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The B3LYP hybrid density functional study on solids

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Abstract The B3LYP hybrid density functional method, which is very successful in the study of thermochemistry of atoms and molecules, has been applied to some periodic systems recently. The applications to solids and surfaces show that the B3LYP hybrid functional reproduces the experimental energy gaps and magnetic moments for a variety of materials.

Keywords B3LYP, solid, surface

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1 Introduction

B3LYP hybrid density functional [1,2] was originally developed to improve the description of the ground state energetics of small molecules. Subsequently, it has been demonstrated to be significantly more reliable than the local density approximation (LDA) and generalized gradient approximation (GGA) functionals for computing atomization enthalpies [3, 4], geometries and vibrational frequencies [5]. The application of this method in periodic calculations of solids has been inhibited by difficulties in computing the nonlocal Fock exchange. These problems have now been overcome and recently a number of solid state studies have been performed for both bulk and surface phases.

In the LDA and GGA calculations on solids especially the transition metal oxides, which are prototypes of Mott insulators [6], some specific properties are not well described because of the strong Coulomb repulsion between the two 3d electrons on the transition metal ions. The conventional

energy band calculations based on the LDA and GGA failed to predict the correct ground states for some of these strongly correlated phases, such as FeO, CoO, CaCuO₂, La₂CuO₄, etc. [7]. And the energy gap of NiO is severely underestimated. These failures result from a serious problem in the LDA and GGA calculations, i.e., the unphysical self-interaction is not cancelled in their energy functionals which is not important in common metals because the quasiparticles are itinerant, but makes them poor for strongly correlated systems with localized 3d or 4f orbitals since the self-interaction tends to delocalize the 3d or 4f electrons. The simple Hartree-Fock (HF) approximation is able to predict the correct ground states for the strongly correlated insulators due to the lack of self-interaction, while the energy gaps and magnetic moments are always overestimated due to the inadequate consideration on correlations.

In the B3LYP hybrid functional scheme, the nonlocal Hartree-Fock (HF) approach is mixed into the energy functional of the GGA. Here, the Perdew-Wang [8] gradient-corrected correlation energy, which was used in the original work of Becke [1], is replaced by Lee-Yang-Parr correlation energy [2]. The exchange-correlation energy functional can be written as:

$$E_{xc} = (1 - A) (E_x^{\text{LDA}} + BE_x^{\text{Becke}}) + AE_x^{\text{HF}} + (1 - C)E_c^{\text{VWN}} + CE_c^{\text{LYP}} \quad (1)$$

in which the local density functional of Vosko, Wilk, and Nusair is used for E_x^{LDA} and E_c^{VWN} . E_x^{HF} is the exact nonlocal HF exchange energy. E_x^{Becke} and E_c^{LYP} are the Becke's and Lee-Yang-Parr's gradient corrections for the local exchange and correlation energies, respectively. The weight coefficients for the gradient-correlated correlation energy, local exchange energy, and the exact HF exchange terms were determined by a linear least-square fitting of the thermochemical properties of some atoms and molecules to the experiments. 20 % of the exact HF exchange energy in the exchange-correlation energy gives theoretical results in good agreement with experiments. The optimum values for the parameters A (Fock exchange percentage), B (exchange

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weight of the non-local part of exchange), and C (weight of the non-local correlation) are 0.20, 0.9, and 0.81, respectively.

