Spin Hamiltonian effective parameters from periodic electronic structure calculations.

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Abstract. This paper presents and discusses a general procedure to extract spin Hamiltonian effective parameters from periodic calculations. The methodology is illustrated through representative examples of increasing complexity covering systems with three dimensional magnetic order or with a two dimensional magnetic structure. Some more complex systems are discussed where physical intuition based on the crystal structure of the system does not provide a reliable guide but where the present approach can be applied in a straightforward way.

1. Introduction
Transition metal compounds such as oxides, sulphides and halides often exhibit magnetic properties which are due to the existence of open $d$ shells. These compounds usually display a rather ionic character and the strong Madelung field induces a high degree of localization of the $d$ electrons to the point that their optical spectra can be adequately interpreted in terms of simple local molecular orbital models. A consequence of the localized character of the unfilled $d$ shells is the concomitant presence of effective magnetic moments also localized on the transition metal cations. The existence of net magnetic moments imply a particular response to applied external magnetic fields which is evidenced by experiment; for instance in the magnetic susceptibility versus temperature plots or by the magnetic dispersion of polarized neutrons. This magnetic response is the result of the interaction between the localized magnetic moments that governs the low energy spectrum, whose features are observable usually at low temperature only. The interaction between the localized magnetic moments can be adequately represented, even quantitatively, by suitable spin model Hamiltonians where the overall physics corresponding to the low energy spectrum is ascribed to the quantum mechanical interactions between the net spin angular momentum resulting from the particular electronic configuration of the transition metal compound. This is readily understood by considering some simple example such as NiO, a paradigm of strongly correlated magnetic insulators. In a simple ionic picture, which indeed is rather physically sound, each metallic site can be viewed as a Ni$^{2+}$ cation with an associated $d^8$ electronic configuration. However, because of the cubic symmetry of the ligand field, the $d$ manifold splits into $t_{2g}$ and $e_g$ levels and the resulting electronic configuration is $(t_{2g})^6 (e_g)^2$. Now, one must recall that the $e_g$ level is twofold degenerate and, hence, leading to a not simple multiplet structure as evidence by the optical spectrum which is easily interpreted in terms of $d-d$ transitions. The electronic ground state corresponding to this open shell electronic configuration can be predicted from simple arguments based on the application of the Hund’s rule: the electronic ground state is usually the one with the highest possible multiplicity. In the NiO case the local ground state has triplet multiplicity.
and $A_{2g}$ point symmetry which follows from the atomic $3^2F$ term of the Ni$^{2+}$ cation when going from the atomic spherical symmetry to the local octahedral one. The fact that Ni$^{2+}$ exhibits a triplet ground state permits one to consider that, in absence of strong external fields which could induce a change in the electronic configuration of this site, Ni$^{2+}$ can be represented as a magnetic particle with effective total spin angular momentum $S=1$ because in this case orbital angular contribution is quenched. To this point, the discussion has omitted the extended nature of bulk NiO. Taking into account periodic symmetry induces some dispersion by the interaction between the local electronic levels but one can still interpret the electronic structure in terms of $d$-like bands of $t_{2g}$ or $e_g$ character.

The low energy spectrum of effective particles with a given effective spin $S$ can be described by the corresponding quantum mechanical operator accounting for the interaction between magnetic moments. In principle, one should include all possible many body terms (two-, three-, four-,... n-body operators) thus resulting in an exceedingly complicated problem even for a model system. Nevertheless, it is expected (and observed for many magnetic systems) that two body terms will dominate and that nearest neighbour two-body interactions will exhibit the larger amplitudes. The simplest case involving isotropic two-body interaction magnetic centers is usually referred to as Heisenberg (or Heisenberg-Dirac-Van Vleck) Hamiltonian as in Eq. (1)

$$\hat{H} = -\sum_{i,j} J_{ij} \hat{S}_i \cdot \hat{S}_j = -J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j$$

