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## Magnetic Exchange Couplings with Range-Separated Hybrid Density Functionals

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**Abstract:** We investigate the effect of Hartree−Fock range-separation on the calculation of magnetic exchange couplings in a set of nine bimetallic transition-metal complexes containing 3d elements (V, Cr, Mn, and Cu). To this end, we have compared magnetic exchange couplings calculated as self-consistent energy differences using two global hybrid functionals, B3LYP (Becke 3-parameter exchange and Lee−Yang−Parr correlation) and PBEh (hybrid Perdew−Burke−Ernzerhof) with the short-range separated HSE (Heyd−Scuseria−Ernzerhof) and the long-range corrected LC-$\omega$PBE. Our results show that, although there is no clear superiority of any of these functionals when compared with experimental data, the LC-$\omega$PBE provides a better description of the magnetization on the metallic centers, yielding self-consistent solutions that mimic more closely a Heisenberg-like behavior.

## Introduction

One of the most interesting properties of molecular complexes containing transition-metal atoms is their ability to behave as single-molecule magnets. Many applications have been proposed exploiting these molecular-size magnets, such as quantum computation units and high-density data storage.[1] The magnetic behavior of these systems has been probed using a variety of experimental techniques. In all cases, an empirical model based on the Heisenberg spin Hamiltonian was found to fit the experimental data very well, provided that the parameters in the model Hamiltonian are chosen properly. Thus, modeling the magnetism of single-molecule magnets can be reduced to analyzing simple statistical models based on a Heisenberg spin Hamiltonian that includes both external parameters (temperature, applied magnetic field, etc.) and internal parameters (magnetic exchange couplings, magnetic anisotropy, etc.).

Internal parameters for a particular molecular magnet can be obtained from first-principles electronic structure calculations by mapping the molecular energies to the energies of the Heisenberg spin Hamiltonian.[2−4] In particular, magnetic exchange couplings, *J*, can be obtained considering the isotropic Heisenberg Hamiltonian

$$H = -2\sum_{\langle i,j \rangle} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{1}$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the (localized) spin operators associated to each magnetic center. The theoretical prediction of magnetic exchange couplings depends mainly on two factors: the approach employed in this mapping and the choice of the electronic structure method. Because of the size of most systems of interest, density functional theory (DFT) represents the most viable electronic structure method to this end.

Several approaches have been proposed for extracting *J* couplings from DFT energies. According to the spin-projected (SP) approach,[2] the energies of a two-center complex *A* and *B* can be related to the *J* coupling as

$$E_{\text{LS}} - E_{\text{HS}} = 4S_A S_B J_{AB} \tag{2}$$

while in the non(spin)projected (NP) approach,[5] the energies of a two-center complex $S_A$ and $S_B$ can be related to the *J* coupling as

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$$E_{LS} - E_{HS} = (4S_A S_B + 2S_B)J_{AB} \qquad (3)$$

where $S_B \leq S_A$. In eqs 2 and 3, $E_{HS}$ is the energy of the high-spin state and $E_{LS}$ is the energy of the low-spin (broken-symmetry) state. Equations 2 and 3 can be straightforwardly generalized to a set of equations for complexes with multiple magnetic centers.[6,7] While the SP and NP methods are fairly popular, other methods have been proposed in the literature such as Nishino's approach[8] and the constrained-DFT approach of Rudra et al.[9,10]

It has been shown that for the calculation of magnetic exchange couplings, hybrid functionals perform the best among several realizations of density functionals available in the literature.[3] In particular, Ruiz et al. have shown that the broken-symmetry approach in combination with the hybrid B3LYP functional[11,12] yields the best exchange couplings between several popular density functionals when compared to experimental values.[5] Valero et al. have recently shown that the M06 realization of the generalized-gradient approximation (GGA) functional yields exchange couplings as accurate as B3LYP.[13] It has been suggested that the presence of self-interaction error (SIE) in approximate density functionals mimics in some way nondynamical electron correlation contributions to the calculated energies.[14,15] Since the use of the NP approximation also accounts for electron correlation that is not included in the spin-projected approximation, it was argued by Ruiz et al. that using the broken-symmetry method in combination with a self-interaction free functional should give accurate exchange couplings,[16] although this led to some controversy.[17−19] Several authors have argued that eq 2 represents a more physically meaningful mapping between the Heisenberg and DFT models[20−24] than eq 3 and that the accuracy of B3LYP combined with eq 3 is fortuitous. Therefore, a density functional that is able to reproduce magnetic exchange couplings in combination with eq 2 would be desirable.