2 Applications on bulks

Bredow and Gerson have calculated the lattice constants, heats of atomization, and electronic structures of MgO, NiO, and CoO [9] using the *ab initio* HF, GGA, and hybrid functionals. The results showed that the B3LYP leads to a consistent description of the electronic and structural properties in comparative studies of the three compounds. And the B3LYP method is the only approach among those investigated that gives reasonable to good agreement with experiment for all properties. They suggested that the B3LYP is the best choice for comparative investigations on different oxides of main-group elements and transition metals. Using the B3LYP functional, Muscat *et al.* [10]. studied the band gaps of a variety of materials, including the semiconductors (Si, diamond, and GaAs), semi-ionic oxides (ZnO, Al₂O₃, and TiO₂), sulphides (FeS₂, ZnS), an ionic oxide (MgO) and the transition metal oxides (MnO and NiO). The B3LYP gives rather accurate energy gaps for some semiconductors [10], which is a significant improvement over LDA results. It has been well known that LDA gives energy gaps of semiconductors underestimated over 30 %. Agreement with experimentally derived band gaps is at least as good as that obtained with sophisticated correlated calculations or perturbation theories. They found the B3LYP functional is straightforward to implement, computationally efficient and produces ground state energy surfaces which are significantly more accurate than those computed with the best GGA methods currently in use. Perry *et al.* [11] performed band-structure calculations on the high-temperature superconductor parent compound, La₂CuO₄ using the B3LYP functional. The result showed that the band structure is in agreement with the SIC-LSD and LDA+U schemes, with the energy gap being in better agreement with experiment [11]. Feng [12] studied the electronic and magnetic properties of CoO and MnO within the B3LYP hybrid density functional method. The ground states have been correctly predicted by the B3LYP functional, and it gives better results for energy gaps, magnetic moments, and core-level binding energies than GGA and the unrestricted Hartree-Fock (UHF) method. The B3LYP results for energy gaps, magnetic moments and core-level binding energies are between the GGA and UHF ones for antiferromagnetic, ferromagnetic and nonmagnetic phases of MnO and CoO. Feng and Harrison [13] applied the B3LYP functional to the electronic structure calculation of the infinite layer compound CaCuO₂. The results showed that the theoretical energy gap and magnetic moment are in excellent agreement with the experiments. The ratio of intralayer to interlayer magnetic coupling constants and lattice parameters are also in good accordance with the experiments.

Ruiz *et al.* [14] calculated the magnetic coupling constant of the high-temperature phase of CuGeO₃ using the HF, LDA, GGA and B3LYP methods. It was found that the hy-

brid method B3LYP gives the most accurate values for the magnetic coupling constant J . And the B3LYP functional was used to predict the magnetic coupling constants of the other solid state transition metal compounds: the silver copper oxide Ag₂Cu₂O₃, and the family of M[N(CN)₂]₂ (M = Cr (II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)). Recently Bredow *et al.* [15] studied the electronic and magnetic structure of the low-temperature phase of ScMnO₃ from B3LYP functional, the optimized structure is in good agreement with the experiments. And in agreement with experimental estimates [16], they found the interband transition at 3.3 eV with B3LYP. However, the B3LYP gives a much larger value (13.9 meV) of magnetic coupling constants than the experimental value (5.5–7.0 meV). The overestimation of magnetic coupling constants within the B3LYP functional is also found in materials of KCuF₃, Sr₂CuO₂Cl₂, La₂CuO₄, La₂NiO₄, K₂NiF₄, KNiF₃, NiF₂, KMnF₃, and MnF₂ [17]. With a hybrid density functional, in which 35 % of the nonlocal HF exchange is mixed in the general gradient approximation to the density functional theory, Feng *et al.* [17] found the calculated magnetic coupling constants for these materials with different structures, spins, and magnetic orderings are in good agreement with experiment. Their results improved 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 % HF exchange, which means that within the current scheme of hybrid density functionals different functionals are needed to better predict different properties of materials.

Besides the bulks, the B3LYP has also been applied to some surface systems. Wander *et al.* [18] studied the structure of the ZnO (10 $\bar{1}0$) surface has been determined by using *ab initio*, all-electron total energy calculations. By employing local basis sets based on Gaussians, and a hybrid density functional (B3LYP), results in excellent agreement with experiment have been obtained for the geometric and electronic structure. In a later work [19], for the first time they performed the B3LYP total energy calculations on the polar surfaces of an oxide material (ZnO) without artificially removing the macroscopic electric field. The experimental and theoretical relaxations are in good agreement. The polar surfaces are shown to be very stable.

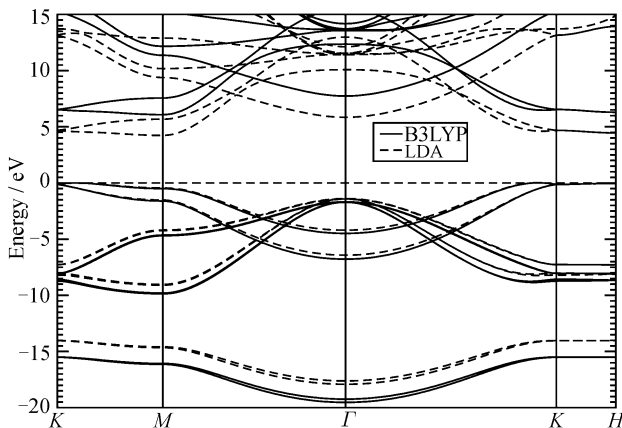
3 Our works

We also applied the B3LYP functional to some solids such as boron nitride (BN) nanotube [20] and Na_{0.5}CoO₂ material [21] using the the CRYSTAL03 software [22]. The CRYSTAL03 package performs *ab initio* calculations of the ground state energy, energy gradient, electronic wave function and properties of periodic systems. The B3LYP hybrid functional can be used directly. It is also possible to incorporate part of the exact HF exchange into some other exchange functional through the keyword HYBRID. Any

