

# The band gap problem: the accuracy of the Wien2k code confronted

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This paper is a continuation of our detailed study [Phys. Rev. B 86, 195106 (2012)] of the performance of the recently proposed modified Becke-Johnson potential (mBJLDA) within the known Wien2k code. From the 41 semiconductors that we have considered in our previous paper to compute the band gap value, we selected 27 for which we found low temperature experimental data in order to pinpoint the relative situation of the newly proposed Wien2k(mBJLDA) method as compared to other methods in the literature. We found that the GWA gives the most accurate predictions. The Wien2k (mBJLDA) code is slightly less precise, in general. The Hybrid functionals are less accurate, on the overall. The GWA is definitely the most precise existing method nowadays. In 88% of the semiconductors considered the error was less than 10%. Both, the GWA and the mBJLDA potential, reproduce the band gap of 15 of the 27 semiconductors considered with a 5% error or less. An extra factor to be taken into account is the computational cost. If one would seek for precision without taking this factor into account, the GWA is the method to use. If one would prefer to sacrifice a little the precision obtained against the savings in computational cost, the empirical mBJLDA potential seems to be the appropriate method. We include a graph that compares directly the performance of the best three methods, according to our analysis, for each of the 27 semiconductors studied. The situation is encouraging but the problem is not yet a closed issue.

*Keywords:* Band gap problem; Wien2k; mBJLDA potential; hybrid functionals; GW approximation.

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## 1. Introduction

Khon-Sham equations [1] are central to the practical application of Density Functional Theory (DFT). To solve them, an approximation to the exchange and correlation energy is required from which an exchange and correlation potential is derived. The way in which this term is approximated is crucial to the proper description of the band structure of solids. The Local Density Approximation (LDA) [2], the Generalized Gradient Approximation (GGA) [3–5] and the meta-GGA [3, 6], among others, describe very well the electronic band structure of even complicated metallic systems. They fail, nevertheless to account for the band gap value of semiconducting systems, a short come known for several years now [7]. Efforts to solve this problem were done since long ago. Approximations as the “scissor operator” [8], the Local Spin Density Approximation, LSDA+U [9] and methods based on the use of Green’s functions and perturbation theory as the GW approximation, GWA [10–12], were proposed. In the last ten years, these efforts gave rise to substantially improved results. Some of the new proposals include, the screened hybrid functional of Heyd, Scuseria and Ernzerhof (HSE) [13–15] and the middle-range exchange and correlation hybrid functional of Henderson, Izmaylov, Scuseria and Savin (HISS) [16, 17]. Another recent proposal is the modified Becke-Johnson potential (mBJLDA) proposed by Tran and Blaha [18]. This potential was introduced to the Wien2k code [19] in 2010.

## 2. The mBJLDA potential

Recently, we made a detailed analysis of the mBJLDA potential based on the calculation of the electronic band structure

of 41 semiconductors [20]. This paper is a continuation of that work. We found an important improvement in the predictions of the band gap as compared to experiment. The mBJLDA potential [18] is an empirical potential of the form

$$V_{x,\sigma}^{\text{MBJ}}(r) = cV_{x,\sigma}^{\text{BR}}(r) + (3c - 2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_{\sigma}(r)}{\rho_{\sigma}(r)}} \quad (1)$$

where  $\rho_{\sigma}(r)$  is the spin dependent density of states,  $t_{\sigma}(r)$  is the kinetic energy density of the particles with spin  $\sigma$ . and  $V_{x,\sigma}^{\text{BJ}}(r)$  is the Becke-Roussel potential (BR) [21]. The  $c$  stands for

$$c = \alpha + \beta \left( \frac{1}{V_{\text{cell}}} \int d^3r \frac{|\nabla\rho(r)|}{\rho(r)} \right)^{1/2} \quad (2)$$

