Magnetic coupling constants from a hybrid density functional with 35% Hartree-Fock exchange

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The magnetic coupling constants of $KCuF_3$, $Sr_2CuO_2Cl_2$, La_2CuO_4, La_2NiO_4, K_2NiF_4, $KNiF_3$, NiF_2, $KMnF_3$, and MnF_2 are calculated with a hybrid density functional, in which 35% of the nonlocal Hartree-Fock exchange is mixed in the general gradient approximation to the density functional theory. The theoretical magnetic coupling constants for these materials with different structures, spins, and magnetic orderings are in good agreement with experiment. Our results improve significantly over the so-called B3LYP hybrid density functional, which usually overestimates the magnetic coupling constants by about 50%. However, the energy gaps from the B3LYP functional are in better agreement with experiment than the hybrid functional with 35% Hartree-Fock exchange, which means that within the current scheme of hybrid density functionals different functionals are needed to better predict different properties of materials.

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I. INTRODUCTION

The discovery of high temperature superconductors has caused great interest in the correlated electronic systems. The parent compounds of high temperature superconductors and some transition metal oxides have antiferromagnetic (AFM) insulating ground states. For example, La_2CuO_4 has a two-dimensional AFM ordering in the CuO_2 plane and weak interlayer magnetic coupling. The low-lying excited states of these magnetic materials are generally described by the Heisenberg Hamiltonian

$$\hat{H} = \sum_{i,j} J_{ij} \hat{S}_i \cdot \hat{S}_j, \tag{1}$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin operators on sites i and j, J_{ij} the magnetic coupling constant between $\hat{S}_i$ and $\hat{S}_j$. J can be extracted from the total energy differences of different magnetic states of Eq. (1). There are several theoretical methods for calculating the magnetic coupling constants with different precisions. In the cluster approach the Heisenberg Hamiltonian can be solved for a cluster with two magnetic sites to get the total energies of various magnetic states, and the total energies of the real materials can be obtained by configuration interaction methods.[1]

In the periodic approach the total energies of materials are calculated with unrestricted Hartree-Fock (UHF) and various approximations to density functional theory, such as local density approximation (LDA) and generalized gradient approximation (GGA). Since a Slater's determinant is not an eigenstate of the Heisenberg Hamiltonian, the coupling constants are extracted from the total energy differences between different magnetic phases of the Ising Hamiltonian

$$\hat{H}_{\mathrm{Ising}} = \sum_{i,j} J_{ij} \hat{S}_{iz} \cdot \hat{S}_{jz}. \tag{2}$$

In the Ising Hamiltonian there are no transverse fluctuations of spins, which have important effects on the magnetic properties of materials. It seems a rude approximation to use the Ising Hamiltonian to extract the magnetic coupling constants. However, it is shown that in some cases the mappings between the Ising and the Heisenberg Hamiltonians justify the extracting of magnetic coupling constants with the Ising Hamiltonian.[2–5]

For a general spin dimer it is proved that the highest spin (HS) state is an eigenstate of both the Heisenberg and the Ising Hamiltonians with the same eigenvalue and that the eigenvalue of the Ising Hamiltonian for the broken symmetry (BS) spin state is the same as the expectation value of the Heisenberg Hamiltonian for the same BS spin state.[5] Since the Heisenberg Hamiltonian has not exactly been solved for dimensions above one, it is not possible to build a general mapping between the Heisenberg and the Ising Hamiltonians. However, some theoretical results from the cluster approach based on the Heisenberg Hamiltonian suggest that J is a local quantity; good results can be obtained with a cluster containing only two magnetic sites.[1]

The UHF approach can recover only about 30% of the experimental values of magnetic coupling constants. For some strongly correlated electronic systems, such as CoO, FeO, and parent compounds of high temperature cuprate superconductors, LDA and GGA could not predict the correct ground states. So, the application of LDA and GGA in calculating the magnetic coupling constants is limited. In the applicable cases the magnetic coupling constants from LDA and GGA approaches are often significantly overestimated. The so-called B3LYP hybrid density functional method could correctly predict the ground states of strongly correlated electronic systems.[6–9] However, the B3LYP magnetic coupling constants are usually 50% larger than the experimental ones.

