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Localized Orbitals *vs.* Pseudopotential-Plane Waves Basis Sets: Performances and Accuracy for Molecular Magnetic Systems

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Summary. Density functional theory, in combination with *a*) a careful choice of the exchange-correlation part of the total energy and *b*) localized basis sets for the electronic orbitals, has become the method of choice for calculating the exchange-couplings in magnetic molecular complexes. Orbital expansion on plane waves can be seen as an alternative basis set especially suited to allow optimization of newly synthesized materials of unknown geometries. However, little is known on the predictive power of this scheme to yield quantitative values for exchange coupling constants J as small as a few hundredths of eV (50–300 cm^{-1}). We have used density functional theory and a plane waves basis set to calculate the exchange couplings J of three homodinuclear Cu-based molecular complexes with experimental values ranging from $+40\,\text{cm}^{-1}$ to $-300\,\text{cm}^{-1}$. The plane waves basis set proves as accurate as the localized basis set, thereby suggesting that this approach can be reliably employed to predict and rationalize the magnetic properties of molecular-based materials.

Keywords. Molecular modeling; Density functional calculations; Molecular magnetism; Magnetic properties.

Introduction

Molecular magnetism owes a large share of its impact on inorganic chemistry and material science to the growing capabilities of theoretical tools in predicting magneto-structural correlations for compounds of increasing complexity [1]. We refer here in particular to open-shell molecular structures containing paramagnetic centers coordinated through closed-shell ligands. The direct calculation of exchange

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couplings is nowadays possible via electronic structure-based techniques, by providing accurate values for quantities that are decisive in the design of molecular-scale magnets. Although in principle less accurate than *ab initio* multiconfiguration approaches as the configuration-interaction (CI), density functional (DFT) methods allow to investigate a wider range of systems sizes [1]. This includes fairly small homo- and heterodinuclear molecules as well as much larger polynuclear compounds and periodic solids. For these reasons, DFT has to be preferred when the primary goal is to obtain reliable quantitative estimate of exchange couplings as small as 50–100 cm^{-1} (0.005–0.01 eV) at an affordable computational cost, within an accessible and yet rigorous theoretical framework.

When adopting a DFT scheme among those made available in computational packages, two kinds of considerations are in order. On the one hand, the performances of DFT are crucially related to the quality of the exchange-correlation part of the energy functional. On the other hand, the desired level of manageability and computational convenience determines the choice of a basis set. For isolated magnetic molecules or magnetic crystals made of weakly interacting molecules, the two above criteria are largely fulfilled by the use of the hybrid B3LYP exchange correlation functional [2] in conjunction with localized orbitals as a basis set. These ingredients are implemented within the Gaussian code [3]. The evaluation of the singlet state $S = 0$ energy is carried out by using the so-called broken-symmetry (*i.e.* spin polarized with total spin $S = 0$) solution (BS) [4]. Indeed, a large amount of calculations has proved that the BS-DFT approach is best suited to provide quantitative estimates of J that are as reliable as those obtained from highly sophisticated (and much more expensive computationally) multireference *ab initio* calculations [1].

Experimentally, the magnetic susceptibility measurements are obtained from solid samples in which the packing forces can produce small deviations from the structure of the isolated molecule. Hence, in the calculations, neither the model nor the complete structures are optimized since very small variations in the geometry such as those induced by the packing forces can produce large changes in the calculated magnetic constant. Given the availability of structural data, calculations are typically performed for a fixed set of experimental coordinates. Along the same lines and by using the CRYSTAL [5] package, which is the periodic extension of the Gaussian scheme, exchange couplings can be obtained for periodic solids. In this case, several spin configurations corresponding to the same total spin (as in antiferromagnetic or ferrimagnetic situations) need to be taken into account. Then, the collection of total energies data resulting from the different spin configurations have to be mapped to an appropriate spin Hamiltonian.

The DFT schemes implemented in Gaussian and CRYSTAL are well suited to find minima in the energy if the starting configurations are close to local configurational minima. However, the methods based on plane waves are usually implemented with more efficient strategies to handle complex structural searches. This is for instance the case of a new family of solid-state molecular-based magnetic materials, the transition metal hydroxides $M_2(\mathrm{OH})_3X$, where M is a divalent transition metal ion and X an exchangeable anion [6, 7]. As in the case of copper hydroxide acetate $\mathrm{Cu_3(OH)_3CH_3COO}$, knowledge of the atomic structure of these solid-state compounds is often incomplete [8]. Accordingly, it appears appropriate to tackle the atomic-scale study of molecular magnetic materials characterized by unknown or poor structural determination by resorting to plane waves (PW), more adapted to a flexible and efficient search of structural minima. The PW basis set is implemented for a periodic cell, by leading to the following expression for the single-particle orbitals entering the *Kohn-Sham* DFT Hamiltonian:

$$\phi_i^{\mathbf{k}} = e^{i\mathbf{kr}} \sum_{\mathbf{g}} c_i^{\mathbf{k}}(\mathbf{g}) e^{i\mathbf{gr}} \tag{1}$$

where **g** is a reciprocal lattice vector of the period cell, the wave vector **k** lies in the *Brillouin* zone of the reciprocal lattice of the periodic cell and the sum runs over the *Fourier* components $c(\mathbf{g})$ of the single-particle orbital. The advantage of PW over a localized basis set stems from the use of fast *Fourier* transform techniques for the calculation of the energy and the forces acting on the ion, operations which are simplified in this scheme since the PW do not depend on ionic coordinates [9]. PW are taken to represent valence orbitals, while the interaction of the valence electrons with the atomic cores is described by pseudopotentials. It should be stressed that pseudopotentials are devised to modify the potential felt by the valence electrons in the core region. The original potential would require an exceedingly high number of plane waves to account for the rapid variation of the valence states at very small distances. Such strong oscillations are induced by the orthogonalization condition between valence and core states. Because of the use of pseudopotentials, this effect is eliminated and the sum of Eq. (1) can be truncated to include an affordable number of plane waves, *i.e.* those with a kinetic energy $E_{\text{kin}} = 0.5(\mathbf{k} + \mathbf{g})^2$ less than a given energy E_{cut}. The value of E_{cut} depends on the nature of the system and on the quality of the pseudopotential [10]. PW are appealing and ‘‘friendly-user’’ since the convergence and the resulting accuracy of the calculations simply depend on the number of *Fourier* components included in the summation of Eq. (1).

By using PW and pseudopotentials, electronic and magnetic properties of copper hydroxonitrate $Cu_2(OH)_3NO_3$ have recently been investigated, providing an instructive picture of frustration effects in a prototypical layered magnetic material [11]. Turning to the quantitative estimate of the exchange coupling constants, the question arises on the predictive power of the PW scheme to evaluate quantities that can be as small as 0.05 eV. Typically, for solid-state and cluster science applications, energy values within this range are not significantly different, as it is the case when different isomers of a same cluster are obtained through structural optimization procedures. A source of error commonly invoked is related to the pseudopotential construction, characterized by a level of tolerance in reproducing the all-electron results close to a few hundredths of eV. We conclude that no clear-cut information exists on the accuracy of DFT-PW approaches for the calculation of singlet-triplet energy splittings in magnetic molecular systems.

In this work we assess the accuracy of DFT-PW calculations for magnetic molecular materials by calculating the exchange coupling of three isolated Cu_2-based complexes. For these molecules, both experimental and DFT results with localized basis have been obtained, yielding J values as low as $50\,\text{cm}^{-1}$. We are able to conclude that the DFT-PW scheme is well suited to provide quantitative information on the exchange couplings and that it can be reliably employed with the same purpose for larger systems and solid-state compounds.

Method

Our calculations are performed in the *Kohn-Sham* DFT framework with the BLYP generalized gradient approximation due to *Becke* (B) [12] for the exchange part and to *Lee*, *Yang* and *Parr* (LYP) [13] for the correlation part. The account of spin polarization for $S = 0$ calculations corresponds to the broken-symmetry approach referred to in DFT applications of quantum chemistry [1]. All valence electrons are treated explicitly and on the same footing, *i.e. via Fourier* expansion of the associated orbitals in plane waves at the $\mathbf{k} = 0$ point of the supercell. Norm conserving pseudopotentials generated following the scheme by *Trouiller* and *Martins* are used to account for core-valence interaction [14]. An energy cutoff E_{cut} equal to 90 Ry yields converged binding energies, equilibrium distances d_{e} and vibrational frequency ω for the Cu_2 and CuO dimers that were used in test calculations. Small differences are found when comparing our calculated d_{e} and ω of Cu_2 and CuO with the corresponding quantities obtained *via* the Gaussian-localized basis scheme. For Cu_2 the values are $d_{\text{e}} = 2.27\,\text{Å}$ (PW) and $d_{\text{e}} = 2.26\,\text{Å}$ (Gaussian), $\omega = 270\,\text{cm}^{-1}$ (PW) and $\omega = 256\,\text{cm}^{-1}$ (Gaussian). For CuO the values are $d_{\text{e}} = 1.73\,\text{Å}$ (PW) and $d_{\text{e}} = 1.75\,\text{Å}$ (Gaussian), $\omega = 660\,\text{cm}^{-1}$ (PW) and $\omega = 641\,\text{cm}^{-1}$ (Gaussian). When calculating the properties of an isolated system within a PW scheme, the simulation box has to be chosen large enough so as to minimize the interaction with the periodic images. This can be checked by recalculating the properties of interest for systems of increasing size. In our case, a converged value for the exchange coupling J is attained for a box length $L = 18.5\,\text{Å}$. We recall that J is defined as