$\alpha$  and  $\beta$  are free parameters. The Wien2k code defines  $\alpha = -0.012$  and  $\beta = 1.023 \text{ Bohr}^{1/2}$ . These values are general but certainly fixed experimenting with several cases. A particular feature of this potential is that a corresponding exchange and correlation energy term,  $E_{xc}[\rho]$ , such that the mBJLDA potential is obtained in the usual way, namely,  $V_{xc} = \delta E_{xc}[\rho]/\delta\rho$ , is not possible. As a consequence, a consistent optimization procedure to obtain the lattice parameters, the Bulk modulus and its derivative with respect to pressure are not actually possible. This is a consequence of the empirical character of this potential. For that reason, Tran and Blaha have proposed the empirical alternative that prior to a band structure calculation with the mBJLDA potential, the lattice parameter is found from either a LDA or a GGA optimization procedure and the result introduced into the code to perform the band structure calculation of the semiconductor system. Such a procedure gives rise to quite improved results as compared to the previous version of

the Wien2k code. It is known that the LDA underestimates as a rule, the lattice parameters and, on the contrary, GGA overestimates them. We have explored the possibility of using the averaged value as the lattice parameter,  $a_{\text{Avg}}$ , where  $a_{\text{Avg}} = (a_{\text{LDA}} + a_{\text{GGA}})/2$ . Here  $a_{\text{LDA}}$  ( $a_{\text{GGA}}$ ) is the lattice parameter obtained from an LDA (GGA) optimization procedure. When  $a_{\text{Avg}}$  is used as input into the Wien2k code implemented with the mBJLDA potential, a better agreement of the band gap value with experiment is obtained as compared to the results with either  $a_{\text{LDA}}$  or  $a_{\text{GGA}}$ . So this procedure turns out to give better results than the one recommended by Tran and Blaha and its extra computational cost is relatively low. A surprising result was, nevertheless, obtained when the experimental low temperature lattice parameter,  $a_{\text{LT}}$ , was introduced instead. Unexpected deviations of the band gap value from experiment as big as 48% were obtained [20]. This is a disturbing result since the lattice parameters obtained from any optimization procedure are judged to be as good as the deviation from the experimental lattice parameter value is small, and so one expects to get the best result (the minimum deviation of the predicted band gap value from experiment) when the experimental lattice parameter is used. This is not the case. This fact throws doubts on the meaning of the optimization procedure altogether when the empirical mBJLDA code is employed. Nevertheless, we stress that the results obtained for the band gap value of semiconductors using the mBJLDA potential represents a relevant improvement at relatively low computational cost, a fact that we will emphasize below.

### 3. The HSE method

Hybrid functionals are a linear combination of Hartree-Fock (HF), LDA and GGA terms and were proposed initially with the aim of improving LDA and GGA in the calculation of the energy bands of molecules [22, 23]. More recently, hybrid functionals were used as an effort to improve the old-standing problem of the band gap of semiconductors; they include the Heyd-Scuseria-Ernzerhof (HSE) functional [13] proposed in 2003. It combines a screened short-range HF term and a screened short- and long-range functional proposed by Perdew, Burke and Ernzerhof (PBE) [4]. The screened terms in HSE result from splitting the Coulomb operator into short- and long-range terms in the following way

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\omega r)}{r}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r)}{r}}_{\text{LR}}, \quad (3)$$

where the complementary error function

$$\text{erfc}(\omega r) = 1 - \text{erf}(\omega r)$$

and  $\omega$  determines the range. The functional form of HSE is based on the hybrid functional of Perdew, Burke and Ernzerhof (PBEh) [24] (also known in the literature as PBE1PBE and PBE0) [25, 26], as follows

$$E_{xc}^{\text{PBEh}} = aE_x^{\text{HF}} + (1-a)E_x^{\text{PBE}} + E_x^{\text{PBE}} + E_c^{\text{PBE}}, \quad (4)$$

The expression for the HSE exchange-correlation energy,  $E_{xc}^{\text{HSE}}$ , is

$$E_{xc}^{\text{HSE}} = aE_x^{\text{HF,SR}}(\omega) + (1-a)E_x^{\omega\text{PBE,SR}}(\omega) + E_x^{\omega\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}, \quad (5)$$

where  $E_x^{\text{HF,SR}}$  is the HF short-range functional (SR),  $E_x^{\omega\text{PBE,SR}}$  and  $E_x^{\omega\text{PBE,LR}}$  are the short-range (SR) and long-range (LR) components of the PBE functional.  $a$  is a mixing constant that is derived from perturbation theory [27]. In the literature, the functional HSE appears as HSE03 and HSE06. The difference is in the choice of the value of  $\omega$ . We will refer to the HSE03 simply as HSE, in this work. In 2005, Heyd *et al.* [14] reported a study of the band gap and lattice parameters of semiconductor compounds using the HSE functional. We will comment on these results below.

