Improved semiconductor lattice parameters and band gaps from a middle-range screened hybrid exchange functional

M J Lucero¹, T M Henderson¹,² and G E Scuseria¹,²,³

¹ Department of Chemistry, Rice University, Houston, TX 77005-1892, USA
² Department of Physics and Astronomy, Rice University, Houston, TX 77005-1827, USA
³ Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

E-mail: guscus@rice.edu (G E Scuseria)

Received 14 November 2011, in final form 24 January 2012
Published 15 March 2012
Online at stacks.iop.org/JPhysCM/24/145504

Abstract
We show that the middle-range exchange–correlation hybrid of Henderson, Izmaylov, Scuseria and Savin (HISS) performs extremely well for elemental and binary semiconductors with narrow or visible spectrum band gaps, as well as some wider gap or more ionic systems used in devices. The lattice parameters are superior to those predicted by the screened hybrid functional of Heyd, Scuseria and Ernzerhof (HSE), and provide a significant improvement over the geometries predicted by typical semilocal functionals, yielding results competitive with PBEsol, which was specially tuned for solids. HISS also yields band gaps superior to those produced by functionals developed specifically for the solid state. Timings indicate that HISS is more computationally efficient than HSE, implying that the high quality lattice constants coupled with improved optical band gap predictions render HISS a useful adjunct to HSE in the modeling of geometry-sensitive semiconductors.

1. Introduction

Reliable theoretical treatment of semiconductors, particularly those in the visible range (20 meV–4 eV) remains non-trivial. While semilocal density functional theory (DFT) methods represent the most computationally tractable approach, the band gaps obtained are generally poor [1–4]. Moreover, many semiconductors, such as the perovskites [5, 6], chalcopyrites [7, 8, 5] or Delafossites [9, 5] have solid state properties that are very sensitive to their geometry. These shortcomings of solid state DFT arise, in part, from the various approximations to the exchange–correlation energy, $E_{xc}$ [10].

In the simplest case, the local spin density approximation (LSDA) [11] assumes that the exchange–correlation energy density at the point $\mathbf{r}$ depends only on the spin densities at $\mathbf{r}$, rendering the exchange interaction local [10]. For solids, the LSDA underestimates lattice constants [12, 13], and severely underestimates band gaps [14]. Generalized gradient approximations (GGAs) such as the functional of Perdew, Burke and Ernzerhof (PBE) [15, 16] improve upon the LSDA by incorporating the local density gradient, while the meta-GGAs such as the functional of Tao, Perdew, Staroverov and Scuseria (TPSS) [17] also add dependence on the kinetic energy density and/or the Laplacian of the density. Because GGAs and meta-GGAs are semilocal in character, they can partially account for inhomogeneities in the density, thus showing significant improvement over the LSDA in atoms and molecules. For extended systems, however, these functionals can often provide predictions of lower quality than the LSDA [18–20].

Hybrid functionals including a percentage of exact non-local Hartree–Fock-type exchange [21, 22] have proven very successful for molecules, as is evident from the popularity of the B3LYP [23] functional. These hybrids
describe the exchange–correlation energy as

$$E_{xc} = E_{xc}^{DFA} + c(E_{x}^{HF} - E_{x}^{DFA}),$$  \(1\)

where \(E_{xc}^{DFA}\) is the exchange–correlation energy of a (semi)local density functional approximation (DFA) and \(E_{x}^{HF}\) and \(E_{x}^{DFA}\) are, respectively, the exact exchange energy and the exchange energy from a DFA. The constant \(c\) typically ranges from 1/10 to 1/2. Unfortunately, even increasingly sophisticated hybrids such as PBEh (also known as PBE0 and PBE1PBE) [24, 25], TPSSh [26], or the highly empirical M06 [27] series of functionals have been unable to supplant the LSDA for applications in extended systems, despite its numerous and well-known insufficiencies.

