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Calculation of semiconductor band gaps with the M06-L density functional

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The performance of the M06-L density functional has been tested for band gaps in seven semiconductors plus diamond and MgO. Comparison with the local spin density approximation (LSDA), Becke-Lee-Yang-Parr (BLYP), Perdew-Burke-Eernzerhof (PBE), Tao-Perdew-Staroverov-Scuseria (TPSS), and Heyd-Scuseria-Ernzerhof (HSE) functionals shows that M06-L has improved performance for calculating band gaps as compared to other local functionals, but it is less accurate than the screened hybrid HSE functional for band gaps. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3076922]

I. INTRODUCTION

Band gap is a critical property for understanding the optical and electrical properties of materials and for the design of semiconductor devices. The accurate calculation of band gaps is an active and important research area in solid-state physics and theoretical chemistry.[1–4] Although Kohn–Sham density functional theory (DFT) has been very successful in theoretical physics and quantum chemistry, local density functionals such as the local spin density approximation (LSDA) and generalized gradient approximations (GGAs) tend to underestimate band gaps due to self-interaction errors. In quantum chemistry, self-interaction errors are also responsible for the underestimation of reaction barrier heights[5] and of orbital energy gaps between highest occupied and lowest unoccupied molecular orbitals and for the overestimation of polarizabilities and hyperoplarizabilities of conjugated systems. Hybrid functionals, which include a portion of nonlocal Hartree–Fock (HF) exchange, ameliorate the self-interaction problems, and they are much more accurate for band gaps than the LSDA or GGAs.[3,6,7] However, the computational cost for HF exchange in solid-state physics calculations is very high,[3,8,9] and recently Heyd *et al.*[3,10,11] developed a screened hybrid functional, called HSE, to circumvent this problem.

Recently we developed a meta-GGA functional, in particular M06-L,[12,13] that is designed for main group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. The M06-L functional has been shown to perform well for many areas of chemistry,[12–22] Of special relevance to solid-state physics is that M06-L is a local functional (depending on local density, local density gradient, and local kinetic energy density) which does not involve HF exchange, so it is well suited for solid-state calculations where more efficient algorithms can be employed in the absence of HF exchange.

In the present study, we assess the performance of M06-L for the prediction of band gaps in group-4, group 3–5, and metal oxide semiconductors. In Sec. II, we describe the test sets and computational details. Section III gives results and discussion, and Sec. IV contains concluding remarks.

II. THEORY

One definition of the band gap is the onset of optical absorption. For local functionals the band gap may be equated to the independent-quasiparticle approximation:[23]

$$\Delta\varepsilon = \varepsilon^{\mathrm{LUCO}} - \varepsilon^{\mathrm{HOCO}}, \tag{1}$$

where $\varepsilon^{\mathrm{LUCO}}$ is the Kohn–Sham orbital energy of the lowest unoccupied crystal orbital and $\varepsilon^{\mathrm{HOCO}}$ is the Kohn–Sham orbital energy of the highest occupied crystal orbital. When these orbital energies correspond to the same wave vector $\boldsymbol{k}$, the band gap is called direct; and when they correspond to different wave vectors, it is called indirect.[24] In this paper we calculate the lowest excitation energy (whether direct or indirect) by Eq. (1), but we note that although this is a good approximation for local functionals and for the screened hybrid HSE functional when the screening parameter is large enough,[4] for global hybrid functionals one should use a higher-level method or a method such as time-dependent DFT to calculate band gaps.[25]

III. TEST SET AND COMPUTATIONAL DETAILS

We tested the M06-L functional for the prediction of band gaps of the DSBG9 database, which consists of nine semiconductors, namely, C (diamond), GaAs, Ge, InAs, InSb, MgO, Si, SiC, and ZnO. We group them into three smaller databases:

- G4BG4 (group-4 band gaps): C, Ge, Si, SiC;
- 35BG3 (groups 3–5 band gaps): GaAs, InAs, InSb;
- MOBG2 (metal oxide band gaps): MgO, ZnO.

All the experimental reference band gaps were taken from Refs. 3 and 24, except for ZnO, which is taken from Ref. 26.

Although the main goal of the present study is to test the performance of the M06-L meta-GGA for calculating band

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TABLE I. Band gap (eV) results.