Recently, Marques *et al.* [28] have proposed to relate the mixing constant  $a$  to dielectric properties of the solid. They took  $a = 1/\epsilon_{\infty}^{\text{PBE}}$ . Their calculation using the hybrid functional PBE0 improves the predictions for the band gap value of the 21 semiconductors considered as compared to the original formulation. Furthermore, they used  $a \sim \bar{g}$ , and  $a \sim \bar{g}^4$  where  $\bar{g}$  takes the form of the term in parenthesis in Eq. (2). They introduced this form of the  $a$  parameter into the hybrid functionals PBE0 and HSE06, respectively, and got an improved result. These proposals improve the performance of the hybrid functionals at no extra cost. We will comment further on these results below.

### 4. The HISS potential

Another successful potential to calculate the band structure of semiconductors is the middle-range hybrid exchange and correlation Henderdon-Izmaylov-Scuderia-Savia functional (HISS) [16, 17]. It also uses the PBE potential but in a different way,

$$E_{xc}^{\text{HISS}} = E_x^{\text{SR-PBE}} + E_x^{\text{LR-PBE}} + E_c^{\text{PBE}} + c_{\text{MR}}(E_x^{\text{MR-HF}} - E_x^{\text{MR-PBE}}), \quad (6)$$

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

$$\frac{1}{r} = \underbrace{\frac{\text{erfc}(\omega_{\text{SR}} r)}{r}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega_{\text{SR}} r)}{r}}_{\text{LR}} + \underbrace{\frac{\text{erf}(\omega_{\text{SR}} r) - \text{erf}(\omega_{\text{LR}} r)}{r}}_{\text{MR}}, \quad (7)$$

In 2012, Lucero *et al.* [29] reported their study of the band gap and lattice parameters of some semiconductor compounds using HISS, with  $\omega_{\text{SR}} = 0.84a_0^{-1}$ ,  $\omega_{\text{LR}} = 0.20a_0^{-1}$  y  $c_{\text{MR}} = 0.60$ . These values were determined by fitting them to some atomization energies, barriers heights and values of the gap for some compounds.

## 5. The GW approximation (GWA)

As it is well known, the many-body Schrödinger equation contains the Coulomb interaction term which is a two-body potential and creates the difficulty to solve it for realistic systems. To address this problem, the Hartree-Fock Approximation (HFA) adds to the average Coulomb potential (the Hartree term) a non-local exchange potential which reflects the Pauli Exclusion principle. The energy gap of semiconductors predicted in this way turns out to be in most cases too large. This is due to the neglect of correlations or screening which are crucial in solids. To simulate the effect of correlations, Slater introduced the  $X\alpha$  approximation which may be regarded as a precursor of the modern DFT. In DFT, the ground state energy can be proved to be a functional of the ground state density but the explicit form of the functional is not known. The minimization of the total energy functional with respect to the density gives the Kohn-Sham equations. The unknown exchange and correlation potential is approximated either by the local density approximation (LDA), the generalized gradient approximation (GGA) or the meta-GGA, among others, which describe metals well but fail to account for the band gap of semiconductors. The empirical mBJLDA potential is a response. An alternative way to deal with this problem is the GW approximation (GWA). It is derived from many-body perturbation theory [30]. The form of the self-energy in the GWA is the same as in the HFA but the Coulomb interaction is dynamically screened remedying the most serious deficiency of the HFA. The corresponding self-energy is therefore non-local and energy dependent. The Green function is obtained from a Dyson equation of the form  $G = G_0 + G_0 \Sigma G$  where  $G_0$  describes the direct propagation without the exchange and correlation interaction and  $\Sigma$  contains all possible exchange and correlation interactions with the system that an electron can have in its propagation. The GWA may be regarded as a generalization of the HFA but with a dynamically screened Coulomb interaction. The non-local HFA is given by

$$\Sigma^x(\mathbf{r}, \mathbf{r}') = \sum_{k_n}^{(\text{occ})} \psi^*(\mathbf{r}) \psi(\mathbf{r}') \nu(\mathbf{r} - \mathbf{r}') \quad (8)$$