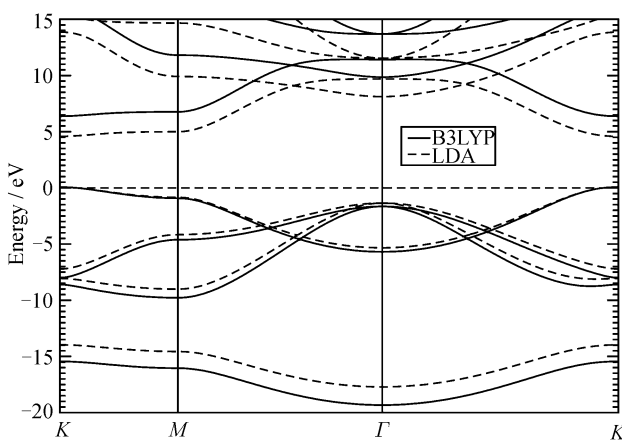
mixing (0–100 %) of exact HF and DFT exchange can be used. NONLOCAL allows modifying the relative weight of the local and non-local part both in the exchange and the correlation potential with respect to standard definition of GGA type potentials. As it is not convenient within the commonly used plane wave basis sets it is implemented readily and very efficiently within a Gaussian basis set in the CRYSTAL package. The main numerical approximation is the selection of the local Gaussian basis set. For many materials high quality basis sets have been developed which are available on the website of <http://www.crystal.unito.it>.

3.1 BN nanotube

In our work of BN nanotube [20], we first studied bulk h-BN and BN sheet. Figure 1 showed the band structures for bulk h-BN and BN sheet. In addition, their LDA band structures were also shown in Fig. 1. We found that both B3LYP and LDA predict an indirect band gap between the bottom of the conduction band at the M point and the top of the valence band near K . The indirect and direct band gaps for bulk h-BN were shown in Table 1. The agreement between our B3LYP band gaps and previous GW values [23] is



(a) Band structure for h-BN



(b) Band structure for BN sheet

Fig. 1 (Dashed line) B3LYP and LDA band structures of (a) Bulk h-BN and (b) An isolated BN sheet.

very good. In fact, besides the band gap agreement, we found the B3LYP band structure also agrees well with the GW result: the difference between B3LYP result and LDA one is strongly dependent on the degree of orbital localization and that the overall corrections can not be reproduced by a rigid band shift of the conduction states with respect to the top of the valence states. For the isolated BN sheet, our results indicated that it is a direct gap at K semiconductor with a energy gap of 4.50 eV and 6.30 eV within LDA and B3LYP respectively. The good agreement between our B3LYP results and GW ones indicates that B3LYP describes very well the band gap and band structure for such systems composed by BN layers.

Table 1 Band gaps of bulk h-BN.

E_g /eV	B3LYP	Our LDA	Others' LDA [23]	GW [23]
Direct	6.33	4.48	4.46	6.47
Indirect	6.06	4.22	4.02	5.95

Then we turned to study the electronic and piezoelectric properties of the BN nanotubes. The result of B3LYP supported previous LDA results that the energy gap of small zigzag BN nanotubes decreases rapidly with the decrease of radius, whereas, the energy gap of armchair BN nanotubes almost remains constant. The obtained B3LYP band gap is larger than the LDA one by almost constant (about 1.8 eV) for nanotubes with various chirality and radius. We gave an alternative interpretation that the absorption lines at 4.45 eV might be due to the electron transition in small zigzag BN nanotubes. The piezoelectric constant within the B3LYP formalism for zigzag BN nanotubes are substantially larger than those in the PVDF polymer family, thus piezoelectric BN nanotubes held promise for application in nanometer scale sensors and actuators.