In part, this failure is a matter of computational affordability, as the lattice sums required to evaluate the non-local exchange energy are slowly convergent, particularly as the band gap of the system decreases. A second problem arises from the fact that hybrid functionals are almost always constructed in the generalized Kohn–Sham (GKS) framework [28], where the non-local exchange energy leads to a non-local exchange ‘potential’ similar to that of Hartree–Fock (HF). Accordingly, hybrid functionals formulated in the GKS sense inherit many of the deficiencies that Hartree–Fock exhibits for extended systems. In fact, for some solid state properties, hybrid functionals yield errors similar in magnitude to those of semilocal functionals, but at much greater computational cost [29, 30].

In order to efficiently recover the benefits of non-local exchange for both solids and molecules, a more flexible scheme to mix exact and semilocal exchange is required. Probably the most promising such route is the use of range separation [31–33, 29], where the amount of non-local exchange included in the functional depends on the distance between electrons. A typical range-separation scheme might split the Coulomb operator \(1/r_{12}\) into short-range (SR) and long-range (LR) pieces, as

$$\frac{1}{r} = \frac{1 - \text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}},$$  \(2\)

where \(\omega\) is a parameter defining the length scale of separation and erf is the error function, chosen for simplicity of integration with Gaussian orbitals. The exchange–correlation energy then becomes

$$E_{xc} = E_{xc}^{DFA} + c_{SR}(E_{x}^{SR-HF} - E_{x}^{SR-DFA}) + c_{LR}(E_{x}^{LR-HF} - E_{x}^{LR-DFA}),$$  \(3\)

so that the amount of non-local exchange used for electrons which are far apart can differ from the amount used for electrons which are close together. In molecules, we generally set \(c_{LR} = 1\) in what is known as a long-range-corrected hybrid. By choosing \(c_{LR} = 1\), the correct long-range portion of the exchange–correlation potential is obtained, resulting in substantial improvements over non-local hybrids for properties which sample density tails, including non-linear optical properties [34], long-chain polarizabilities [35], and charge transfer or Rydberg excitations [36]. Solids, however, have no density tails, and the long-range portion of the exact exchange becomes problematic if left unscreened, not only because it is expensive to compute, but also because it yields unphysical results. We, therefore, set \(c_{LR} = 0\) in what are known as screened hybrids.

The screened hybrid functional of Heyd, Scuseria and Ernzerhof [37–39] uses 25% HF exchange in the short range, with \(\omega = 0.11a_{0}^{-1}\), where \(a_{0}\) is the Bohr radius. This value of \(\omega\) corresponds to a range of \(\sim 5\) Å, so that non-local exchange extends over two to three nearest neighbors. Note that for practical purposes this range is quite long. The HSE screened hybrid performs acceptably for metallic systems, but significantly improves upon the predictions of regular hybrids for semiconductors. For molecular systems, it yields results of the same quality as unscreened hybrids. Nevertheless, despite some ability to describe long-range properties [39], HSE does not adequately describe quantities sensitive to the long-range portion of the exchange–correlation potential [40, 41].

A functional successfully coupling the accuracy for solids of a screened hybrid with the accuracy for molecules of a long-range-corrected hybrid would be of considerable utility in modeling extended systems, as surface phenomena such as molecular adsorption, catalysis, and surface reconstruction could then be reliably addressed. This was the motivation behind the development of the HISS functional of Henderson, Izmaylov, Scuseria and Savin [42, 43], which has three ranges rather than just two. Like HSE, HISS uses PBE as the underlying GGA, but HISS is written as

$$E_{xc}^{HISS} = E_{xc}^{PBE} + c_{MR}(E_{x}^{MR-HF} - E_{x}^{MR-PBE}),$$  \(4\)

where the last two terms in parentheses are the middle-range (MR) exact exchange and middle-range PBE exchange energies, given by

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\omega_{SR} r_{12})}{r_{12}} + \frac{\text{erf}(\omega_{LR} r_{12})}{r_{12}},$$

$$\frac{1}{r_{12}} = \frac{\text{erf}(\omega_{SR} r_{12}) - \text{erf}(\omega_{LR} r_{12})}{r_{12}}.$$