Where  $\nu(\mathbf{r} - \mathbf{r}')$  is the bare Coulomb interaction. The GWA corresponds to replacing the bare Coulomb interaction  $\nu$  by a screened interaction  $W$ . In the language of perturbation theory this corresponds to

$$\Sigma^x(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') \quad (9)$$

For details see Ref. 11. We will analyze the results obtained for the semiconductor gap value using this approximation in what follows.

In 2005, Rinke *et al.* [31] using the so called OEPx(cLDA)+GW approximation obtained a reasonable agreement with experiment when calculating the band gap of a certain number of semiconductors. In 2007, Shishkin

*et al.* [32, 33] using a self-consistent GWA (GWA + DFT), and the self-consistent GW approximation with attractive electron-hole interaction, scGW(e-h) accounted quite well for the experimental band gap of several semiconductors.

Now we proceed to analyze some of the different offers in the literature in what the calculation of the band gap of semiconductors is concerned and compare their results among themselves and with experiment.

## 6. Analysis

In Table I, we present the results obtained for the band gap using different methods and approximations. The first two columns refer to our calculation. The resulting values using LDA and mBJLDA [20] as in version 2011 of Wien2k code are presented. We have used as lattice parameter the average of the values obtained from an LDA and a GGA optimization which, as we found [20], gives the best results for the gap as compared to experiment when the mBJLDA potential is used. Next we report the values obtained with the hybrid HISS and HSE06 functional [29], HSE [13, 14] and GWA. In the column denoted as GWA, we include the most precise predictions for the gap reported in the literature using either the self consistent GW (scGWA) [33–40] or the scGWA with attractive electron-hole interaction, scGW(e-h) [32].

In Fig. 1, the band gap value is given in the horizontal axis. Each vertical line is drawn at the experimental low temperature band gap value for each of the 27 semiconductors considered. The vertical axis represents the absolute percent error, ( $|\text{Error}(\%)|$ ) calculated as shown at the bottom of Table I. The three data on each vertical line correspond to the result obtained using the mBJLDA potential, the HSE method and the GWA. So, for a particular semiconductor, the graph compares directly the performance of each of the three best methods as found in this work. (see Table I).

As it is very well known [7] and as it appears in Table I, the LDA does not reproduce the experimental values of the band gap of semiconductors. Furthermore, The Wien2k (LDA) code produces for MgS and MgTe a band structure which shows a direct band gap in contradiction with experiment [20].

The results of the predictions obtained with the GWA are the most accurate with an averaged error of 5.7%. The empirical mBJLDA potential produces results with an averaged error of 8.4%. Next, the errors obtained with the HSE potential result in an averaged error of 10.2%, HSE06 (11.5%) and HISS (34.1%). The GWA, the mBJLDA potential, and HSE functional do better than the ones reported by Marques *et al.* [28]. They get results with averaged errors 16.5%, 14.4% y 10.4% using the hybrid functional PBE0 <sub>$\epsilon_\infty$</sub> , PBE0<sub>mix</sub> and HSE06<sub>mix</sub>, respectively. In this paper, the authors suggest the possibility that the mixing parameter should be related to physical variables. The performance of the GWA is highly accurate, 88% of the calculated results recorded here show less than 10% error. This is to be compared to the one obtained when using mBJLDA (74%), HSE (54%), HSE (42%),

TABLE I. We compare the results for the gap ( $E_g$ ), in eV, that we obtained with the Wien2k(LDA) code and with mBJLDA potential, with the hybrid functionals HISS, HSE06, HSE and with the GWA (see text). The crystal structure and percentage difference with respect to the experiment is shown in parenthesis. The minus sign means that the calculation underestimates the experimental value. The experimental data are from Refs. 41 to 49.