3.2 $\text{Na}_{0.5}\text{CoO}_2$

The B3LYP hybrid density functional method has been adapted to examine the electronic and magnetic properties of $\text{Na}_{0.5}\text{CoO}_2$ [21]. A charge ordered AFM insulating state was unambiguously identified as the ground state of $\text{Na}_{0.5}\text{CoO}_2$. Figure 2 showed the band structures for the FM and AFM states of $\text{Na}_{0.5}\text{CoO}_2$. Both the FM and AFM states are insulating with a direct band gap at M , as can be seen from the band structures. The insulating ground state agrees with the experimental findings. In addition, by comparing the hybrid density functional results with our previous DFT+ U results [24], we found when $U = 4$ eV the electronic and magnetic properties of $\text{Na}_{0.5}\text{CoO}_2$ is similar except for the band discrepancy. The results suggest that the hybrid density functional method is good in dealing with strongly correlated systems such as Na_xCoO_2 .

The Fermi surface topology of the paramagnetic Na_xCoO_2 was also studied by the B3LYP method. We first studied a single $(\text{CoO}_2)^{0.5-}$ layer model with the percentage of the nonlocal Hartree-Fock exchange changing from 0 % to 20 %. The results were shown in Fig. 3. Only when the mixed

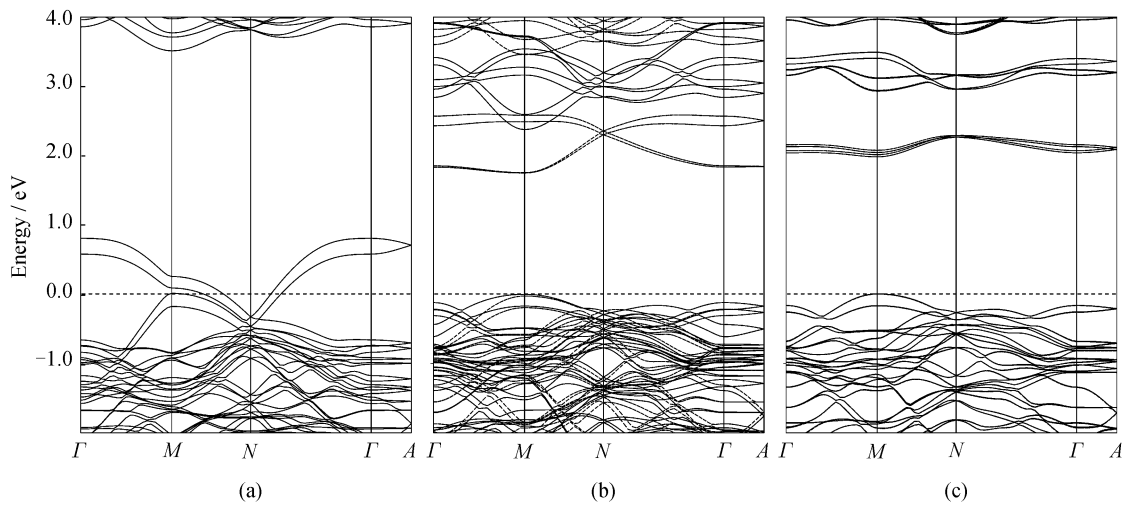


Fig. 2 Electronic band structure of $\text{Na}_{0.5}\text{CoO}_2$ in the B3LYP scheme: (a) The PM state, (b) The FM state, and (c) The AFM state. For an insulating state the top of the valence band is taken as the reference energy.