where $J$ is the two-body spin amplitude, hereafter referred to as magnetic coupling constant, between $i$ and $j$ equivalent sites with $\hat{S}_i$ and $\hat{S}_j$ total effective spin operators and $<i,j>$ denotes that the summation runs over all equivalent pairs of nearest neighbor sites only -- an infinite number in a bulk solid. The minus sign here is a convention that states that negative $J$ values correspond to an antiferromagnetic interaction (state with antiparallel spins is more stable) between sites $i$ and $j$. The amplitudes of the corresponding spin operators are usually derived from experiment although quite often in a rather indirect way because hypothesis about the magnitude and sign of the dominant terms are required. In other words, a microscopic spin model is assumed and statistical mechanics is used to derive the macroscopic observable quantity which is then compared or fitted to experiment. For cases with one dominant interaction this procedure is very reliable. However, when several terms are important this procedure may even lead to a qualitative incorrect description. To avoid misleading results it is then highly desirable to come in handy unbiased and reliable estimates of the magnitude of the leading terms in the spin Hamiltonian. An interesting and appealing possibility is to make use of the powerful electronic structure methods which are nowadays available to the scientific community. The goal of the present paper is precisely to present a general procedure to extract the magnitude of the amplitudes of spin operators in a given spin Hamiltonian for extended or periodic systems. The term periodic needs to be emphasized since it makes a huge difference with respect to discrete or molecular systems. In fact, for a molecular system, the Heisenberg Hamiltonian takes a simple form because the summation in Eq. (1) runs over a finite number of pairs only. This implies that the spectrum of this Hamiltonian can be easily derived. Imagine a simple Cu dinuclear complex which can be seen as a magnetic system with two localized $S=1/2$ spins. The corresponding Heisenberg Hamiltonian has two spin eigenfunctions — a singlet (S) and a triplet (T) — with energies $+3J/4$ and $-J/4$, respectively. In this case $E(S)-E(T)=J$ and, hence, to appropriately represent the magnetic coupling between these two $S=1/2$ magnetic centers it is enough to have accurate values for the corresponding singlet and triplet electronic states. Notice that the magnetic spectrum involves excitations between the lowest possible electronic states and, hence, the singlet and triplet states defining $J$ are simply the ones with lowest energy. Using pure spin electronic ab initio configuration interaction wave functions to describe these electronic states permits one to obtain these energies with sufficient accuracy so as to quantitatively predict the magnetic coupling constant of the system. The procedure outlined above is the basis of a general mapping procedure which relies in the one-to-one correspondence between the eigenfunctions of the Heisenberg Hamiltonian and the lowest electronic states of the discrete magnetic system of interest. However, this simple mapping cannot be used when
dealing with an extended solid since, on the one hand, in a periodic approach one is constrained to write the wave function (or the electron density) by means of a single Slater determinant and, on the other hand, the eigenfunctions and eigenenergies of the Heisenberg Hamiltonian of periodic spin systems are not known, except in the case of a one-dimensional system and some simplified two dimensional magnetic arrays. The main goal of the present paper is to describe a general procedure that allows one to provide unbiased estimates of magnetic coupling constants in magnetic solids from periodic calculations. Numerical results are not included on purpose since these are known to be strongly dependent on the computational methods used. We note that agreement with experiment cannot be taken as a valid argument since this can arise from a combination of a given computational method and a wrong mapping procedure.