Solid	Gap						$E_g^{\text{Expt.}}$
	$E_g^{\text{LDA}}$	$E_g^{\text{mBJLDA}}$	$E_g^{\text{HISS}}$	$E_g^{\text{HSE06}}$	$E_g^{\text{HSE}}$	$E_g^{\text{GWA}}$	
The experimental band gap at Low temperature							
C(A1)	4.16 (-24%)	4.95 (-9.7%)	6.11 (11.5%)	5.42 (-1.1%)	5.49 (0.2%)	5.6 <sup>a</sup> (2.2%)	5.48
Si(A1)	0.45 (-62%)	1.17 (0.0%)	1.45 (23.9%)	1.22 (4.3%)	1.28 (9.4%)	1.24 <sup>†</sup> (6.0%)	1.17
Ge(A1)	0.00 (-100%)	0.80 (8.1%)	1.08 (45.9%)	0.54 (-27.0%)	0.56 (-24.3%)	0.75 <sup>a</sup> (1.4%)	0.74
MgO(B1)	5.00 (-36%)	7.22 (-7.1%)	7.87 (1.3%)	6.40 (-17.6%)	6.50(-16.3%)	7.7 <sup>b</sup> (-0.9%)	7.77
AlAs(B3)	1.32 (-41%)	2.17 (-2.7%)	2.40 (7.6%)	2.16 (-3.1%)	2.24 (0.4%)	2.18 <sup>c</sup> (-2.2%)	2.23
SiC(B3)	1.30 (-46%)	2.26 (-6.6%)	2.74 (13.2%)	2.32 (-4.1%)	2.39 (-1.2%)	2.53 <sup>†</sup> (4.5%)	2.42
AlP(B3)	1.43 (-42%)	2.33 (-4.9%)	2.71 (10.6%)	2.44 (-0.4%)	2.52 (2.9%)	2.57 <sup>†</sup> (4.9%)	2.45
GaN(B3)	1.90 (-46%)	2.94 (-10.9%)	4.05 (22.7%)	2.97 (-10.0%)	3.03 (-8.2%)	3.27 <sup>†</sup> (-0.9%)	3.30
GaAs(B3)	0.47 (-69%)	1.56 (2.6%)	1.86 (22.4%)	1.18 (-22.4%)	1.21 (-20.4%)	1.52 <sup>‡</sup> (0.0%)	1.52
InP(B3)	0.45 (-68%)	1.52 (7.0%)	2.23 (57.0%)	1.61 (13.4%)	1.64 (15.5%)	1.44 <sup>d</sup> (1.4%)	1.42
AlSb(B3)	1.14 (-32%)	1.80 (7.1%)	2.05 (22.0%)	1.85 (10.1%)	1.99 (18.5%)	1.64 <sup>d</sup> (-2.4%)	1.68
GaSb(B3)	0.07 (-91%)	0.90 (9.8%)	1.31 (59.8%)	0.70 (-14.6%)	0.72 (-12.2%)	0.62 <sup>d</sup> (-24.4%)	0.82
GaP(B3)	1.39 (-41%)	2.24 (-4.7%)	2.67 (13.6%)	2.42 (3.0%)	2.47 (5.1%)	2.55 <sup>d</sup> (8.5%)	2.35
InAs(B3)	0.0 (-100%)	0.55 (31.0%)	0.93 (121.4%)	0.36 (-14.3%)	0.39 (-7.1%)	0.40 <sup>d</sup> (-4.8%)	0.42
InSb(B3)	0.0 (-100%)	0.31 (29.2%)	0.80 (233.3%)	0.28 (16.7%)	0.29 (20.8%)	0.18 <sup>d</sup> (-25%)	0.24
CdS(B3)	0.93 (-63%)	2.61 (5.2%)	2.72 (9.7%)	2.10 (-15.3%)	2.14 (-13.7%)	2.45 <sup>e</sup> (-1.2%)	2.48
CdTe(B3)	0.49 (-69%)	1.67 (4.4%)	2.00 (25.0%)	1.49 (-6.9%)	1.52 (-5.0%)	1.76 <sup>f</sup> (10.0%)	1.60