The three parameters were determined by fitting to small test sets of atomization energies, barrier heights, and band gaps, resulting in \(\omega_{SR} = 0.84a_{0}^{-1}\), \(\omega_{LR} = 0.20a_{0}^{-1}\), and \(c_{MR} = 0.60\). The fraction of exact exchange included in HISS rises from zero at \(r_{12} = 0\) to roughly 0.35 near \(r_{12} = 1.5a_{0}\), then decays to zero again for large distances; HISS has more exact exchange than HSE over one or two chemical bonds, but the fraction of exact exchange decays even more rapidly than it does in HSE, producing a speed-up in solid state calculations. As expected, enhanced mid-range non-local exchange was demonstrated to reduce the calculated errors for the thermochemistry, low-lying Rydberg states, atomization energies, barrier heights and polarizabilities of H2 chains [43]. For the semiconductor band gaps tested, HISS did not perform as well as HSE, overestimating them by 0.4 eV [43]. However, given the excellent reproduction of molecular properties and the fact that only a small set of solids was examined, we
chose to more thoroughly assess the performance of HISS in semiconductors, and here focus on sp-type semiconductors against which HSE has previously been benchmarked [44]. We should note that HSE is less successful for metallic systems, where it overestimates band widths, and HISS is expected to be worse than HSE. Similarly, neither HSE nor HISS is well suited to ionic solids, which generally require more exact exchange than the semiconductor systems for which HISS and HSE perform so well.

2. Computational methods

Density functional calculations were performed using the periodic boundary-condition code [45–47] within the GAUSSIAN suite of programs [48]. Gaussian basis sets optimized for solids were discussed and provided in the supplementary material of the earlier study by Heyd et al. [44]. While these basis sets may not approach the basis set limit, they are deemed adequate for band structure calculations and yield lattice constants which agree with plane wave results to within a few pm [30].

The band gaps and related properties reported here are for fully relaxed, equilibrium structures (lattice parameters and geometries) obtained using the LSDA (with SVWN5 [49]), PBE, TPSS, PBEsol [50], the HSE screened hybrid, and the HISS middle-range hybrid. The equilibrium structures are optimized in redundant internal coordinates [51] using the GAUSSIAN09 defaults. The SCF convergence criterion was set to $10^{-7}$ on the density matrix ($\text{SCF} = \text{TIGHT}$) with Brillouin space integration performed using the GAUSSIAN09 default; this corresponds to at least ten points in each dimension and usually more, depending on the size of the unit cell. All extended systems studied are for three-dimensional ‘bulk’ crystalline materials.

3. Benchmarks

3.1. The SC40 test set

The solids used in this study were previously published as the SC40 test set [44]. The forty compounds are here separated into three groups. Group 1 contains twenty commercially relevant bulk semiconductors absorbing in the optical (0.20 meV–4 eV) range. This set includes the most commonly used or benchmarked elemental and binary compounds adopting the diamond (di), zincblende (zb), or wurtzite (wu) lattices, and each compound is referenced to a complete set of low (LT) and room temperature (RT) band gap data. Group 2 consists of a smaller set of wide gap semiconductors and ionic solids known to be challenging computationally or for various intriguing experimental properties. Group 3 encompasses a collection of binary compounds useful for simultaneously benchmarking lattice parameters and providing an opportunity for band gap prediction as these materials have gaps that are either unknown or not particularly well-established. Each group is further subdivided according to the lattice structure, with the diamond, zincblende and wurtzite structures preceding any rock salt (rs) structures within each group. Separations between groups are indicated by horizontal lines in tables 2 and 4.

To facilitate evaluation of the relative performance of each functional, the experimental band gaps have been updated to reflect half a decade of experimental progress and further augmented to include, and discriminate between, room temperature and low temperature (LT) values. It should be noted that the low temperature data set is not exhaustive and the experimental measurements range from extrapolated 0 K values up to 27 K, providing no consistent basis by which to judge the quality of the predicted optical gaps, particularly if the temperature dependence of a given material is uncertain. Alternatively, the more complete room temperature data set, which has gaps typically ca 0.2 eV higher in energy than the measured LT results, can provide a useful baseline for estimations of the low temperature gaps where unavailable or extrapolated. The majority of the experimental reference data (gaps and lattice constants) are taken from the third edition of the Springer semiconductor handbook [52] and any references included therein. All experimental data for group 3 are taken from [44] except for the lattice constants of MgSe (which are taken from [52]). Other alternate tabulations are cited where applicable.