A new generation of density functionals that incorporate screened Hartree−Fock (HF) exchange became recently available. Such is the case of the Heyd−Scuseria−Ernzerhof (HSE) functional,[25−27] which includes a portion of short-range HF exchange in its definition that makes it suitable to treat electronic localization effects and, at the same time, computationally more efficient than traditional (global) hybrids. The LC-$\omega$PBE,[28] which incorporates long-range HF exchange to partly remove SIE, provides a not exactly one-electron, but most often "many-electron self interaction-free" functional.[29] Rivero et al. have analyzed the reliability of these range-separated hybrid functionals for describing magnetic exchange interactions using a reference database proposed by Valero et al.[13] In view of these developments, it is important to investigate the performance of these new models for the prediction of magnetic parameters. It is the purpose of this work to compare magnetic exchange couplings calculated with the range-separated HSE and LC-wPBE with those calculated with global hybrid functionals.

## Methodology

All magnetic exchange couplings were calculated from self-consistent field (SCF) energy differences for the HS and LS states, as given by eqs 2 and 3 for the SP and NP approaches, respectively. The Gaussian Development Version was used through this work.[30] The low-spin solution was obtained from an initial SCF guess generated by flipping the local spin-density in one of the metal centers of the high-spin solution. We have verified that the SCF solutions approximately represent the target Heisenberg solutions by comparing Mulliken atomic spin densities for each particular case. All calculations converged the SCF procedure to an accuracy of $10^{-8}$ hartree = 0.27 $\mu$eV in the total energy. An atom-centered numerical integration grid of 99 radial and 590 angular points (grid = ultrafine keyword in Gaussian) was employed in all cases. Geometrical structures were taken from experimental crystallographic data. All calculations were carried out using the Ahlrich's double-$\zeta$ valence plus polarization Gaussian basis for atoms other than transition metals[31] and all-electron Ahlrich's triple-$\zeta$ valence plus polarization for the metal centers.[32] Molecular data (spin configurations, total charge, and spin multiplicities), geometrical structures, and complete basis sets are available as Supporting Information.

To assess the effect of range separation in density functionals we have chosen a set of nine bimetallic transition-metal complexes containing 3d elements (V, Cr, Mn, and Cu). Five of them (compounds 1−5) present antiferromagnetically coupled magnetic centers ($J_{AB} < 0$), while the remaining four (compounds 6−9) are ferromagnetically coupled ($J_{AB} > 0$). These systems have been employed by Rudra et al. to assess the performance of a proposed methodology to evaluate magnetic exchange couplings based on constraint DFT.[9] Here we have evaluated magnetic exchange couplings for these 9 complexes using the global hybrid functionals B3LYP and PBEh,[33−35] and the range-separated hybrid functionals HSE and LC-wPBE.

## Results and Discussion

In Table 1, we show our results for the magnetic exchange couplings. Experimental values and their corresponding reference are also shown. For all four hybrid functionals, exchange couplings evaluated using the NP approach are in slightly closer agreement with the available experimental data. Our NP and SP results for the B3LYP functional are in line with those of Rudra et al.[9] (not shown in Table 1), although the calculated couplings are somewhat different. We attribute this discrepancy to the different basis set employed by Rudra et al. and this work.

For all antiferromagnetically coupled complexes (compounds 1−5), the PBEh functional yields a weaker coupling between magnetic centers as compared to B3LYP, while the trend for ferromagnetically coupled complexes is not uniform. On the other hand, the effect of truncating the long-range HF exchange in the HSE functional effectively reduces ferromagnetic exchange couplings (compounds 6−9) and increases antiferromagnetic couplings (compounds 1−5), as evidenced by comparing HSE and PBEh results. Contrarily, the LC-$\omega$PBE functional produces the opposite effect in most cases, with the exception of the $Mn^{III}Mn^{IV}$ (compound 5) and $Cu^{II}Cr^{III}$ (compound 8) complexes. In particular, PBEh and HSE show a very large deviation for the latter complex

