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REGULAR ARTICLE

How to compute the magneto-electric tensor from ab-initio calculations?

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Abstract This paper shows how to properly combine different ab-initio methods to determine the magneto-electric tensors. To reach this goal it proposes a thorough analysis of the different aspects of the problem and of the different tools at our disposal. Using this analysis, we proposed a methodology in which each step uses the best state of the art method according to its specificities.

Keywords Multiferroics · Magneto-electricity · Ab-initio calculations · Correlated systems · Magnetism

1 Introduction

Multiferroic materials have attracted a lot of attention over the last decade. They are characterized by the coupling between at least two different ferroic orders: ferroelectricity, ferromagnetism, ferro-elasticity or ferro-toroidicity. Out of all the possible multiferroic systems, those involving the coupling between magnetic and electric properties have attracted the largest attention. Indeed, not only colossal magneto-electric effects have been discovered a decade ago[1–3], but the possibility to trigger the magnetic order of a material, using an electric field, opens lots of possibilities for applications in electronics or spintronics devices. One of the direct applications of multiferroics is, for instance, data storage. The electrical control of magnetization via the magneto-electric coupling in a single device [4], offers the opportunity to write a magnetic information by the application of a small voltage instead of a large current. Multiferroics could thus combine sub-nanosecond switching speeds and write-operation with low energetic costs (due to low power voltage), with non-destructive standard read operations. In addition, the magneto-electric coupling stabilizes the magnetic information by the atomic displacements, associated with the electric polarization. This is an important point for non volatile memories.

Using a strict definition, such a multiferroic material should exhibit both a magnetic moment, a polarization and a linear magneto-electric coupling between the two of them. However the community have extended the multiferroic denomination to any system showing a coupling between a long range magnetic order of any kind, and the polarization of a system, even when the magneto-electric coupling is not linear but of higher order.

Multiferroic systems are generally classified into type I and type II. The type I compounds are characterized by a paraelectric/ferroelectric transition distinct from the magnetic transition. In such systems the polarization is usually large, however the magneto-electric coupling remains weak. In type II systems the ferroelectricity appears at a magnetic transition and is often magnetically induced, the inset of the magnetic order being responsible for the polar atomic displacements. In such systems, the magneto-electric coupling is large, even though the polarization usually remains quite small.

The linear magneto-electric coupling is experimentally determined by the measure of the linear magneto-electric tensor, $\overline{\overline{\alpha}}$. $\overline{\overline{\alpha}}$ is the linear response of a system polarization as a function of an applied magnetic field, or reversely the linear response of the magnetic order parameter

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(magnetization, $\vec{M} = \sum_j \vec{\mu}_j$, in a ferromagnetic system, staggered magnetization, $\vec{M} = \sum_j (-1)^j \vec{\mu}_j$, in antiferromagnetic ones, etc.) as a function of an electric field.

The aim of this paper is to develop a method in order to compute the magneto-electric tensor, $\overline{\overline{\alpha}}$, from ab-initio calculations of the electronic structure.

2 The magneto-electric tensor

In a Landau theory, $\overline{\overline{\alpha}}$ corresponds to the second derivative of the free energy with respect to both electric and magnetic fields

$$\overline{\overline{\alpha}} = -\left.\frac{\partial^2 \mathcal{F}}{\partial \vec{\mathcal{E}}\, \partial \vec{\mathcal{H}}}\right|_{\substack{\mathcal{E}=\vec{0}\\ \mathcal{H}=\vec{0}}} \tag{1}$$

Multiferroic systems are magnetic insulators, therefore their low-energy excitations are magnetic excitations. It results that one can describe their low-energy properties, by an effective Hamiltonian taking explicitly into account only the magnetic degrees of freedom. Heisenberg or related Hamiltonians are good example of such effective models of the low-energy physics. Let us suppose, for the sake of example, that our system can be described by such an Hamiltonian for its Fermi level properties, that is magnetic properties,

$$\hat{H} = E_0 - \sum_{<i,j>} J_{i,j}\, \hat{\vec{S}}_i \cdot \hat{\vec{S}}_j \tag{2}$$

where $< i, j >$ means that the i and j sites are nearest neighbors and the energy E_0 is the energy associated with all non magnetic degrees of freedom.

