the final values were determined to be -1.28 (cis-coupling) and -3.48 cm^{-1} (trans-coupling) respectively (Tandon, Venkatesan, et al., 2020). The use of the `suscep` code calculates the temperature dependence of susceptibility which is shown in Figure 1 (b). This package has been used in a similar manner for probing the magnetic properties of a Mn_8 complex (Tandon, Soriano-López, et al., 2020).

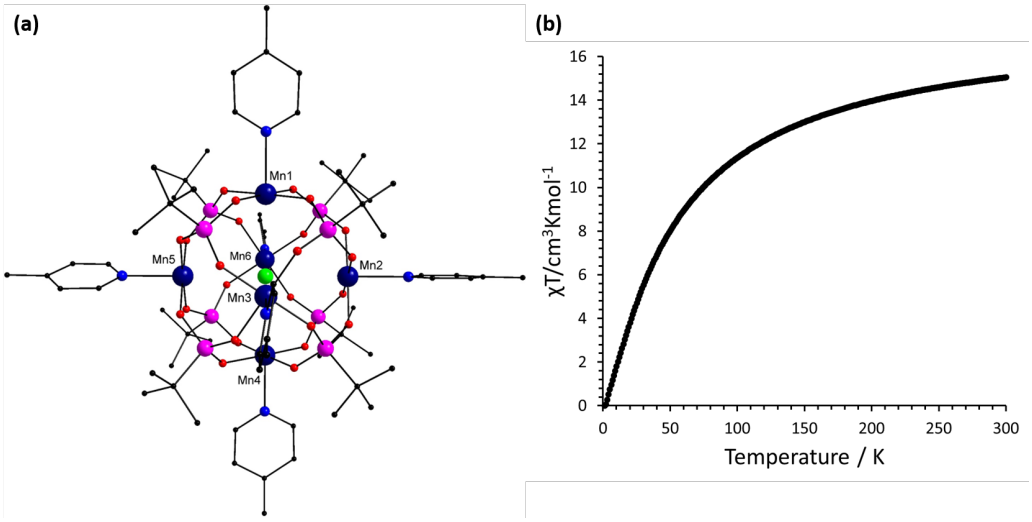

Figure 1: (a) Structure of the Mn_6 complex and (b) the temperature dependence of magnetic susceptibility obtained using the suscep code. Colour scheme: Mn (dark blue), P (pink), Cl (green), C (black), N (blue) and O (red). Hydrogen atoms have been removed for clarity.

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