**Table 1.** Magnetic Exchange Couplings (in cm$^{-1}$) Calculated with Different Hybrid Density Functionals[a]

| complex | B3LYP | | PBEh | | HSE | | LC-$\omega$PBE | | ref 9 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SP | NP | SP | NP | SP | NP | SP | NP | C-DFT | exptl |
| (**1**) Cu$^{II}$−Cu$^{II}$ | −84.2 | −42.1 | −59.5 | −29.8 | −63.5 | −31.8 | −40.3 | −20.1 | −16 | −30.9[b] |
| (**2**) Cu$^{II}$−Cu$^{II}$ | −101.8 | −50.9 | −79.0 | −39.5 | −83.4 | −41.7 | −58.2 | −29.1 | −44 | −37.4[c] |
| (**3**) Mn$^{II}$−Cu$^{II}$ | −36.4 | −30.4 | −27.8 | −23.2 | −29.7 | −24.8 | −18.5 | −15.4 | −128 | −15.7[d] |
| (**4**) V$^{IV}$−V$^{IV}$ | −100.2 | −50.1 | −82.3 | −41.1 | −87.4 | −43.7 | −62.4 | −31.2 | −83 | −107[e] |
| (**5**) Mn$^{III}$ Mn$^{IV}$ | −171.0 | −136.8 | −138.0 | −110.4 | −142.5 | −114.0 | −152.7 | −122.1 | −128 | −110[f] |
| (**6**) Cu$^{II}$−Cu$^{II}$ | 103.5 | 51.7 | 140.6 | 70.3 | 133.8 | 66.9 | 247.7 | 123.8 | 112 | 84[g] |
| (**7**) Cu$^{II}$−Cu$^{II}$ | 131.9 | 66.0 | 119.9 | 60.0 | 119.2 | 59.6 | 120.2 | 60.1 | 57 | 57[h] |
| (**8**) Cu$^{II}$ Cr$^{III}$ | 14.6 | 11.0 | 170.9 | 128.2 | 169.1 | 126.8 | 8.1 | 6.1 | 23 | 18.5[i] |
| (**9**) Cu$^{II}$ Mn$^{III}$ | 75.6 | 60.5 | 28.8 | 23.1 | 10.8 | 8.7 | 46.9 | 37.5 | 75 | 54.4[i] |
| MAE | 36.2 | 19.8 | 48.1 | 26.1 | 50.1 | 28.4 | 40.6 | 19.9 | 25.4 | |
| MAE excluding (**8**) | 40.2 | 21.3 | 35.0 | 15.6 | 37.5 | 18.4 | 44.3 | 20.9 | | |

[a] MAE indicates the mean absolute error compared with experimental data. Magnetic exchange couplings taken from ref 9 are based on constraint-DFT (C-DFT) calculations. [b] Taken from ref 43. [c] Taken from ref 44. [d] Taken from ref 45. [e] Taken from ref 46. [f] Taken from ref 47. [g] Taken from ref 48. [h] Taken from ref 49. [i] Taken from ref 50.

compared with the B3LYP and LC-$\omega$PBE functionals and experimental results. In most cases, HSE and PBEh exchange couplings differ a few cm$^{-1}$, with the exception of compound 9 where the difference is about 14 cm$^{-1}$. This implies that the truncation of the long-range HF exchange in the HSE functional has little impact on the calculated magnetic exchange couplings.

Overall, B3LYP and LC-$\omega$PBE provide a very good agreement with experimental values when the NP approximation is employed to map the DFT energies to the model Hamiltonian energies. This has been noted by different authors,[3,13,16] although there is some discrepancy about the physical grounds of this approach.[18,36] LC-$\omega$PBE and B3LYP yield very similar mean absolute errors (MAEs), although individual magnetic exchange couplings are somewhat different. Using the open-shell database of Valero and co-workers,[13] Rivero et al. have shown that the HSE functional is able to provide better magnetic exchange couplings when the SP instead of the NP approximation is used.[37] The reference database employed in that work consisted of 10 systems with two spin 1/2 magnetic centers: the H−He−H model system, two first-row compounds, and seven Cu−Cu complexes. Our results, however, do not show such conclusive evidence: Magnetic exchange couplings calculated with PBEh, HSE, and LC-$\omega$PBE are comparable to those calculated with B3LYP, being the latter slightly better. However, if complex 8 is excluded, the B3LYP MAE in Table 1 is the largest of all the functionals included in this work. Notably, in this case, PBEh and HSE provide the best agreement with the experimental data, although all four functionals give close MAEs.

It should be pointed out that it is not the purpose of this work to assess the performance of different functionals against experimental data. Instead, we aim to compare the effect of range-separation on the calculation of magnetic exchange couplings. The comparison of our results with existing assessments suggest that larger test sets need to be employed to assess the performance of different methods for magnetic exchange couplings.