In the polar magnetic phase, where the magneto-electric coupling takes place, the free energy can thus be written as

$$\mathcal{F} = E_0 - \sum_{<i,j>} J_{ij} \langle \hat{\vec{S}}_i \cdot \hat{\vec{S}}_j \rangle \tag{3}$$

$$- \sum_i g\, \mu_{\mathrm{B}}\, \langle \vec{S}_i \rangle \cdot \vec{\mathcal{H}} - \vec{P} \cdot \vec{\mathcal{E}} - T\, S \tag{4}$$

where $\langle\rangle$ means the thermal average, J_{ij} are the effective magnetic integrals, T the temperature and S the entropy, $\vec{\mathcal{E}}$ and $\vec{\mathcal{H}}$ are the electric and magnetic fields. At this point one may remember that the thermal probability of a state (in a gapped system such as the present ferroelectric ones) is varying very fast as soon as one is a little away from the transition. In other words, in the paramagnetic phase ($T > T_c$, that is when $\forall I, k_{\mathrm{B}} T \gg E_I - E_0$, with E_I the energy of the Ith excited magnetic state) all magnetic states, $|\psi_I\rangle$, have an equivalent probability $p_I = \mathrm{e}^{-\beta E_I}/Z \simeq 1/N$. Z is the partition function and N the number of magnetic states. It results that the free energy is dominated by the entropy part, the energy part being constant. On the contrary in the magnetically ordered phase, ($T < T_c$), the ground state probability strongly dominates and the free energy is dominated by its energetic part. The direct consequence of this analysis is that one can neglect the entropy contribution in the calculation of the magneto-electric tensor, as soon as one is a bit away from the paramagnetic/magnetically ordered state transition.

In a first approximation, the magneto-electric tensor can thus be written as

$$\overline{\overline{\alpha}} = \sum_{<i,j>} \left.\frac{\partial J_{i,j}}{\partial \vec{\mathcal{E}}}\right|_{\mathcal{E}=\vec{0}} \otimes \left(\left.\frac{\partial \langle \vec{S}_i \rangle}{\partial \vec{\mathcal{H}}}\right|_{\mathcal{H}=\vec{0}} \cdot \langle \vec{S}_j \rangle + \langle \vec{S}_i \rangle \cdot \left.\frac{\partial \langle \vec{S}_j \rangle}{\partial \vec{\mathcal{H}}}\right|_{\mathcal{H}=\vec{0}} \right) \tag{5}$$

One therefore needs to be able to evaluate the derivative of the effective magnetic integrals as a function of an applied electric field and the derivative of the local magnetic moments as a function of a magnetic field. The former will require accurate ab-initio evaluation of the magnetic integrals and while the later can be reached using a spin-wave calculation, a usual method in solid state physics [5–9]. In fact the difficulty resides in the first part, that is the evaluation of the magnetic couplings derivatives as a function of an applied electric field. For this purpose we will rely on accurate ab-initio calculations.

3 Accurate ab-initio calculation of an effective magnetic interaction

Prior to dealing with the effect of an applied electric field, one needs to be able to accurately calculate the effective magnetic interactions appearing in a magnetic Hamiltonian, such as the Heisenberg Hamiltonian.

The most popular method in first principle quantum chemistry is nowadays the density functional theory (DFT) [10]. DFT is a highly efficient method that provides good results on numbers of problems, such as geometry optimization, phonons spectra etc. At this point let us recall that DFT calculations are based on the Kohn–Sham approximation [11], and thus solve a non-interacting effective problem, supposed to have the same (spin)-density as the real correlated problem. The energetic effect of the electronic correlation and exchange are treated using the so-called exchange correlation functionals. As far as the electronic correlation is concerned, the different DFT functionals have proved over and over again their reliability, as long as the electron–electron interactions remains sub-dominant compared to the kinetic energy. In strongly

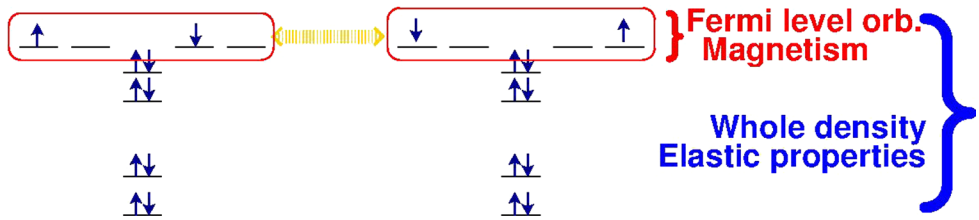

Fig. 1 Schematic electronic structure of a strongly correlated compound

correlated systems, things are more complicated. Indeed, DFT calculations encounters difficulties to describe properties dominated by the Fermi level electrons. This is, for instance, the case for the evaluation of the effective magnetic interactions [12, 13]. Indeed, the predictability and accuracy is not insured [13] and different functionals may yield quite different values for the magnetic integrals [14]. On the other end, geometries, lattice dynamics and many other properties are still well described in strongly correlated systems within a DFT scheme (except on some spurious cases). Let us try to analyze the reasons of this simultaneous success and failure of DFT for strongly correlated systems.