$$J = E(\text{S} = 0) - E(\text{S} = 1) \tag{2}$$

where $E(\text{S} = 0)$ and $E(\text{S} = 1)$ are the total energies for the singlet and triplet state respectively. The above definition corresponds to the non spin-projected energy [15]. As discussed by several authors, the best results from DFT methods when calculating the singlet-triplet gap are obtained when the broken symmetry state is considered without spin projection, *i.e.* by using Eq. (2) [16–18]. This fact is due the inclusion of the non-dynamical correlation effects in the commonly used exchange functionals. The use of the spin projection simultaneously produces a suppression of such effects, as discussed recently by *Polo et al.* [19].

For each molecule, atomic positions are taken equal to the experimental values. Total energy minimization is carried out with respect to the coefficient of the PW expansion and stops when the largest gradient is smaller than 10^{-6} a.u. Our calculations are carried out by using the CPMD plane waves code [20]. For one of the studied systems, we have performed calculations with the Gaussian code, in order to complete previous results of Ref. [1]. We used analytical small core pseudopotentials proposed by *Hay* and *Wadt* [21] combined with B3LYP [2] and BLYP [12, 13] functional (using the LANL2DZ keyword in Gaussian code [3]) and all electron calculations using the PBE [22] and PBE0 [23] functionals.

Results and Discussion

The first molecule we considered is copper(II) acetate (Fig. 1). Copper(II) acetate has been adopted in extensive benchmark calculations comparing different electronic structure approaches for magnetic molecular materials [1]. The results reported in Ref. [1] are shown in Table 1, together with the value calculated in this work. The optimal performances of the hybrid B3LYP functional ($J = -299\,\mathrm{cm}^{-1}$ against $J = -297\,\mathrm{cm}^{-1}$, experimental value [24]) are clearly highlighted by the data. The present PW-BLYP calculations yield a J value ($J = -518\,\mathrm{cm}^{-1}$) which is closer to the experiment than the one obtained within Gaussian with the same functional using all electron basis sets or using *Hay-Wadt* pseudopotentials ($J = -779$ and $-754\,\mathrm{cm}^{-1}$, respectively). This change in the localized basis sets does not produce the same effect on the BLYP and B3LYP functionals, since for the BLYP the all electron value is more negative, while the opposite is found for the B3LYP one. The use of other GGA schemes with the localized basis sets, such as the PBE functional, also provides values close to the BLYP result with the same basis set. Due to the larger exact exchange contribution than within the B3LYP functional, the free parameter hybrid functional PBE0 gives less negative J values. We note that the inclusion of the exact exchange improves considerably the results in comparison with the other GGA functionals when using localized basis sets.

In a second test case, which belongs to the family of the extensively studied hydroxo-bridged Cu(II) dinuclear complexes [25], we considered a Cu-based dinuclear transition metal molecular complex, $[\mathrm{Cu}_2(\mu\text{-OH})_2(bipym)_2](\mathrm{NO}_3)_2 4\mathrm{H}_2\mathrm{O}$ (*bipym* = bipyrimidine) (Fig. 2). In Ref. [15] the exchange coupling for this molecule was calculated *via* several energy functionals to elucidate the differences between the BLYP results and those obtained with hybrid methods. These latter were found to be dependent on the amount of exact exchange included.