An implicit assumption in the evaluation of magnetic exchange couplings by equating the DFT and Heisenberg energy differences is that the DFT model is able to mimic the behavior of the Heisenberg model (eq 1), which implies

**Table 2.** Deviation from the Heisenberg Model As Given by the Parameter $\eta(\times 10^{-3})$ as Defined in Equation 4[a]

| complex | B3LYP | PBEh | HSE | LC-$\omega$PBE |
|---|---|---|---|---|
| (**1**) Cu$^{II}$−Cu$^{II}$ | 1.67 | 2.69 | 2.75 | 2.97 |
| (**2**) Cu$^{II}$−Cu$^{II}$ | 10.10 | 7.24 | 7.90 | 3.77 |
| (**3**) Mn$^{II}$−Cu$^{II}$ | 9.52 | 7.41 | 7.81 | 5.96 |
| (**4**) V$^{IV}$−V$^{IV}$ | 4.23 | 2.93 | 3.19 | 2.21 |
| (**5**) Mn$^{III}$ Mn$^{IV}$ | 22.05 | 16.85 | 17.35 | 16.02 |
| (**6**) Cu$^{II}$−Cu$^{II}$ | 3.96 | 6.39 | 6.07 | 11.09 |
| (**7**) Cu$^{II}$−Cu$^{II}$ | 4.73 | 4.56 | 4.56 | 4.15 |
| (**8**) Cu$^{II}$ Cr$^{III}$ | 26.56 | 28.16 | 84.90 | 10.61 |
| (**9**) Cu$^{II}$ Mn$^{III}$ | 40.98 | 14.15 | 18.65 | 0.29 |

[a] Smaller values of $\eta$ indicate lesser variation of the local magnetization at the metallic centers between both high-spin and low-spin solutions.

that the magnetization at each center is the same for both spin configurations. Although this concept is difficult to quantify, a masure of the deviation of the DFT system from an ideal Heisenberg model can be given by the parameter

$$\eta = \left| \frac{S_A^{HS} S_B^{HS} + S_A^{LS} S_B^{LS}}{2(S_A^{HS} S_B^{HS} - S_A^{LS} S_B^{LS})} \right| \qquad (4)$$

where $S_{A,B}^{HS,\,LS}$ are the local magnetic moments (or integrated spin densities) at magnetic centers $A$ and $B$ for the HS and LS configurations. The parameter $\eta$ is zero for the ideal case where both the HS and LS spin states hold the same local magnetization at both, $A$ and $B$, magnetic centers. It should be commented that in the approximation proposed by Rudra et al.[9,10] the parameter $\eta$ is exactly zero because of the constraint imposed in the local magnetic moements. Although there are several methods for partitioning the density and spin density into atomic contributions, we have chosen Mulliken population to estimate $S_{A,B}^{HS,\,LS}$ since it is the most widely used method, although other partitioning methods based on local projectors[38−41] might be more suitable for large systems with many magnetic centers. Importantly, since the parameter $\eta$ is based on differences of atomic spin populations between the LS and HS states, one would not expect that the values of $\eta$ obtained using other population methods will follow the same trend for different density functionals. In Table 2 we show calculated values of $\eta$ for all the complexes and density functionals employed in this

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work. In all cases, $S_{A, B}^{HS, LS}$ include atomic spin densities of the metallic centers and surounding atoms with non-negligible magnetization. Overall, the parameter $\eta$ is smaller for LC-$\omega$PBE followed by PBEh, HSE, and B3LYP, in that order. This indicates that among the four hybrid functionals utilized in this work, B3LYP does the worst job in mimicking the Heisenberg behavior of all nine bimetallic complexes. This is in line with the observation of Rivero et al. that LC-$\omega$PBE and HSE enhance the localization of the spin-density with respect to B3LYP, improving the description of spin localization (and hence magnetic exchange couplings) in these type of systems.[37,42]

## Conclusions

We have investigated the effect of Hartree−Fock range-separation on the calculation of magnetic exchange couplings by comparing magnetic exchange couplings using two global hybrid functionals, B3LYP and PBEh, with the short-range separated HSE and the long-range corrected LC-$\omega$PBE in a test set of nine bimetallic transition-metal complexes containing 3d elements. Although our results show that there is no clear superiority of any of these functionals when comparing with experimental data, the LC-$\omega$PBE provides a better description of the magnetization on the metallic centers, yielding self-consistent solutions for the high-spin and low-spin states that mimic more closely a Heisenberg-like behavior. The comparison of our results with existing assessments involving these same functionals separately suggest that larger test sets including all these functionals need to be employed to assess their performance for the prediction of magnetic exchange couplings.

**Supporting Information Available:** Molecular data (spin configurations, total charge and spin multiplicities), atomic Cartesian coordinates, and complete basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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