Correlated systems are characterized by a strong Coulomb repulsion (larger than the typical kinetic energy scale) between electrons close to the Fermi level. It results in wave functions, for the ground and low lying excited states, involving many (an infinity for infinite systems) Slaters determinants with equivalent weights, and differing only by the occupation or spins of the Fermi level orbitals (see Fig. 1). Since all those configurations are strongly coupled, it is quite understandable that an effective free electrons representation encounters some difficulties to describe such systems. In fact, as long as the desired property involves the whole electron density (as geometry, phonons, elastic properties, etc.), the error introduced by a ill-representation of the Fermi electrons remains weak, and does not significantly affect the results. Indeed, the Fermi level strongly correlated electrons represent a (very) small part of the total electron density. On the contrary, when the desired property is dominated by the Fermi level electrons (as it is the case in effective magnetic interactions, see reference [15]), then DFT encounters difficulties to yield accurate predictions.

One will thus have to rely on specifically designed wave function correlated methods, such as DDCI [16–18] or for systems with numerous open-shells per atom SAS+S [13], in order to accurately determine the effective magnetic integrals. Indeed, these highly multi-reference methods allow, on embedded fragments, to accurately compute the low-energy magnetic spectrum in strongly correlated systems. Based on a Complete Active Space (CAS), as in the DDCI method, or on an appropriate zeroth-order multi-reference space retaining the dominant configurations for both the ground state and the magnetic excited states, as in the SAS+S method, both methods include the dynamical correlation corrections, on each of the reference determinants. It results highly accurate spectra, from which effective exchange integrals can be extracted using an effective Hamiltonian method. Such ab-initio evaluations are highly predictive and systematically yield exchange integrals within the error bar of inelastic neutrons scattering results [19, 20].

The ab-initio calculations provide ground and low-energy excited states eigenvalues and wave functions for a set of fragments designed to suit all the crystallographically independent effective interactions in the compound. In order to extract the effective spin Hamiltonian (such as the Heisenberg Hamiltonian) one can use the effective Hamiltonian theory. Let us recall quickly the main principles. The goal is that, on each fragment the effective Hamiltonian does not only mimic the ab-initio spectrum, but also that its eigenvectors reproduce the main configurations of the ab-initio wave functions. This projection must be on a subset of the zeroth-order multi-reference space chosen for the ab-initio calculation, and must represent at least about 90 % of the wave function of all involved states. Once the projection operator chosen, this can be achieved in minimizing the following Lagrangian over the effective Hamiltonian parameters

$$\min_{J_{ij}} \mathcal{L}(J_{ij}) = \min_{J_{ij}} \sum_I ||\hat{H}(J_{ij})\hat{P}|\Psi_I\rangle - E_I\hat{P}|\Psi_I\rangle||^2 \quad (6)$$

where $\hat{H}(J_{ij})$ is the spin Hamiltonian, $|\Psi_I\rangle$ the ab-initio wave function of the Ith excited state and E_I its energy, and $\hat{P}$ is the projector over the chosen reference configurations. The correctness of the chosen spin effective Hamiltonian is insured by the fact that $\sqrt{\mathcal{L}(J_{ij})} \ll J_{ij}$ and $\sqrt{\langle\Psi_I|\hat{P}|\Psi_I\rangle} \gtrsim 0.9$, for all fragments.

4 Effect of an electric field on the magnetic interactions

The method for an accurate determination of the magnetic integrals being designed, the question is how to describe the effects of an applied electric field on these magnetic interactions. According to Iñiguez [21], it is the nuclear displacements induced by the electric field that constitute the dominant effect. Indeed, in most cases, the external field is efficiently screened, and the orbital polarization due to the

applied field can be neglected [21, 22]. Similarly, the spin polarization (important when a magnetic field is applied) only comes through the spin-orbit term when an electric field is applied. In compounds with $3d$ elements, it thus remains quite negligible. Of course, such effects should be taken into account in systems where the spin-orbit is rather large [23, 24].

In condensed matter, the response of a system to an electric field is given by the born tensor $\overline{\overline{Z}}^*_{ij} = -e\ \delta\mathcal{F}_i/\delta\mathcal{E}_j$. $\overline{\overline{Z}}^*$ is thus the modification of the force applied on the system ions, when an electric field is applied. In other words the forces equilibrium yields the following equation

$$\overline{\overline{Z}}^\star \cdot \vec{\mathcal{E}} = \overline{\overline{\mathrm{H}}} \cdot \vec{d} \quad \Leftrightarrow \quad \vec{d} = \overline{\overline{\mathrm{H}}}^{-1} \cdot \overline{\overline{Z}}^\star \cdot \vec{\mathcal{E}} \tag{7}$$

where $\overline{\overline{\mathrm{H}}}$ is the energy Hessian of the system, and $\vec{d}$ the system ions displacement vector. The main response of a ferroelectric compound to an applied electric field will thus be a geometry modification that can be evaluated by the displacement $\vec{d}(\vec{\mathcal{E}})$ of the system ions [21]. This displacement vector will then induce a change in the magnetic interactions. Computing the magnetic integrals for different electric fields displacements allows to numerically evaluate the derivative of the spin Hamiltonian parameters as a function of an applied electric field, as needed in Eq. 5.

