

On the prediction of band gaps from hybrid functional theory

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Abstract

Details of the band gap and band widths within materials are of fundamental importance to a wide range of applications. A hybrid scheme is used to predict the band gaps of a variety of materials. The electronic structure of silicon is examined in some detail and comparisons with alternative theories are made. Agreement with experimentally derived band gaps is at least as good as that obtained with sophisticated correlated calculations or perturbation theories. The functional is straightforward to implement, computationally efficient and produces ground state energy surfaces which are significantly more accurate than those computed using the best gradient corrected density functionals currently in use. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Density functional theory (DFT) provides an efficient and reliable method for computing the ground state energetics for a wide variety of materials. In recent years the use of functionals based on the generalised gradient approximation (GGA) has significantly improved the accuracy of computed energies when compared to the original local density approximation (LDA). The eigenvalues in DFT calculations do not formally correspond to excitation energies. This is particularly apparent in their use to estimate band gaps where the non-analytic dependence of the effective potential on the density [1] often leads to a gap which is less than half of that observed. The poor estimation of the band gap has a number of unfortunate con-

sequences. For example, in some systems the band gap closes completely and a qualitatively incorrect description of the ground state (as a metal rather than an insulator) is obtained [2]. Consequently the utility and reliability of DFT calculations is limited especially when properties depending explicitly on excited state energies (such as optical adsorption spectra) are of interest.

In recent years a number of methods for obtaining a better approximation to the band gap have been put forward. GW perturbation theory [3] yields highly accurate gaps in weakly interacting systems such as semi-conductors [4,5]. In these systems the screened exchange approximation has also been successful [6,7]. The quantum monte carlo (QMC) method [8] has also been used to estimate excitation energies based on explicitly correlated wavefunctions [9–11]. Excitation energies can also be extracted from the frequency dependent linear response which may be computed within time-dependent DFT [12,13]. Few calculations

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have been reported with these latter methods as yet due to the complexity and computational cost involved in their implementation.

In order to study the electronic and optical properties of complex materials an approach providing a reliable estimate of band gaps while retaining the reasonable ground state description of the GGA is required. In the current work we demonstrate the fact that these requirements are satisfied by a simple hybrid scheme which contains an admixture of non-local Fock exchange.

Hybrid functionals were originally developed to improve the description of the ground state energetics of small molecules [14]. Subsequently, they have been demonstrated to be significantly more reliable than the best GGA functionals for computing atomisation enthalpies [15], geometries and vibrational frequencies [16]. The application of these methods in periodic calculations of solids has been inhibited by difficulties in computing the non-local 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 [17–19].

The hybrid exchange functional used in the current study is the B3LYP functional which has the following form

$$E_X = E_X^{\text{LSDA}} + 0.2(E_X^{\text{Fock}} - E_X^{\text{LSDA}}) + 0.72\Delta E_X^{\text{GGA}}, \quad (1)$$

where the LSDA and GGA energies are taken from widely used functionals [14] and E_X^{Fock} is the non-local Fock exchange energy. The correlation energy is taken to be the gradient corrected functional of Lee et al. [20] scaled by 0.81. The empirical parameters in this functional were determined by Becke in order to optimise the atomisation energies, ionisation potentials and proton affinities of a number of small molecules [14].

In the current scheme, we explicitly evaluate the non-local Fock energy. 20% of this value is then utilised as shown in Eq. (1). Hence we exactly value the original derivation and meaning of B3LYP given by Becke [14]. While this is not convenient within the commonly used planewave basis sets it can be implemented readily and very

efficiently within a Gaussian basis set as used in the CRYSTAL software [21]. The main numerical approximation is the selection of the local Gaussian basis set. For each of the materials studied here high quality basis sets (typically containing triple valence plus polarisation functions) have been generated in previous work [22] except for FeS₂ and ZnS. For these materials basis sets were developed during the current study and are available from the authors. For each system a full structural optimisation of the cell and internal co-ordinates was performed. Typically the optimised structural parameters are within $\pm 2\%$ of the experimental values. The band structure of the optimised system was then used to determine the band gaps which are evaluated as difference in the converged eigenvalues.