Dai and Whangbo suggested a method for calculating magnetic couping constants within the density functional theory on the basis of transition state concept.[10] By expanding the total energies of the HS and BS states around the transition state the difference of total energies of the HS and BS states are calculated with orbital energies which are obtained by a single calculation. The theoretical results for

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Rb_2MnF_5 and Cs_2MnF_5 are in much better agreement with experiment than the usual total-energy-difference method. The theoretical values deviate from the experimental ones by about 20%. The problem with the method is that self-consistent convergences are not reached for some materials, such as Na_2MnF_5, Li_2MnF_5, and $(NH_4)_2MnF_5$.[10]

Recently, I. de P. R. Moreira *et al.* have studied the effects of the Hartree-Fock (HF) exchange on the electronic structure and magnetic couplings in NiO by changing the percentage of HF exchange in the B3LYP hybrid functional.[11] It is found that 35% HF exchange mixed in the GGA density functional gives a reasonably balanced description of some structural, electronic, and magnetic properties of NiO. NiO has a three-dimensional AFM ordering with ferromagnetic (111) planes and alternating spins in neighboring planes. In this paper we apply the hybrid density functional with 35% HF exchange to several materials with different structures, spins, and magnetic orderings, i.e., La_2CuO_4, La_2NiO_4, $Sr_2CuO_2Cl_2$, $KCuF_3$, $KMnF_3$, $KNiF_3$, K_2NiO_4, MnF_2, and NiF_2. $KCuF_3$ is a one-dimensional antiferromagnet. La_2CuO_4, La_2NiO_4, and $Sr_2CuO_2Cl_2$ are usually thought of as two-dimensional square Heisenberg antiferromagnets. $KMnF_3$ and $KNiF_3$ have ferromagnetic (111) planes and alternating spins in the neighboring planes. In MnF_2 and NiF_2 the magnetic coupling between the next nearest magnetic ions are not negligible compared with the one between the nearest magnetic ions. Our results show that the theoretical J values extracted from the total energy differences obtained with the hybrid density functional with 35% HF exchange are in good agreement with experiment.

II. CALCULATION METHOD

The hybrid density functional used in the present work and in Ref. 11 is a variant of the so-called B3LYP hybrid density functional. In the B3LYP hybrid density functional the HF exchange energy is mixed into the total energy functional of GGA.[6] The argument for mixing the HF exchange into the exchange-correlation energy is based on the adiabatic connection formula.[6] The weights for the gradient-corrected correlation energy, local exchange energy, and the nonlocal HF exchange were determined by a linear least-squares fitting of the thermochemical properties of some atoms and molecules to experiments. Twenty percent of the nonlocal HF exchange gives theoretical results in good agreement with experiment. In the B3LYP scheme the Perdew-Wang[12] gradient-corrected correlation energy, which was used in the original work of Becke,[6] is replaced by Lee-Yang-Parr correlation energy.[13]

The admixture of HF exchange has important effects on the electronic and magnetic properties of materials, especially for correlated electronic systems. It has been realized that the success of the B3LYP functional in strongly correlated antiferromagnetic materials results from the reduction of the self-interaction due to the introduction of HF exchange. However, the removal of self-interaction is not enough to get good results for highly correlated systems. A better correlation energy is also essential to take the correlation effects into account. The successful application of the method to semiconductors, where self-interaction is not important, indicates that the B3LYP hybrid functional has a better correlation energy than LDA and GGA have.

In this paper the percentage of the nonlocal HF exchange has been changed from 20% in the B3LYP approach to 35%. The calculations are carried out with the CRYSTAL package.[14] The basis vectors for expanding the Kohn-Sham orbitals are linear combinations of atom-centered Gaussian basis sets.[15] In the calculations on $KCuF_3$, 60 and 80 points in the irreducible part of the first Brillouin zone were used for the ferromagnetic and antiferromagnetic states, respectively. For La_2CuO_4, La_2NiO_4, and $Sr_2CuO_2Cl_2$, 59 and 105 points were used for ferromagnetic and antiferromagnetic phases, respectively. For the other materials, a shrinking factor of 8 has been adopted for forming a regular reciprocal mesh in the first Brillouin zone. We adopt 7, 7, 7, 7, and 14 as the integral tolerances to obtain high precision in monoelectronic and bielectronic integrals. The total energy convergence threshold exponent is set as 7. Supercells have been built to take the antiferromagnetic orderings into account. For comparisons, B3LYP calculations were also carried out with the same basis sets and precisions.