3.2. Lattice parameters

In principle, our theoretical lattice constants should be compared to vibrationally corrected 0 K experimental values. Unfortunately, a complete set of low temperature results is unavailable. However, [53] contains extrapolated 0 K reference data for roughly half of the solids in our test set, as well as 0 K lattice constants corrected with the zero point anharmonic expansion (ZPAE). Table 1 shows calculated lattice constants for these sixteen solids, as well as extrapolated 0 K and ZPAE-corrected 0 K results from [53] and room temperature experimental data from [52]. We use the \textit{ab initio} ZPAE correction of [53]. Note that, for example, the literature value [53] for the 0 K lattice constant of InSb is quoted as 6.479 Å, which is equal to the room temperature value given in Madelung [52]. It is not our intent to sort out any discrepancies in the low temperature values, but we note that, in practice, the difference between 0 K and room temperature lattice constants has only a minor effect on our error statistics.

Our data suggest that HISS generally overestimates the ZPAE-corrected 0 K lattice constants and underestimates the room temperature results, which is reflected in the mean error (ME). The mean absolute error (MAE), however, is essentially unaffected. As is well known, the LSDA provides reasonable, but generally contracted, lattices, while gradient-corrected functionals tend to over-correct and extend them, instigating the development of functionals specifically tailored to produce...
To better illustrate the lattice parameter predictions, figure 1 shows the errors for all forty three lattice parameters contained in table 2 in the form of histograms. The ME for each functional is depicted by the vertical dotted line on each plot. While the results from HISS are sharply peaked around zero error, it is clear that the LSDA underestimates the lattice constants, HSE produces highly clustered overestimations, nearly as accurate as the LSDA, while the well-known PBE and TPSS overestimations are evident. The PBEsol distribution is somewhat narrower than that of the LSDA, but, as with other GGAs, skews toward expanded lattice constants.

Figure 2 shows the mean absolute errors of the equilibrium lattice parameters for the twenty commercially relevant semiconductors in group 1. Remarkably, HISS provides excellent lattice parameters, with an MAE of less than half that of the LSDA (see table 3), despite producing bond lengths in molecules that are not particularly impressive [43].

3.3. Band gaps

Table 4 contains the calculated gaps for all the solids in the SC40 set and the experimental gaps where available. It is readily apparent that HISS and especially HSE more accurately predict the band gaps than the semilocal functionals, which is well known. It should be emphasized that hybrid functionals such as HISS and HSE which use...
the GKS approach predict fundamental gaps as band energy (conduction band–valence band) differences [54]. They also provide excellent approximations of optical gaps, particularly for visible-range semiconductors and other materials [55]. This is particularly well-illustrated in figure 3, which plots the calculated HISS, HSE, LSDA and PBEsol band gaps.
of the twenty semiconductors in group 1 of table 4 against the low temperature experimental optical gaps. The dashed lines indicate deviations of ±0.3 eV. Almost all the HSE data are within the ±0.3 eV range, while HISS tends toward larger gaps and, as one expects, the semilocal functionals consistently underestimate all the band gaps by more than 0.3 eV. We should point out that the many body GW method and the semilocal modified Becke–Johnson potential [56] seem to yield semiconductor gaps comparable in accuracy to those of HSE.

The LSDA metalizes the narrow gaps of Ge and the indium pnictides, as is evident from the clustering on the x-axis between 0 and 1 in figure 3, whereas HISS and HSE do not. On the other hand, HISS strongly overestimates these gaps, which is why we expect HISS to perform poorly for metallic systems. Previously, our group demonstrated that HSE is capable of correctly describing the Mott metal–insulator transition in actinide oxides. All of the semilocal functionals predict these systems to be metallic as well, yet they are known to be narrow gap semiconductors [57–59]. Whether HISS can also describe the Mott transition in the actinide oxides is an open question, but it seems likely to be capable of doing so provided that a metallic phase can be found.