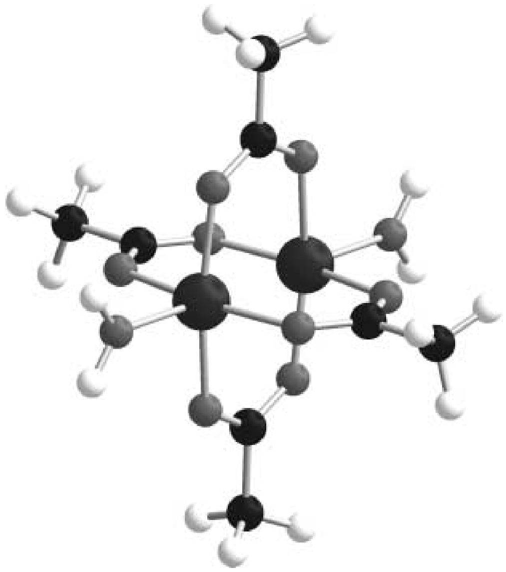

Fig. 1. Representation of the structure of the copper acetate molecule

Table 1. Value of exchange coupling constant, J, for copper(II) acetate calculated using several *ab initio* and density functional methods. Most of the results are taken from Ref. [1]. The calculation performed with the *Hay-Wadt* pseudopotentials combined with localized basis set are labeled as "pseudo". The BLYP-PW result corresponds to that obtained with the plane wave approach. All DFT and HF calcalations make use of the broken symmetry approach

Method	J (cm^{-1})
Experimental (Ref. [24])	-297
DDCI-2 (Ref. [1])	-77
DDCI-3 (Ref. [1])	-224
CASSCF (Ref. [1])	-24
CASPT2 (Ref. [1])	-117
UHF (Ref. [1])[a]	-54
Xα (Ref. [1])	-848
SVWN (Ref. [1])	-1057
B3LYP (Ref. [1])	-299
BLYP (Ref. [1])	-779
B3LYP pseudo	-346
BLYP pseudo	-754
PBE	-776
PBE0	-237
BLYP-PW	-518

[a] Using spin projection

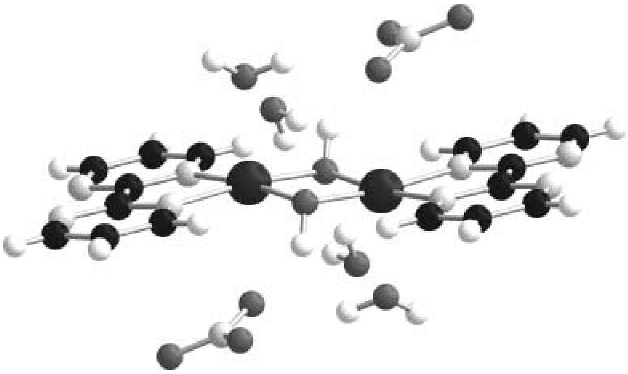

Fig. 2. Representation of the structure of $Cu_2(\mu\text{-}OH)_2(bipym)_2](NO_3)_2 4H_2O$

Again, the best agreement with experiments was obtained *via* the B3LYP functional in the spin non-projected version, which performs much better than spin-projected unrestricted *Hartree-Fock* calculations [15]. As shown in Table 2, the PW approach improves upon the localized basis one, yielding a value for J closer to experiments (BLYP-PW, $J = +95\,\mathrm{cm}^{-1}$, experiment, $J = +114\,\mathrm{cm}^{-1}$ [26]). A non-negligible difference is found between the two BLYP results ($+95\,\mathrm{cm}^{-1}$ against $+221\,\mathrm{cm}^{-1}$ with Gaussian).

In a final test, we look for a third molecule containing a pair of Cu centers and a smaller coupling constant, $[(dpt)Cu(\mu\text{-}Cl)_2Cu(dpt)]Cl_2$, ($dpt$ = dipropylenetriamine) (Fig. 3). This complex is an interesting example of dinuclear copper(II)

Table 2. Value of the exchange coupling constant, *J*, for $[Cu_2(\mu\text{-}OH)_2(bipym)_2](NO_3)_2$, calculated *via* DFT (broken symmetry) methods within Gaussian (Ref. [15]) and by using a PW basis set within DFT-BLYP (present calculations)

Method	J (cm^{-1})
Experimental (Ref. [26])	-114
B3LYP	-113
BLYP	-221
BLYP-PW	-95

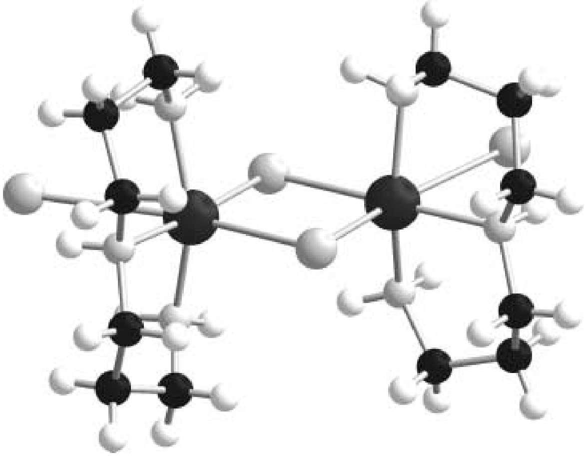

Fig. 3. Representation of the structure of $[(dpt)Cu(\mu\text{-}Cl)_2Cu(dpt)]Cl_2$, ($dpt$ = dipropylenetriamine)