2. A general mapping procedure to extract magnetic coupling constants in solids from broken symmetry solutions

The main approach to the electronic structure of extended systems is based on exploiting the translational symmetry, the outcome being the well-known band structure theory. Many implementations of band theory have been developed with different level of sophistication: from the simple tight-binding models to the ab initio periodic Hartree-Fock and modern density functional theory based methods. However, a common feature of all these approaches is, as mentioned above, the use of a single Slater determinant as trial wave function or trial density. For magnetic systems, a single Slater determinant does not always permit one to have a well-defined total spin quantum number (per cell or formula unit) which indeed is an observable quantity. The practical way to circumvent the problem is to rely on the expectation energies of the single Slater determinant ferromagnetic (\(\text{FM}^\dagger\)) and several antiferromagnetic, broken symmetry, (\(\text{AFM}^\dagger\)) solutions, usually obtained by carrying out the calculations on suitable supercells. While these functions are not spin eigenfunctions and hence it is not possible to assign a well-defined value to the total spin, they are eigenfunctions of the \(z\)-component of the total spin operator and, hence, this observable is well defined and simply corresponds to the total number of alpha electrons minus the total number of beta electrons per cell which is fixed in the calculation. It is now possible to define a simplified spin Hamiltonian which, at variance of the Heisenberg Hamiltonian as in Eq. (1), does only commute with the \(z\)-component of the total spin operator. The corresponding model Hamiltonian (Eq. 2) is usually referred to as Ising Hamiltonian

\[
\hat{H}_{\text{Ising}} = -\sum_{\langle i,j \rangle} J_{ij} \hat{S}_i^z \hat{S}_j^z = -J \sum_{\langle i,j \rangle} \hat{S}_i^z \hat{S}_j^z
\]

where \(\langle i,j \rangle\) denotes that the summation runs over all equivalent pairs of nearest neighbor sites only. The eigenfunctions of the Ising Hamiltonian and the broken symmetry solutions mentioned above all have a well-defined total \(S_z\) quantum number and, hence, it is possible to establish a one-to-one correspondence between broken symmetry solutions and Ising eigenfunctions. This one-to-one correspondence permits one to use a mapping procedure similar to the one described above for non-periodic systems between the energy corresponding to suitable approximations to wave functions of low energy states with a well-defined spin and the eigenenergies of the Heisenberg Hamiltonian. However, in the case of periodic systems the mapping involves broken symmetry single determinant functions and energies and eigenenergies of the Ising Hamiltonian. In the following sections we will show how to derive these mappings for systems with increasing complexity. A point deserving further comments concerns the identity of the magnetic coupling parameters in the Heisenberg and Ising Hamiltonians, usually assumed without further proof. A rather easy way to solve the problem consists in carrying out the mapping procedure for expectation values of exact and Heisenberg Hamiltonians using the same type of trial function; for instance a broken symmetry solution written in a localized basis set. This is because for any spin-only function (not necessarily spin eigenfunctions) written in terms of localized spins (i.e. any Slater determinant such as \(\left| \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \ldots \right\rangle\), the diagonal
terms of Heisenberg and Ising Hamiltonian always coincide. This is clear when the Heisenberg Hamiltonian is written as in Eq. (3).

\[
\hat{H} = -J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j = -J \sum_{<i,j>} \left\{ \frac{1}{2} (\hat{S}_i \cdot \hat{S}_j + \hat{S}_j \cdot \hat{S}_i) + \hat{S}_z \hat{S}_z \right\}
\]

(3)

where \( \hat{S}_i \) and \( \hat{S}_j \) are the well known ladder operators for spins on site \( i \) and \( j \), respectively. \(^1,3\) From the form of the Heisenberg Hamiltonian as in Eq. (3) it immediately follows that the eigenvalues of the Ising Hamiltonian are the expectation values of the Heisenberg Hamiltonian for the same spin function. This permits one to map broken symmetry solution energies into Heisenberg expectation values or Ising eigenvalue indistinctly. The latter leads to easier expressions and is the one which we will use in the remaining of this article. Finally, we note that the above arguments are completely general and hence apply indistinctly to molecules and solids. \(^11\) The molecular cases have been described in detail in previous works and the interested reader is referred to the pertinent references. \(^12-14\) The description of how to apply to solids is the main goal of the present paper.

2.1. Simple cubic isotropic system with \( S=1/2 \)

Let us now consider a simple case, corresponding to a cubic system with equivalent magnetic centers, one unpaired electron per magnetic center in a well localized atomic orbital and such that only nearest neighbor interaction between the localized spins are relevant. This is quite a hypothetical system which is used here only to introduce the general mapping procedure. The corresponding Heisenberg and Ising Hamiltonians take the form as in Eqs (1) and (2), respectively, where the \(<i,j>\) symbol is used to indicate that only nearest neighbor interactions are included.