HISS accurately predicts the gaps of the zinc chalcogenides and both the α- and β-polytypes of GaN, which are, again, somewhat problematic for the semilocal functionals (table 4). The performance of all functionals for group 1

Table 4. Band gaps for the SC40 solid test set [44] at the equilibrium lattice parameters in table 2. The reference sets for band gaps are either room temperature (RT) or low temperature (LT), with LT implying less than 77 K. (Note: the experimental low temperature set is neither consistent, nor complete. Reference [52] is the source unless otherwise noted. 0 K (extrapolated): Si, GaP, GaAs, GaSb, CdTe [76], MgS [77], MgO, ≤ 2 K: Ge, β-SiC, AIP, InP, InSb, ZnTe, α-GaN, MgTe [78]; ~4–6 K: AlAs, InN [79], InAs, ZnS [67]; 7–10 K: β-GaN, BN [80], AlN; 14 K: ZnS [67]; 27 K: AlSb; others: CdSe [81], CdS [81], BAs.) The abbreviations I or D refer to indirect or direct gap transitions. The room temperature experiment for InN is taken from [60] and that for C from [61].
Figure 1. Histograms of the calculated lattice constant errors (pm) relative to the experimental values from table 2. The dashed lines indicate MEs for HISS, HSE, LSDA, PBE, TPSS and PBEsol: 0.9, 3.7, −4.8, 7.3, 6.0 and 0.5 pm, respectively.

Table 5. Error statistics for the band gaps at equilibrium geometries (pm) relative to the low and room temperature experiments. Groups 1 and 2 are as defined in table 4.

| Error (eV) | HISS | HSE06 | LSDA | PBE | PBEsol | TPSS |
|-----------|------|-------|------|-----|--------|------|
| LT group 1 | ME   | 0.39  | −0.17| −0.98| −1.00  | −0.99| −0.88|
|            | MAE  | 0.37  | −0.25| −1.16| −1.19  | −1.19| −1.05|
| LT groups 1 + 2 | ME  | 0.50  | −0.07| −0.88| −0.90  | −0.89| −0.78|
|            | MAE  | 0.50  | 0.15 | 0.88 | 0.90   | 0.89 | 0.78 |
| RT group 1 | ME   | 0.50  | −0.12| −1.02| −1.06  | −1.06| −0.93|
|            | MAE  | 0.50  | 0.20 | 1.02 | 1.06   | 1.06 | 0.93 |

Semiconductors relative to both temperature ranges is summarized in figure 4, which illustrates the systematic deviations alluded to in section 3.1. The MAEs for groups 1 and 2, in both temperature ranges, are summarized in table 5. As expected, HSE has the lowest errors, on the order of 0.20 eV for either the low or the room temperature data sets.
3.4. Difficult cases

Having discussed the bulk of the statistics above, we now turn our attention to a few cases worthy of note. As is pointed out in the Springer handbook \cite{52}, there are conflicting experimental data regarding the magnitude of the AlSb indirect transition, and, at one time, there was some uncertainty regarding the location. One set of experiments indicates that the indirect transition occurs somewhere near $\Gamma \rightarrow X$, with a magnitude of 1.6–1.7 eV \cite{62, 63}, while another set supports a $\Gamma \rightarrow L$ transition \cite{64} with a gap closer to 2 eV. Among several common texts, the gap is reported to be ca 1.5, 1.6 or 1.7 eV in \cite{5}, \cite{65} and \cite{66}, respectively. We calculated the band structure using LSDA, HSE and HISS. Interestingly, all three indicate that the indirect transition is clearly in the vicinity of $\Gamma \rightarrow X$, figure 5, and the 0 K HSE gap of 1.82 eV compares favorably with the 1.69 eV (27 K) band gap and shows the characteristic camel’s back structure. The slightly larger 2.05 eV band gap predicted by HISS might encourage preference of the $\Gamma \rightarrow L$ transition but, as is evident from the figure, the smallest indirect gap occurs near X and there is little difference between the structure of the highest valence and lowest conduction bands for either calculation. The fact that HISS systematically overestimates the band gaps but shows similar structure to HSE thus tends to favor the smaller transition as well.