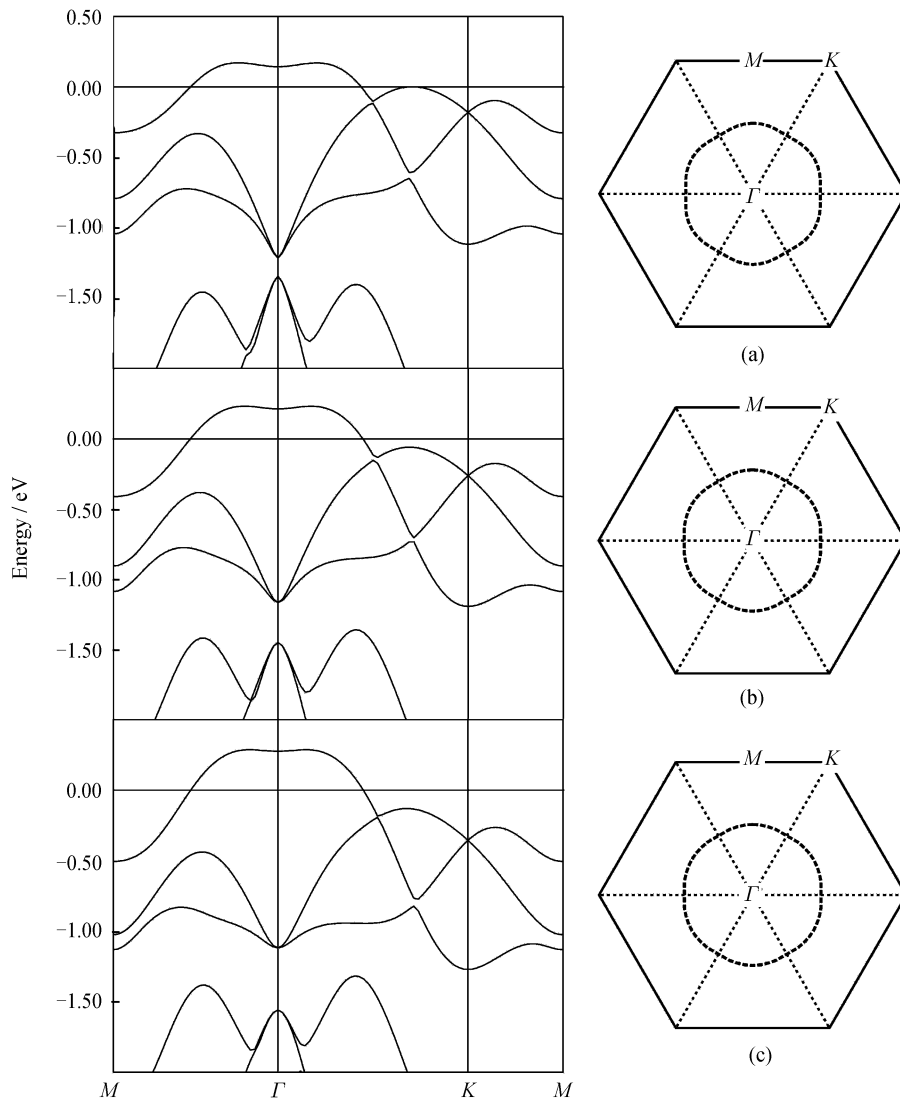


Fig. 3 (a) The FS topology of $(\text{CoO}_2)^{0.5-}$ with 1 % HF exchange in the hybrid density functional; (b) The FS topology of $(\text{CoO}_2)^{0.5-}$ with 3 % HF exchange in the hybrid density functional; (c) The FS topology of $(\text{CoO}_2)^{0.5-}$ with 5 % HF exchange in the hybrid density functional.

nonlocal Hartree-Fock exchange is between 1 % and 5 %, the Fermi surface topology is similar with the experimental one. Then considering the effects of Na ions in the $\text{Na}_{0.5}\text{CoO}_2$ system, and with 3 % HF exchange in the B3LYP hybrid functional, we found that the Fermi surface is split to double holes and small gaps open near the intersections between Brillouin zone and Fermi surface. These gaps in the FS curvature were also proposed by Bobroff *et al.* recently [25], who suggested that in the presence of any small lattice potential, the gaps should open at the intersections between BZ and FS. As they did not consider the splitting the a_{1g} states in their construction of FS, their FS curvature seemed to be an average hole of ours.

4 Other hybrid functionals studies

Besides B3LYP, some other hybrid functionals such as B3PW [1, 26], PBEh (also known in the literature as PBE1PBE and PBE0) [27–29], and a newly developed HSEPBE hybrid functional [30, 31] have also been applied to some solid systems. Kudin *et al.* [32] applied the PBEh hybrid functional to the electronic structure of the traditional Mott insulator UO_2 , and found that it correctly yields an antiferromagnetic insulator as opposed to the ferromagnetic metal predicted by the LDA and GGAs. The gap, density of states, and optimum lattice constant are all in good agreement with experiment. A set of 40 simple and binary semiconductors have been calculated very recently using the HSEPBE hybrid functional [33]. HSEPBE hybrid functional correctly predicts semiconducting behavior in systems where pure functionals erroneously predict a metal, such as, for instance, Ge. The short-range nature of the exchange integrals involved in HSEPBE calculations makes their computation notably faster than regular hybrid functionals. These results, paired with earlier work, suggest that HSE is a fast and accurate alternative to established density functionals, especially for solid state calculations.

5 conclusion

In this article, the applications of B3LYP hybrid density functional to solids are summed up. The applications to bulks and surfaces show that B3LYP hybrid functional are computationally efficient, produces ground state energy surfaces and significantly improve energy gaps for a variety of materials. The B3LYP functional is also used to predict the magnetic coupling constants of solid state transition metal compounds.

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