system containing chloro bridging ligands with a $Cu(\mu\text{-}Cl)_2Cu$ motif. In Ref. [27] magnetic susceptibility data showed a ferromagnetic coupling between the two Cu centers, as corroborated by extended *Hückel* calculations. The data collected in Table 3 confirms that the combination of PW and BLYP is capable of reproducing fairly accurately the experimental J (BLYP-PW, $J = +61\,cm^{-1}$, experiment, $J = +42.9\,cm^{-1}$). As in the previous case, the value obtained *via* PW is about a factor of 2 lower than the one resulting from the localized orbital calculations with the same energy functional ($J = +100\,cm^{-1}$, Ref. [28]). While

Table 3. Value of the exchange coupling constant, *J*, for $[(dpt)Cu(\mu\text{-}Cl)_2Cu(dpt)]Cl_2$, calculated *via* DFT (broken symmetry) methods within Gaussian (Ref. [28]) and by using a PW basis set within DFT-BLYP (present calculations)

Method	J (cm^{-1})
Experimental (Ref. [27])	$+42.9$
B3LYP	$+56$
BLYP	$+100$
BLYP-PW	$+61$

further investigation are in order to elucidate the origins of this discrepancy, we recall that the use of pseudopotentials corresponds to the neglect of an explicit description of the atomic cores. On a quantitative basis, this may inhibit comparison with Gaussian basis results, as recently pointed out [29].

Overall, these results demonstrate that the DFT-PW is a reliable and accurate tool to calculate exchange coupling of transition metal complexes as small as $\sim 50\,\mathrm{cm}^{-1}$. A general recipe to investigate theoretically magnetic molecular-based materials becomes available. Provided the atomic structure is experimentally known, the DFT-PW method can be used directly to extract the exchange couplings from the mapping of a suitable spin Hamiltonian. For this, a collection of microscopic spin configurations compatible with the total magnetic character of the system is required. For each microscopic configuration, the ground state electronic structure can be efficiently attained within the DFT-PW scheme. Whenever a knowledge of the atomic structure is not available, structural optimization becomes a necessary prerequisite. The DFT-PW scheme is well suited to this task, allowing for a simultaneous optimization of both electronic and ionic degrees of freedom. This step can be followed by the determination of the coupling constant along the lines sketched above.

Despite the encouraging indications of this study the DFT-PW approach is also characterized by a few weak points that do not have to be overlooked. First and foremost the above mentioned difficulty to reproduce at the same level of accuracy all-electron results by using PW and pseudopotentials. In addition, we recall that using plane waves as a basis set corresponds to filling all portions of space with the same density of *Fourier* components, irrespective of the presence of atoms. The number of plane waves N_{pw} grows linearly with the volume and follows a power law $(E_{\mathrm{cut}})^{3/2}$ as a function of the energy cutoff. For the third molecule we considered, $[(dpt)\mathrm{Cu}(\mu\text{-}\mathrm{Cl})_2\mathrm{Cu}(dpt)]\mathrm{Cl}_2$, this cutoff amounts to as much as $2.4 \cdot 10^6$ plane waves for the expansion of the electronic density. In this case, the calculation of the electronic ground state required 5 hours of CPU time on 48 processors of an IBM-SP4 computer. These data point out the relatively high cost of these runs, together with the need of powerful parallel computers.

It was already mentioned that the hybrid B3LYP is the functional of choice for calculations of exchange couplings within the DFT formalism, at least in most transition metal complexes. However, this functional has not yet become operational in a PW code, as it would be desirable to exploit the flexibility of the plane waves basis set at a quantitative level. As a further point, we note that the non-localized character of this basis set prevents from a straightforward assignment of the initial spin density distribution. This is necessary to build up the catalog of all microscopic spin topologies corresponding to a given value for the total spin. Finally, by focusing on isolated molecules, it has to be reminded that the periodicity of the calculation cell is not well suited to calculations for charged systems, because of the long-range *Coulomb* interaction between the periodic images. Given the current pace of developments and improvements in this area, none of these shortcomings are stumbling blocks [29, 30]. Therefore, we are confident on the appearance of an increased number of DFT-PW applications for the theoretical study of molecular-based magnetic materials.

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