The zincblende CdS, Hawleyite, is not as widely used as wurtzite CdS, Greenockite, and neither is widely used now as bulk crystal—most of the available, reliable experimental data for cubic CdS are for thin films, which typically have larger gaps than for the bulk, and hexagonal CdS is the structure generally used in thin film solar cells and quantum dots. Nevertheless, the HISS and HSE results are within what would be anticipated and the consistently low errors HISS yields are encouraging.

Finally, the wide gap nitrides of aluminum and boron are worthy of comment because BN is an unusual zincblende compound while the isoelectronic AlN adopts a rather polar wurtzite structure. Boron nitride, ‘borazone’ is almost as hard as diamond, has excellent refractory properties \cite{67}, and, atypical of most zincblende structures, has a band gap (6.3 eV) well into the UV spectrum. Surprisingly, the predicted screened hybrid band gaps are still good.

3.5. Timings

In addition to its excellent performance for lattice parameters, HISS possesses another advantage over HSE: because the range-separation parameter $\omega_{LR}$ for HISS is roughly twice
Figure 5. Band structures for the relaxed geometries of AlSb as calculated with LSDA (left), HSE (middle) and HISS (right). Note that all functionals show that the two observed experimental transitions near $\Gamma \rightarrow X$ and $\Gamma \rightarrow L$ are close in energy, but that the $\Gamma \rightarrow X$ gap is smaller.

Table 6. CPU time per SCF cycle relative to PBE for representative systems. The numbers in parentheses are the numbers of SCF cycles required for convergence.

| Solid | PBE | HISS | HSE06 | PBEh |
|-------|-----|------|-------|------|
| C     | (9) | 1.95 (9) | 2.92 (10) | — |
| Si    | (10) | 2.04 (12) | 2.38 (10) | 36.50 (11) |
| BP    | (8) | 2.12 (9) | 2.88 (9) | 42.47 (9) |
| SiC   | (8) | 1.89 (8) | 2.97 (9) | 48.45 (9) |
| MgO   | (10) | 1.85 (10) | 2.18 (8) | 49.15 (15) |
| InN   | (18) | 2.84 (14) | 5.24 (14) | — |
| Mean  | —  | 2.12 | 3.10 | 44.14 |

the parameter $\omega$ of HSE, the long-range exchange in HISS is screened more aggressively. Accordingly, the computational cost for HISS is smaller than that for HSE. The claim in [68] that HISS is quite expensive because one must do the two-electron integrals twice is simply incorrect. While this is true in the most naive implementation, computationally efficient implementations of HISS will only carry out the so-called $[0]^{(m)}$ integrals twice, and the expensive steps of contraction and angular moment recurrence are done once, just as in HSE.

Table 6 shows the CPU time per SCF cycle relative to that of PBE for BP, C, InN, MgO, Si, and SiC. These materials include both wide gap and narrow gap materials adopting diamond, zincblende or wurtzite lattices. All calculations are performed at the experimental geometries. We see that HISS is only twice as expensive as PBE, and that HSE costs about 50% more than HISS, both producing much better band gaps and lattice parameters. We also include results for the PBEh [25, 24] global hybrid to illustrate the enormous savings resulting from range separation. PBEh calculations on C and InN were not possible at high accuracy in our code because they required more memory than we had available. The PBEh band gaps for Si, SiC BP, and MgO are respectively 1.81, 3.22, 2.74, and 7.31 eV. Comparison with table 4 shows that the PBEh band gaps are in error by approximately 0.7 eV, offering minimal improvement over PBE but at an enormously larger computational cost.

Global hybrid functionals like B3LYP and PBEh have been benchmarked against HSE for a few systems and properties, and it has been shown that their increased computational cost (observed for both plane waves and Gaussian orbitals) does not lead to improved answers compared to HSE. This is more true for band gaps of semiconductors, which are over-estimated by both B3LYP and by PBEh [69].

4. Concluding remarks

The middle-range screening utilized in the HISS functional allows for accurate reproduction of lattice parameters with concomitant band gap prediction at nearly the quality of HSE. The HISS screened hybrid band gap errors are systematically over-estimated, but are of increased accuracy for larger gap systems, while the lattice parameters are superior to those produced by LSDA—or even PBEsol—for commercially relevant semiconductors, including non-cubic systems.