The last question to solve is how to evaluate the Hessian matrix $\overline{\overline{\mathrm{H}}}$ and the Born tensor $\overline{\overline{Z}}^\star$. Going back to our analysis of the electronic structure of strongly correlated compounds, as pictured in Fig. 1, one sees that since both the Hessian (as for the dynamical matrix and the phonons modes) and the Born tensor depend of the whole electron density, the correlation among the Fermi level electrons will induce only minute modifications of these two tensors. It results that one can safely evaluate them using standard DFT calculations, provided the use of a functional accounting reasonably for the ferroelectric gap and distortions, such as hybrid functionals (for instance B1WC [25] or even B3LYP [26]).

This method has been successfully applied to the multiferroic $YMnO_3$ compound [27]. Indeed, we showed that the magneto-electric tensor can be expressed as the sum of the 2×3 terms, associated with the three Mn subsystems composing the manganese triangular pattern in two layers of the unit cell. Each of these terms can be associated with a set of Mn–Mn bonds orientated in a specific direction. It was shown that derivative of the exchange integrals when the electric field is applied perpendicular to the MnO_3 planes is negligible. When the field is applied along a direction within the MnO_3 plane, its effect differs from bond to bond. It slightly increases the absolute value of the magnetic coupling when it is parallel to a Mn–Mn bond. It more substantially decreases it when applied perpendicular to the Mn–Mn bond. It was also shown that the spin-orbit coupling, the only explicit coupling between the spin and charge degrees of freedom, plays a negligible role in the $YMnO_3$ magneto-electric coupling, its effect being 10^{-3} weaker than the effect mediated by the elastic response.

5 Conclusion

The magneto-electric tensors are macroscopic tensors measuring the cross response of a system to applied electric and magnetic fields. The linear response tensor ($\overline{\overline{\alpha}} = -\partial^2\mathcal{F}/\partial\vec{\mathcal{E}}\,\partial\vec{\mathcal{H}}\Big|_{\substack{\mathcal{E}=\vec{0}\\ \mathcal{H}=\vec{0}}}$) can also be seen as the derivative of the macroscopic dipole moment or polarization as a function of a magnetic field ($\partial\vec{P}/\partial\vec{\mathcal{H}}$), or the derivative of the magnetic order parameter as a function of the electric field ($\partial M/\partial\vec{\mathcal{E}}$). When the polarization ($\vec{P}$, which is the ferroelectric order parameter) and the magnetic order parameter (M that describes the long range ordering of spin part of the wave function) belong to the same irreducible representation, the linear response tensor is non nill. When M does not belong to the totally symmetric representation of the system symmetry group, $\overline{\overline{\alpha}} = \overline{\overline{0}}$. This is due to the fact that the polarization, $\vec{P} = \sum_N Q_N\vec{R}_N$, has the same symmetry as the total electron density, that is the same symmetry as the nuclei. It thus always belongs to the totally symmetric irreducible representation of the system's symmetry group. This is not necessarily the case for the magnetic order parameter. Indeed, it has the same symmetry as the spin part of the ground state wave function, and thus may belong to any of the irreducible representations of the group. Third order tensors may or may not be zero (since the free energy must be a totally symmetric scalar), but in all cases the quadratic order tensor ($-\partial^4\mathcal{F}/(\partial\vec{\mathcal{E}})^2\,(\partial\vec{\mathcal{H}})^2\Big|_{\substack{\mathcal{E}=\vec{0}\\ \mathcal{H}=\vec{0}}}$) is symmetry allowed.

In the present paper we developed a methodology for the ab-initio evaluation of the linear magneto-electric tensor. This methodology combines different ab-initio methods (correlated wave function calculations of embedded fragments and DFT calculation), with effective Hamiltonian theory along the quasi-degenerate perturbation theory scheme [28], and condensed matter spin-wave theory. While exemplified in this paper using an Heisenberg spin Hamiltonian, one sees that it can easily be extrapolated to any kind of spin Hamiltonian accurately representing the Fermi level spin excitations, and to higher level magneto-electric tensors.

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