In order to establish the reliability of the hybrid functional a variety of materials exemplifying different types of chemical bonding have been studied. The materials chosen include semi-conductors (Si, diamond and GaAs), semi-ionic oxides (ZnO, Al₂O₃, TiO₂), sulphides (FeS₂, ZnS), an ionic oxide (MgO) and the transition metal oxides (MnO, NiO). In Table 1 bands gaps computed using the current scheme are compared to those observed [23–25]. Typically the most accurate determination of band gaps and widths is obtained from a combination of optical adsorption measurements, photoemission and inverse photoemission experiments [26]. Consequently, even band gaps measured under very well controlled conditions are

Table 1
A comparison of observed band gaps with those calculated using the B3LYP functional for a wide range of materials

Material	Expt	B3LYP
Si[25]	≈ 3.5	3.8
Diamond[25]	5.5	5.8
GaAs[25]	1.4	1.5
ZnO[23]	3.4	3.2
Al ₂ O ₃ [23]	≈ 9.0	8.5
Cr ₂ O ₃ [23]	3.3	3.4
MgO[23]	7.8	7.3
MnO[23]	3.6	3.8
NiO[23]	3.8	3.9
TiO ₂ [23]	3.0	3.4
FeS ₂ [24]	1.0	2.0
ZnS[24]	3.7	3.5

All values are given in electron volts (eV).

reliable to about 5%. In addition, thermal effects and structural disorder within the crystalline lattice, which are particularly important in the oxide materials, may lead to further discrepancies. In view of this the discrepancies between observed and computed band gaps are within, or close to, those to be expected from experimental uncertainties with the exception of FeS₂. The remarkable ability of the hybrid functional to predict band gaps with this accuracy is unexpected. In semi-conductors the existence of a mean field potential capable of reproducing band gaps has been exploited previously in the semi-empirical screened exchange approximation [6,7]. The B3LYP functional appears to provide a more universal potential yielding reliable band gaps for a much wider variety of materials. The reproduction of the

gaps in the transition metal oxides is particularly notable.

In FeS₂ the experimental evidence for the 1 eV band gap [27] is highly dependant on defect concentrations with measured values actually ranging from 0.7 to 2.6 eV [28]. Real crystals of FeS₂ are always sulphur deficient and it has been suggested previously that defects result in a narrowing of the observed gap [29]. Hence, the apparent large overestimate of the gap in FeS₂ found in the current study may, in part, arise from the effects of defects on the experimental measurement.

The electronic structure of silicon is analysed in more detail in Fig. 1 and Table 2 including a comparison with the observed excitations and with alternative theoretical approaches [30–35]. The current approach yields a direct band gap in