In fact, as was recently demonstrated for the perovskite SrTiO$_3$ system [70, 82], HISS can rapidly reproduce difficult lattice distortions while producing near-HSE-quality band gaps. The predictive power provided by such systematic errors was also nicely demonstrated by the challenge of the experimental geometry for the novel Delafossite material CuBO$_2$ [71–73], where both the accuracy of the band gaps and the generally systematic deviations in lattice parameters produced by HSE were used to justify theoretical arguments. Given that HISS performs well for molecules [42], it is reasonable to assume that the molecule–surface interactions will be an improvement over what is currently available.

The timing data indicate that HISS is more computationally efficient than HSE, yet more accurate than the semilocal functionals PBEsol or PBEh, imbuing HISS with yet another advantage: reliable theoretical data for semiconductors may be acquired by running one job that will complete at a computational expense of merely twice that of PBE, without necessitating additional high-level corrections. Such easily obtained, high quality lattice constants coupled with improved optical band gap predictions will render HISS a useful adjunct to HSE in the modeling of geometry-sensitive semiconductors or any material necessitating accurate lattice parameters in order to obtain reliable band gaps.

Acknowledgments

The work at Rice University was supported by the Qatar National Research Fund (QNRF) through the National Priorities Research Program (NPRP Grant No. 09-431-076) and The Welch Foundation (C-0036). MJL would like to...
[62] Alibert C, Joullie A, Joullie A M and Ance C 1983 Phys. Rev. B 27 4946
[63] Matthieu H, Auvergne D, Merle P and Rustagi K C 1975 Phys. Rev. B 12 5846
[64] Joullie A, Girault B, Joullie A M and Zien-Eddine A 1982 Phys. Rev. B 25 7830
[65] Safa Kasap P C E 2007 Springer Handbook of Electronic and Photonic Materials ed S Kasap and P Capper (Berlin: Springer)
[66] Economou E N 2010 The Physics of Semiconductors Essentials and Beyond (Berlin: Springer)
[67] Berger L I 1997 Semiconductor Materials (Boca Raton, FL: CRC Press)
[68] Song J W, Yamashita K and Hirao K 2011 J. Chem. Phys. 135 071103
[69] Marsman M, Paier J, Stroppa A and Kresse G 2008 J. Phys.: Condens. Matter 20 064201
[70] El-Mellouhi F, Brothers E N, Lucero M J and Scuseria G E 2011 Phys. Rev. B 84 115122
[71] Snure M and Tiwari A 2007 Appl. Phys. Lett. 91 092123
[72] Scanlon D O, Walsh A and Watson G W 2009 Chem. Mater. 21 4568
[73] Trani F, Vidal J, Botti S and Marques M A L 2010 Phys. Rev. B 82 085115
[74] Heyd J, Scuseria G E and Ernzerhof M 2006 J. Chem. Phys. 124 219906
[75] Perdew J P, Ruzsinszky A, Ernzerhof M, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2009 Phys. Rev. Lett. 102 039902
[76] Doorn C V and Nobel D D 1956 Physica 22 338–42
[77] Davidson I A, Moug R T, Izdebski F, Bradford C and Prior K A 2010 Phys. Status Solidi b 247 1396–8
[78] Hartmann J M, Cibert J, Kany F, Mariette H, Charleux M, Alleysson P, Langer R and Feuillet G 1996 8 6257–65
[79] Anderson P A, Kendrick C E, Kinsey R J, Kennedy V J, Markwitz A, Reeves R J and Durbin S M 2006 Smart Mater. Struct. 15 S87–91
[80] Evans D A, McGlynn A G, Towlson B M, Gunn M, Jones D, Jenkins T E, Winter R and Poolton N R J 2008 J. Phys.: Condens. Matter 20 075233
[81] Zakharov O, Rubio A, Blase X, Cohen M L and Louie S G 1994 Phys. Rev. B 50 10780–7
[82] El-Mellouhi F, Brothers E N, Lucero M J and Scuseria G E 2011 Phys. Rev. B 84 199907