![Figure 1. Magnetic phases used for the simple cubic case. The conventional unit cell (one magnetic center per cell) for the FM phase and two simple double cells used to generate the AFM1 and AFM2 magnetic phases are shown in dashed lines. Notice that 3 equivalent AFM1 phases can be generated depending on the stacking of planes containing parallel spins only along \( a, b \) or \( c \) directions. These can be used to check that the magnitude of \( J \) does not depend on the direction.](image)

Note that for such a periodic system, the structural unit cell involves only one magnetic center. Therefore, to obtain the necessary broken solutions and make use of the mapping procedure described above it is necessary to use supercells. From the simple cubic system under consideration a double cell is required which allows one to obtain five different magnetic solutions (although only three of them are not related by symmetry) as in Figure 1 and to calculate the corresponding energies either through Unrestricted Hartree-Fock (UHF) or spin polarized DFT using any of the available exchange-correlation potentials. Now let us consider the spin functions (not spin eigenfunctions) corresponding to the broken symmetry solutions to derive the corresponding energies within the Ising Hamiltonian. For the \( \text{FM} = \uparrow \uparrow \) solution each localized spin moment in the double unit cell has six nearest
neighbors, but since each magnetic interaction $J$ involves by definition two magnetic centers, the energy per center is $-6J S_z^2/2$. For the AFM2 case a similar reasoning leads to a total energy of $-2J S_z^2/2$ per center. For the simplest case considered here with one localized unpaired electron per center $S_z=1/2$, therefore one has $E(\text{FM})=-3J/4$; $E(\text{AFM2})=+3J/4$; $E(\text{AFM1})=-J/4$ (4)

and

$E(\text{AFM2})-E(\text{FM})=6J S_z^2$ (5)

$E(\text{AFM1})-E(\text{FM})=2J S_z^2$ (6)

which permits one to obtain the value of the $J$ parameter provided the energies of the AFM2 and FM magnetic solutions are known. Note that one can also use the energy of the AFM1 solution and this provides an internal test of the procedure and permits one to check the consistency of the model (isotropy, other spin terms, ...). In case the $J$ value obtained from the two possible energy differences does not coincide one should revise the topology used. On the one hand, to include two body terms other than nearest neighbors and consider higher order terms and, on the other hand, check for possible anisotropies in the magnetic interactions. In the forthcoming discussion we will explicitly consider some of these cases.

2.2. Simple cubic isotropic system with $S>1/2$

The simple KNiF$_3$ and KMnF$_3$ cubic perovskites provide representative examples of cubic isotropic systems with $S=1$ and $S=5/2$, respectively. The study of these systems constitute the first attempts to use UHF periodic calculations to estimate the magnetic coupling constants. Considering nearest neighbor interactions only; which indeed is in agreement with experimental evidence, permits one to use a double cell and to obtain three solutions which are topologically identical to those discussed in the previous subsection and then

$E(\text{FM})=-3J S_z^2$; $E(\text{AFM2})=+3J S_z^2$; $E(\text{AFM1})=-J S_z^2$ (7)

and

$E(\text{AFM2})-E(\text{FM})=6J S_z^2$ (8)

$E(\text{AFM1})-E(\text{FM})=2J S_z^2$ (9)

For KNiF$_3$ and KMnF$_3$, the value of the total magnetic moment per center introduced through $S_z^2$ is 1 and 25/4, respectively. Numerical results from these equations shows that the magnetic interaction is consistently the same along $a$, $b$ or $c$ directions and no other spin terms are relevant. 11,15

2.3. Cubic system with competing exchange paths: NiO

The simple NiO antiferromagnetic provides a beautiful example of a system with two different magnetic coupling parameters: a next nearest neighbor (or NNN) dominant interaction $J_2$ along the Ni-O-Ni path involving angles with 180 degrees and a smaller nearest neighbor interaction ($J_1$) involving Ni-O-Ni bond with 90 degrees. 17 This gives rise to two antiferromagnetic subnets ferromagnetically coupled and the corresponding Heisenberg and Ising Hamiltonians are