Solid	Expt.	HSE[a]	M06-L	BLYP	TPSS[a]	LSDA[a]	PBE[a]
			Group 4 (G4BG4)				
C	5.48[b]	5.49	4.77	4.41	4.21	4.23	4.17
Ge	0.74[b]	0.56	0.14	0.00	0.00	0.00	0.00
Si	1.14[c]	1.28	1.12	1.01	0.82	0.59	0.75
SiC	2.31[c]	2.39	1.66	1.82	1.42	1.40	1.46
All four	MUE[d]	0.10	0.49	0.61	0.81	0.86	0.82
			Groups 3–5 (35BG3)				
GaAs	1.48[c]	1.21	0.89	0.00	0.52	0.43	0.19
InAs	0.39[c]	0.39	0.15	0.00	0.00	0.00	0.00
InSb	0.21[c]	0.29	0.00	0.00	0.00	0.00	0.00
All three	MUE[d]	0.12	0.34	0.69	0.52	0.55	0.63
			Metal oxides (MOBG2)				
MgO	7.22[b]	6.50	4.88	4.48	4.56	4.92	4.34
ZnO	3.40[e]	2.90[f]	0.98	0.94	0.94	0.91	0.88
Both	MUE[d]	0.61	2.38	2.60	2.56	2.40	2.70
			Diverse solids (DSBG9)				
All nine	MSE[g]	−0.15	−0.86	−1.08	−1.10	−1.10	−1.17
All nine	MUE[d]	0.19	0.86	1.08	1.10	1.10	1.17

[a] Results for these functionals were taken from Ref. 3 except that the band gaps for ZnO are calculated in the present work.
[b] Taken from Ref. 3.
[c] Average of the experimental data in Refs. 3 and 24.
[d] MUE denotes mean unsigned error.
[e] From Ref. 26.
[f] This band gap is taken from Ref. 33 and is computed with a smaller basis set than all the other band gaps in this paper.
[g] MSE denotes mean signed error.

gaps, we also carried out calculations by the popular BLYP functional for comparison. In order to put the present results in a broader perspective, the results for the LSDA, Perdew-Burke-Eernzerhof (PBE), Tao-Perdew-Staroverov-Scuseria (TPSS), and Heyd-Scuseria-Ernzerhof (HSE) functionals from Ref. 3 are also included.

All density functional calculations were carried out using a locally modified GAUSSIAN03 (Refs. 27 and 28) program. The calculated band gaps were obtained at the optimized structures for each functional. The algorithms for periodic-boundary-condition calculations of band gaps are described elsewhere.[3,29]

For lighter elements (C, Mg, O, and Si), a modified 6-311G* basis[3] was employed, whereas for the heavier elements (Ga, Ge, In, Sb, and Zn), we use a small-core relativistic effective core potential (RECP) with a double zeta valence basis set.[3] All basis sets and RECPs were taken from the supporting information of Ref. 3.

IV. RESULTS AND DISCUSSION

Table I presents the results for band gaps, with the last two rows being mean signed error (MSE) and mean unsigned error (MUE) for all nine band gaps. All local functionals in Table I underestimate band gaps, as shown by their negative MSE. Table I shows that only HSE and M06-L predict a nonzero band gap for Ge and InAs, whereas other tested functionals predict Ge and InAs are metallic. For InSb, only HSE predicts that it is a semiconductor; all other functionals predict it is metallic.

If we use MUEs to judge the performance of the tested density functionals, Table I shows that the screened hybrid HSE functional gives excellent performance for band gaps, and this result[3] shows that the inclusion of the short-range HF exchange removes some short-range self-interaction errors. Among the local functionals, M06-L gives the best performance for all three band gap databases. BLYP is the second best local functional for the G4BG4 database, TPSS is the second best local functional for the 35BG4 database, and LSDA is the second best local functional for the MOBG2 database. Table I shows that the PBE GGA does not improve upon LSDA, and the TPSS meta-GGA performs only slightly better than PBE.

Table II gives MUEs for the three band gap databases and for the HTBH38 database[30] of barrier heights for hydrogen transfer reactions. As can be seen from Table II, the rank performance for group-4 band gaps is the same as the rank performance for barrier heights except that M06-L outperforms HSE for barrier heights. The performance of the M06-L functional has been compared to that of the LSDA, BLYP, PBE, and TPSS functionals in previous studies;[12–14,22,31,32] the good performance of M06-L as compared to other local functionals for band gaps, as found here, is particularly encouraging since M06-L also has the best

TABLE II. MUEs for the three band gap databases and the HTBH38 database.

Method	G4BG4 (eV)	35 BG3 (eV)	MOBG2 (eV)	HTBH38 (kcal/mol)
HSE	0.10	0.12	0.61	4.6[a]
M06-L	0.49	0.34	2.38	4.2[b]
BLYP	0.61	0.69	2.60	7.5[b]
TPSS	0.81	0.52	2.56	7.7[b]
PBE	0.82	0.63	2.70	9.3[b]
LSDA	0.86	0.55	2.40	17.7[b]

[a] This MUE is taken from Ref. 29.

[b] These MUEs are taken from Ref. 12.

performance of any of the these local functionals for noncovalent interactions, barrier heights, transition metal chemistry, NMR chemical shielding constants, and olefin metathesis.

V. CONCLUDING REMARKS

In the present study, we tested the M06-L meta-GGA density functional for the prediction of band gaps. We found that

(1) M06-L has improved performance for calculating band gaps for group-4 and group 3–5 semiconductors, but it does not reach the accuracy of the screened hybrid HSE functional;

(2) only HSE and M06-L predict that Ge and InAs have a band gap, and the other four functionals predict that Ge and InAs are metallic.

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