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On the applicability of hybrid functionals for predicting fundamental properties of metals



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ABSTRACT

The repercussions of an inaccurate account of electronic states near the Fermi level by hybrid functionals in predicting several important metallic properties are investigated. The difficulties include a vanishing or severely suppressed density of states (DOS) at E_F , significantly widened valence bandwidth, greatly enhanced electron–phonon (el–ph) deformation potentials, and an overestimate of magnetic moment in transition metals. The erroneously enhanced el–ph coupling calculated by hybrid functionals may lead to a false prediction of lattice instability. The main culprit of the problem comes from the simplistic treatment of the exchange functional rooted in the original Fock exchange energy. The use of a short-ranged Coulomb interaction alleviates some of the drawbacks but the fundamental issues remain unchanged.

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1. Introduction

As one of the most successful and extensively implemented theories in electronic structure methods, the importance of density functional theory (DFT) [1,2] cannot be overstated. However, despite its tremendous triumph in describing many ground state properties, DFT within the local density approximation (LDA) [2,3] or the generalized gradient approximation (GGA) [4–6] has serious limitations when it comes to describing excited state properties of materials, a problem that is often loosely referred to as the LDA band gap problem.

Strictly speaking, the Kohn–Sham (KS) eigenvalues cannot be interpreted as the quasiparticle energies in solids. Nevertheless, there has been much effort put into the development of better energy functionals that can also provide a more faithful description of the quasiparticle energies. One class of such functionals, known as hybrid functionals [7], in which the conventional LDA or GGA exchange–correlation functional is mixed with a fraction of the Hartree–Fock (HF) exchange energy, has the promises of providing a better description of a wide range of materials properties [8–15], including the band gap of semiconductors. There are notable exceptions, however. For example, the experimental band gap of FeS₂, an earth abundant material with a very high optical

absorption coefficient in the visible region, is about 0.95 eV [16,17], but the Heyd–Scuseria–Ernzerhof (HSE) [18,19] hybrid functional predicts a band gap of about 2.7 eV [20].

Hybrid functionals have been unbiasedly applied to the study of various materials systems and properties involving metals, and, in some cases, improved or similar results compared with the LDA or GGA functionals have been obtained [12,21–25]. In this work, however, we point out that hybrid functionals have to be used with great caution for metallic systems. In particular, for metallic properties that are sensitive to (or determined by) the Fermi surface properties (electronic structure near the Fermi energy), hybrid functionals are likely to give significantly worse results compared with the LDA or GGA. We show that the application of hybrid functionals to metallic systems gives rise to a range of false or inaccurate results. These include, but not limited to, (1) enlarged valence bandwidth, (2) vanishing or greatly suppressed density of states (DOS) at the Fermi level, (3) significantly overestimated el–ph deformation potentials, (4) false predictions of lattice instability for systems (e.g., MgB₂) with a strong el–ph coupling, and (5) enhanced magnetism in transition metals. The occupied band width and the electronic structure near the Fermi level are among the most important properties of metals. Many fundamental thermal and transport properties of metals are controlled or strongly affected by the electronic structure near the Fermi level. The inaccurate prediction of the strength of the el–ph coupling, lattice stability, and

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magnetism are just a few manifestations of the fundamental difficulties that are inherent to hybrid functionals when they are applied to metallic systems. We believe that the aforementioned problems are serious enough to justify a thorough re-evaluation of the applicability of hybrid functionals to metals and degenerate semiconductors.

2. Computational details

Our density functional calculations are performed using the Quantum Espresso [26] package. The GGA functional of Perdew, Burke, and Ernzerhof (PBE) [27] and hybrid functionals, both the PBE0 [28] and the HSE06 [18,19] functionals, are used in this work. Electron–ion interactions are described by norm-conserving pseudopotentials [29]. The plane wave basis has an energy cutoff of 20 Ry for the calculations of Na, 50 Ry for MgB_2 , and 180 Ry for transition metals. For transition metals, all semicore subshells (i.e., 3s, 3p, and 3d) are included as valence electrons.

3. Results and discussion

We first investigate the electronic structure of metals calculated with the PBE0 and HSE06 functionals using Na as an example. Fig. 1 compares the DOS of Na calculated using both the PBE (blue), HSE06 (green), and the PBE0 (red) functionals. The DOS are calculated using a very high k -point density of $40 \times 40 \times 40$ with a small Gaussian smearing parameter of 0.01 eV. It is well-established that the PBE functional gives a satisfactory description of the electronic structure for a wide range of materials including metals. In fact, the calculated bandwidth (3.15 eV) of Na agrees very well with that obtained from the free-electron model (shown in Fig. 1 with the black curve superimposed on the PBE result). The PBE (and free-electron model) result also compares reasonably well with experiment [30,31] other than a well-understood quasiparticle renormalization factor [32]. The PBE0 functional, in contrast, gives an overly exaggerated occupied bandwidth of 4.2 eV. Perhaps a more alarming issue is that the PBE0 functional predicts a vanishing DOS at E_F as shown in Fig. 1. Note that the singularity is not clearly shown in the figure because of a finite smearing parameter used in our calculation. Nevertheless, the significant dip in the DOS at the E_F can be clearly seen.