$\hat{H} = -J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{\langle k,l \rangle_{\text{NNN}}} \mathbf{S}_k \cdot \mathbf{S}_l$ (10)

$\hat{H}^{\text{Ising}} = -J_1 \sum_{\langle i,j \rangle} \mathbf{S}_{z,i} \cdot \mathbf{S}_{z,j} - J_2 \sum_{\langle k,l \rangle_{\text{NNN}}} \mathbf{S}_{z,k} \cdot \mathbf{S}_{z,l}$ (11)

Again, a double cell is enough to obtain these two magnetic coupling constants by considering the energy of the three broken symmetry solutions depicted in Figure 2.
Now, let us work out the energy of each of these solutions according to the Ising Hamiltonian. For the FM solution one needs to count 6 interactions along \( J_2 \) and 12 interactions along \( J_1 \) per magnetic center. However, since these interactions necessarily involve pairs of magnetic centers, the total energy contribution from \( J_2 \) is \(-6J_2S_z^2/2\) and the one from \( J_1 \) is \(-12J_1S_z^2/2\) and the total energy per magnetic center of this FM solution is \((-3J_2-6J_1)S_z^2/2\). In a similar way, for the totally antiferromagnetic AFM2 phase each magnetic center interacts again with 6 other centers with antiparallel spin through \( J_2 \) and with 12 through \( J_1 \), half parallel and half antiparallel leading to a \( 0J_1S_z^2/2 \) contribution. Similarly, for AFM1 phase each magnetic center interacts again with 6 other centers with parallel spin through \( J_2 \) and with 12 through \( J_1 \), 4 parallel and 8 antiparallel, leading to a \((-6J_2-4J_1)S_z^2/2\) energy per Ni atom.

To summarize, for NiO (for which \( S_z^2=1 \))
\[
E_{(FM)}=-6J_2-3J_2; \quad E_{(AFM1)}=2J_2-3J_2; \quad E_{(AFM2)}=3J_2
\]
and
\[
E_{(AFM1)}-E_{(FM)}=8J_1; \quad E_{(AFM2)}-E_{(FM)}=6J_1+6J_2
\]
which shows how to obtain the two relevant magnetic coupling constants from the energies of the pertinent broken symmetry solutions.\(^{18}\) Note, that for MnO the corresponding equations, similar to Eqs. (12) and (13), can be easily derived by simply considering that \( S_z=5/2.\)

2.4. Two dimensional systems with S=1/2: \( \text{La}_2\text{CuO}_4 \) and lamellar cuprates

These correspond to a broad family of well-known high critical temperature superconductor parent compounds. The common feature of these compound is the existence of \( \text{CuO}_2 \) planes where each \( \text{Cu}^{2+} \) cation bears a \( S=1/2 \) magnetic moment and interacts with 4 nearest neighbors through \( J_1 \) and 4 second neighbors through \( J_2 \).

In principle it is possible to add the interaction between \( \text{Cu}^{2+} \) cations on different planes \( (J_3) \) and four-body and higher order terms.\(^{20}\) In this example we will assume that only \( J_1 \) and \( J_2 \) are important, handling the four body terms is more involved and has been discussed at length recently.\(^{21}\) Considering a double unit cell as in Figure 3, three broken symmetry solutions are enough to extract \( J_1 \) and \( J_2 \). For the FM solution the total energy per magnetic center through the \( J_1 \) magnetic path is simply \(-4J_1S_z^2/2 \) or \(-J_1/2 \) and that through \( J_2 \) is \(-4J_2S_z^2/2 \) or \(-J_2/2 \). For the AFM it is enough to realize that nearest neighbor interactions \( (J_1) \) now involve antiparallel spins and hence account for \(+4J_1S_z^2/2 \) or \(+J_1/2 \) whereas those through \( J_2 \) are as in the FM solution. The same reasoning is used for AFM1 and AFM2 phases to derive the energies per formula unit as in Eqs. 14 and 15,
\[
E_{(FM)}=(-J_1-J_2)J_2/2; \quad E_{(AFM)}=(+J_1-J_2)/2; \quad E_{(AFM1)}=0
\]
and hence
\[
E_{(AFM)}-E_{(FM)}=J_1; \quad E_{(AFM1)}-E_{(FM)}=J_1/2+J_2/2;
\]
\[
E_{(AFM2)}-E_{(FM)}=J_1/2+J_2
\]
Notice that the lack of numerical consistency of these equations has been recently used to estimate the magnitude of four-body terms in cuprates.\cite{20,21}