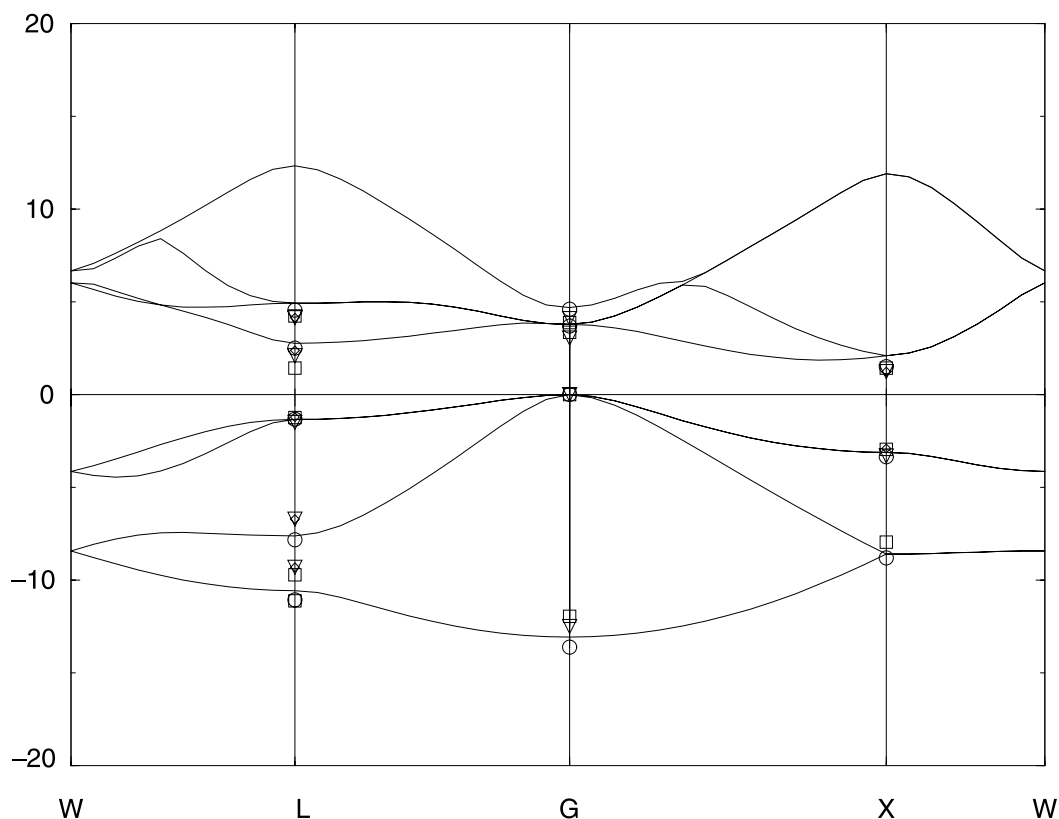


Fig. 1. A comparison of different theoretical approaches and observed values for the band structure of bulk silicon. GW values are indicated by squares, QMC values by circles, and experimental values by triangles. The solid lines are the B3LYP values. The data has been aligned at $\Gamma_{25'}$.

Table 2

A comparison of the observed band mapping of bulk silicon with that computed using correlated wavefunctions, perturbation theory, empirical and single-particle band theories

<i>k</i> -point	QMC[30]	GW[31]	HF[32]	LDA[33]	Emp.[34]	Expt.[35]	B3LYP
$\Gamma_{2'}$	4.6	3.89	9.0	3.19	4.23	4.1	4.68
Γ_{15}	3.7	3.36	8.0	2.55	3.40	3.05	3.78
$\Gamma_{25'}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_1	-13.6	-11.95	-18.9	11.95	-12.5	-12.5	-13.08
X1c	1.51	1.43	5.3	0.63	1.25		1.57
X4	-3.35	-2.93	-4.7	-2.84	-3.3	-2.9	-3.69
X1v	-8.79	-7.95	-12.5	-7.81			-9.24
L1c	2.51	2.19	6.5	1.44	2.4	2.1	2.71
L3	4.55	4.25	8.7	3.31	4.15		5.34
L3'	-1.32	-1.25	-2.0	-1.19	-1.2	-1.5	-1.83
L1v	-7.81	-7.14	-11.1	-6.96	-6.96		-8.37
l2'	-11.05	-9.70	-15.4	-9.61	-9.3		-11.29

The data are in eV and have been aligned at $\Gamma_{25'}$.

excellent agreement with that observed. In addition, the entire band mapping of silicon is highly comparable to that obtained with the sophisticated QMC and GW approaches. The current approach is clearly a systematic and significant improvement over the LDA, GGA and Hartree-Fock (HF) approximations. Since the use of hybrid energy functionals is wide spread in the literature, the fact that they can produce accurate estimate of the band gaps in a range of materials is extremely encouraging.

The correspondence of eigenvalues in a single particle calculation to measured excitation energies is essentially fortuitous. Indeed it is clear that corrections to the current functional are likely to worsen the correspondence. This is particularly true of the transition metal oxides where the single particle picture of the electronic structure is not a qualitatively correct description. Nevertheless, it is clear that in studies of the variation of the band gap with, for instance, chemical composition or structure the current approach provides an extremely useful computational tool. In addition the approach may be used to underpin more reliable calculations of related properties such as the dielectric function for which the linear response theory depends critically on the band gap.

In summary, an hybrid functional (B3LYP) has been applied to ab initio calculations of the geometric and electronic structure of a wide variety of materials. This functional has been shown to reproduce observed band gaps reliably in a wide

variety of materials. Agreement with experimentally derived band gaps is at least as good as that obtained with more sophisticated correlated calculations or perturbation theories. The functional is straightforward to implement, computationally efficient and produces ground state energy surfaces which are significantly more accurate than those computed using the best gradient corrected functionals currently in use.

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