III. RESULTS AND DISCUSSION

For La_2CuO_4, La_2NiO_4, and $Sr_2CuO_2Cl_2$ the antiferromagnetic ordering is mainly of two-dimensional character. The interlayer magnetic coupling is about two orders of magnitude weaker than the intralayer one. Due to the Jahn-Teller distortion of CuF_6 the Cu-Cu distance along the c-axis is shorter than the Cu-Cu distance in the ab plane. $KCuF_3$ is of one-dimensional antiferromagnetic ordering along the c-axis with weak ferromagnetic coupling in the ab plane. Our calculations show that both B3LYP and the hybrid density functional with 35% HF exchange can correctly predict that the antiferromagnetic states are lower than the ferromagnetic states for all the materials studied in this paper.

For materials with leading nearest neighbor magnetic coupling constants the coupling constants can be obtained from the difference of total energies of ferromagnetic and antiferromagnetic phases, $\Delta E = Js^2Z$. ΔE is the energy difference per magnetic ion, Z the nearest number of magnetic ions ($Z=2$ for $KCuF_3$ and $Z=4$ for the other three materials). s is the spin, $\frac{5}{2}$ for Mn, 1 for Ni, and $\frac{1}{2}$ for Cu. In Table I the magnetic coupling constants from the hybrid density functional with 35% HF exchange are compared with UHF, B3LYP, and experimental results. The experimental lattice parameters are used in the calculations. For MnF_2 and NiF_2 the supercells and equations reported in Ref. 16 are adopted to extract the nearest and next nearest magnetic coupling constants. The lattice parameters of $Sr_2CuO_2Cl_2$, La_2CuO_4, La_2NiO_4, and untwisted $KCuF_3$, K_2NiF_4, $KMnF_3$, $KNiF_3$, MnF_2 and NiF_2 are taken from Refs. 17–25 respectively. From Table I one can see that magnetic coupling constants from the hybrid density functional with 35% HF exchange are in good agreement with experiment. As for other magnetic materials UHF approach recovers only about 30% of the experimental values. B3LYP results are about 50% larger than the experimental ones. The magnetic coupling constants

TABLE I. The magnetic coupling constants (in milli-electron volt) from UHF, B3LYP, and the hybrid density functional with 35% HF exchange are compared with experimental results of $Sr_2CuO_2Cl_2$, La_2CuO_4, untwisted $KCuF_3$, La_2NiO_4, $KNiF_3$, K_2NiF_4, and NiF_2.

	UHF	B3LYP	35% HF	Exp.
$Sr_2CuO_2Cl_2$	27.95, 26.21[a]	189.83	121.60	125[b]
La_2CuO_4	36.1[c]	205.34	133.55	128,[d] 135[e]
$KCuF_3$	7.9[f]	57.13	31.67	32.2–35.0[g]
La_2NiO_4	9.2[c]	40.65	27.51	30[h]
$KNiF_3$	2.57[i]	14.86	9.32	8.75[j]
K_2NiF_4	5.39[k]	15.38	9.74	8.27–8.96[j]
$NiF_2(J_1)$	−0.400[l]	−0.592	−0.0357	−0.0273[j]
$NiF_2(J_2)$	0.223[l]	2.91	1.63	1.72[j]
$KMnF_3$	0.214[i]	1.36	0.950	0.64[j]
$MnF_2(J_1)$	−0.206[l]	−0.120	−0.0581	−0.0545[j]
$MnF_2(J_2)$	0.0734[l]	0.627	0.408	0.304[j]

[a]Reference 26.
[b]Reference 27.
[c]Reference 4.
[d]Reference 28.
[e]Reference 29.
[f]Reference 30.
[g]Reference 31.
[h]Reference 32.
[i]Reference 33.
[j]Reference 34.
[k]Reference 35.
[l]Reference 16.