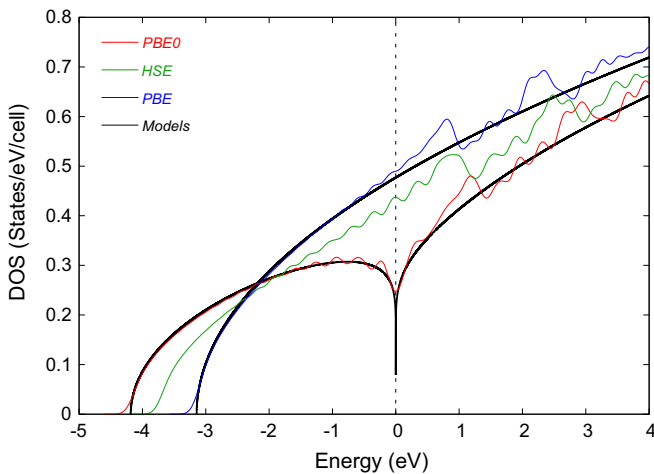


Fig. 1. (Color online) Calculated DOS of sodium using the PBE (in blue) HSE06 (green), and PBE0 (red) functionals. The PBE result agrees well with that of the free-electron model (solid black curve), and the PBE0 result can be well understood within the HF theory of free electrons (solid black curve) that shows vanishing DOS at the E_F (shown with the dashed line).

The abnormal DOS calculated with the PBE0 functional is a direct result of the HF exchange energy incorporated in the functional. A simple free-electron calculation using the HF theory [33] (with the HF exchange-energy rescaled by a factor of 0.25 as it is used in the PBE0 functional) gives nearly identical results as shown with the black curve superimposed on the red curve (PBE0 results). The HSE06 functional gives results that are somewhat in between those calculated with PBE and PBE0 functionals. The bandwidth is still significantly overestimated, however. Although there is no singularity in the calculated DOS, the HSE06 functional gives a suppressed DOS near the Fermi energy.

The Fermi-surface property is perhaps one single most important property of metals. A wrong description of the Fermi-surface properties, including the DOS and the electron energy dispersion near the Fermi level, will have serious consequences when it comes to predicting other fundamental properties of metals, especially for properties that are sensitive to the Fermi surface properties (electronic structure near the Fermi energy). These properties include, but not limit to, el–ph coupling strength, magnetism, thermal properties such as electronic free energy and specific heat of metals, and transport properties.

In order to demonstrate the repercussion of the incorrect description of the electronic structure of metals near the Fermi level, we investigate some electron–phonon coupling related aspects of metals using MgB_2 , a well-established multi-gap phonon-mediated superconductor [34–38], as an example. Quantitative predictions of the superconductivity in MgB_2 , including the precise calculation of the superconducting transition temperature T_C , are one of the celebrated [36–38] successes of modern electronic structure methods. We mentioned that all previous calculations [36–40] used either LDA or GGA functionals. This success would not be possible without an accurate description of the electronic structure near E_F . Fig. 2 shows the DOS of MgB_2 calculated using the PBE0 (shown in red) and PBE (in blue) functionals. Similar to the case of Na, the PBE0 functional gives a significantly widened occupied bandwidth and a greatly suppressed DOS near E_F . In fact, a fully converged PBE0 calculation (with respect to the k -grid density) should give a precisely zero DOS at E_F .

It is now well-established that the strong coupling between the E_{2g} phonons (shown in Fig. 3) and the boron-derived $p\sigma$ states is largely responsible for the enormously high T_C of MgB_2 , and previous work [36–40] has demonstrated the accuracy of LDA or GGA functionals in the prediction of the phonon energies and their coupling with electrons. Fig. 4 shows the band structure of MgB_2 calculated with boron atoms displaced by 0.05 a.u. from their equilibrium position along one of the E_{2g} phonon modes shown in

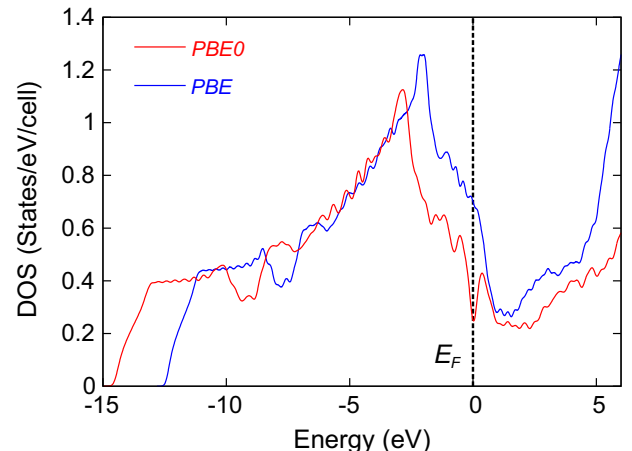


Fig. 2. (Color online) Density of states of MgB_2 calculated using the PBE (blue) and PBE0 (red) functionals. The dashed line indicates the Fermi level E_F .

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