2.5. Difficult cases without symmetry and several competing interactions

The cases discussed above correspond to highly symmetric systems where the magnitude of the magnetic coupling can be inferred by means of the Anderson-Kanamori-Goodenough rules which provide a qualitative model to rationalize the sign and magnitude of exchange interactions in terms of the interaction between electronic open shells (or magnetic orbitals) of a pair of magnetic ions and the bridging ligands in the particular structure. There are, however, cases where symmetry is much lower and where the magnetic structure can wear little resemblance to main features of the crystal structure. This is the case of magnetic systems with spin chains, ladders and other low dimensional magnetic structures. Unbiased prediction of the most important magnetic interaction becomes crucial and first principles periodic calculations become extraordinarily important. The general procedure involves defining a sufficiently large supercell to generate a large enough set of broken symmetry magnetic solutions. After identifying all possible magnetic interaction by the distance to a reference center ($J_1$, $J_2$, $J_3$ and so on) one can deduce the total energy of each magnetic solution within the Ising Hamiltonian by counting the contribution per unique magnetic center included in the (super)cell of each of the $J_i$ interaction which is simply $-(n-m)J_iS_z^2/2$ where $n$ stands for the number of interactions through $J_i$ involving $n$ parallel spins and $m$ is the equivalent for interactions involving antiparallel spins. The number of contributions for each $J_i$ must be added and the procedure repeated for all unique centers in the cell. This procedure needs to be repeated for each broken symmetry solution and the different energies normalized to a given formula unit. Taking appropriate energy differences allows one to define a large set of equations which should permit to obtain the desired set of magnetic coupling parameters. It is important to verify that some of the $J_i$ parameters included in the treatment are really small meaning that the dominant interactions have been identified and predicted. Otherwise, it is necessary to enlarge the unit cell and to repeat the procedure until a consistent set of parameters has been obtained. CuF$_2$ is a paradigmatic example of a complex magnetic system. Periodic UHF calculations by Reinhardt et al.\cite{22} have included $J$ values up to $J_6$ but results show that only $J_1$, $J_2$ and $J_3$ are significant. Moreover, this permitted to unambiguously show that this system with complex crystal structure exhibits a quasi two dimensional magnetic structure.

3. Concluding remarks

Periodic calculations provide an excellent tool to investigate the magnetic structure of many relevant systems and provide an unbiased and independent way to estimate the magnitude of the leading terms in the spin Hamiltonian. The procedure to follow is general and makes use of the various broken symmetry solutions that can be obtained within suitable periodic supercells. The procedure permits one to perform self-consistency checks so that the final form of the spin Hamiltonian and the amplitudes of the corresponding parameters can be determined without making use of previous
hypothesis. The procedure illustrated in this article provides the proper mapping to extract the amplitude of magnetic coupling constants in spin Hamiltonians and has been previously applied to a broad variety of systems.\cite{23,26} The quality of the predicted values depends solely on the computational method chosen to compute the energy of the different broken symmetry solutions. Generally, results obtained from UHF calculations provide qualitative estimates only whereas those arising from hybrid density functional calculations exhibit accuracy comparable to available experimental data. We close this section by recalling that numerical results are, however, strongly dependent on the choice of the exchange correlation functional\cite{10} and that appropriate predictions often require validation of the DFT method used by proper comparison to experiment for similar systems.

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