from the hybrid density functional with 35% HF exchange are comparable to the results of cluster approaches, in which sophisticated configuration interaction calculations are used to extract J directly from the Heisenberg Hamiltonian for clusters containing two magnetic ions.[1,36] The cluster approaches give magnetic coupling constants of 31.28 meV for untwisted $KCuF_3$,[36] 119.5 and 144.8 meV for $Sr_2CuO_2Cl_2$ and La_2CuO_4, respectively.[1]

The reason for the underestimation of magnetic coupling constants by UHF is well-known. The kinetic exchange mechanism in the Hubbard model gives magnetic coupling constant $J=t^2/U$, where t and U are the transfer integral and the on-site Coulomb interaction, respectively. In the UHF approach the correlation effects have been ignored, which leads to a large U and a small J. For the B3LYP hybrid density functional the mixing of nonlocal HF exchange has greatly reduced the self-interaction inherent in the usual LDA and GGA approximations to the density functional theory. This mechanism enables B3LYP to correctly predict that the ground states of some strongly correlated electronic systems are antiferromagnetic insulators, such as parent compounds of high temperature superconductors, for which LDA and GGA give nonmagnetic metallic ground states. The B3LYP functional presents significant improvement over UHF in describing the electronic properties of materials, such as energy gaps and core level energies. However, the B3LYP results of magnetic coupling constants did not improve much over the UHF ones. The above results indicate that the correlation energy in the hybrid density functional with 35% HF exchange is better than that in the B3LYP functional in describing magnetic properties of materials.

TABLE II. The energy gaps (in electron volt) of the antiferromagnetic insulating ground states from UHF, B3LYP, and the hybrid density functional with 35% HF exchange are compared with experimental results of $Sr_2CuO_2Cl_2$, La_2CuO_4, La_2NiO_4, and untwisted $KCuF_3$.

	$Sr_2CuO_2Cl_2$	La_2CuO_4	La_2NiO_4	$KCuF_3$
UHF	15.9[a]	~17[b]	~17[b]	17.7[c]
B3LYP	2.52	2.17	2.62	3.93
35% HF	4.85	4.38	4.30	7.01
Exp.	1.65[d]	2.0[e]	~4[f]	

[a]Reference 26.
[b]Reference 4.
[c]Reference 30.
[d]Reference 37.
[e]Reference 38.
[f]Reference 39.

To see if the hybrid density functional could also be used for studying other properties of materials, the energy gaps from the hybrid density functional containing 35% HF exchange are shown in Table II. They are larger than the experimental and B3LYP results. This is also the case for other materials, such as NiO. The energy gaps of some semiconductors and strongly correlated electronic systems predicted by B3LYP density functional are usually in good agreement with experiment.[40] The 20% HF exchange in the B3LYP density functional is obtained by fitting the theoretical results of atomization energies, ionization potentials, proton affinities, and total atomic energies of some atoms and molecules to experiment. These properties are related to the electronic properties. Especially, the ionization potential is directly related to the orbital energies of electrons. This is the reason why the energy gaps from the B3LYP functional, which is obtained by optimizing the coefficients with respect to the electronic properties, are in good agreement with experiment. The systematic deviation of B3LYP magnetic coupling constants from experiment means that its coefficients, especially the weight coefficient representing the percentage of nonlocal HF exchange, are not the optimum set of parameters for studying magnetic properties of materials. The results shown in Table I suggest that 35% HF exchange is especially suitable for calculating the magnetic coupling constants of magnetic materials. The theoretical results of magnetic coupling constants and energy gaps from the two hybrid density functionals suggest that to get better theoretical predictions on a specific property of materials different percentage of HF exchange is needed.

IV. CONCLUSION

The hybrid density functional with 35% HF exchange can correctly predict that ground states of $KCuF_3$, $Sr_2CuO_2Cl_2$, La_2CuO_4, La_2NiO_4, K_2NiF_4, $KNiF_3$, NiF_2, $KMnF_3$, and

MnF_2 are antiferromagnetic insulators. The magnetic coupling constants for the nine materials which have different structures, spins, and magnetic orderings, obtained from the hybrid density functional improved significantly the B3LYP results and are in good agreement with experiment. However, 35% HF exchange gives larger energy gaps than B3LYP and experimental results. Within the current scheme of hybrid density functionals different percentages of HF exchange are needed to obtain more accurate results of different properties of materials.

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