CdSe(B3)	0.38 (-79%)	1.87 (5.6%)	1.90 (7.3%)	1.36 (-23.2%)	1.39 (-21.5%)	2.01 <sup>f</sup> (13.6%)	1.77
ZnS(B3)	2.08 (-45%)	3.70 (-2.9%)	4.12 (8.1%)	3.37 (-11.5%)	3.42 (-10.2%)	3.86 <sup>‡</sup> (1.3%)	3.81
ZnSe(B3)	1.19 (-58%)	2.74 (-2.8%)	2.93 (3.9%)	2.27 (-19.5%)	2.32 (-17.7%)	2.84 <sup>f</sup> (0.7%)	2.82
ZnTe(B3)	1.20 (-50%)	2.38 (-0.4%)	2.77 (15.9%)	2.16 (-9.6%)	2.19 (-8.4%)	2.57 <sup>f</sup> (7.5%)	2.39
MgS(B3)	-	5.18 (-4.1%)*	5.17 (-4.3%)	4.48 (-17.0%)	4.78 (-11.5%)	-	5.40
MgTe(B3)	-	3.59 (-2.2%)*	3.91 (6.5 %)	3.49 (-4.9%)	3.74 (1.9%)	-	3.67
GaN(B4)	2.06 (-41%)	3.13 (-10.6%)	4.23 (20.9%)	3.14 (-10.3%)	3.21 (-8.3%)	3.5 <sup>g</sup> (0.0%)	3.50
InN(B4)	0.03 (-96%)	0.82 (15.5%)	1.51 (112.7%)	0.66 (-7.0%)	0.71 (0.0%)	-	0.71
AlN(B4)	4.11 (-34%)	5.53 (-10.7%)	6.62 (6.9%)	5.50 (-11.2%)	6.45 (4.2%)	5.8 <sup>g</sup> (-6.3%)	6.19
ZnO(B4)	0.76 (-78%)	2.76 (-19.8%)	-	-	-	3.2 <sup>†</sup> (-7.0%)	3.44
$\Delta$ (%)	60.2%	8.4%	34.1%	11.5%	10.2%	5.7%	-
The experimental band gap at room temperature							
BP(B3)	1.15 (-43%)	1.83 (-8.5%)	2.43 (21.5%)	2.21 (10.5%)	2.16 (8.0%)	-	2.00
BN(B3)	4.39 (-29%)	5.85 (-5.6%)	6.69 (7.90%)	5.90 (-4.8%)	5.99 (-3.4%)	7.14 (15.2%)	6.20
MgSe(B1)	1.71 (-31%)	2.89 (17.0%)	3.05 (23.5%)	2.58 (4.5%)	2.62 (6.1%)	-	2.47
BaS(B1)	1.93 (-50%)	3.31 (-14.7%)	3.61 (-7.0%)	3.21 (-17.3%)	3.28 (-15.5%)	3.92 (1.0%) <sup>h</sup>	3.88
BaSe(B1)	1.74 (-51%)	2.87 (-19.8%)	3.14 (-12.3%)	2.80 (-21.8%)	2.87 (-19.8%)	-	3.58
BaTe(B1)	1.37 (-56%)	2.24 (-27.3%)	2.48 (-19.5%)	2.22 (-27.9%)	2.50 (-18.8%)	-	3.08
BAAs(B3)	1.23 (-16%)	1.72 (17.8%)	2.14 (46.6%)	1.89 (29.5%)	1.92 (31.5%)	-	1.46

\*with mBJ( $a_{LDA}$ ). <sup>†</sup>scGW(h-e) in Ref. 32. <sup>‡</sup>scGW in Ref. 33. <sup>a</sup>Ref. 34. <sup>b</sup>Ref. 35. <sup>b</sup>Ref. 36. <sup>d</sup>Ref. 37. <sup>e</sup>Ref. 38. <sup>f</sup>Ref. 39. <sup>g</sup>Ref. 40. <sup>h</sup>Ref. 50.  $\Delta$ (%) is the average of the absolute percent deviations. We calculate the percent deviation as follows  $\text{Error}(\%) = (E_g^{\text{Teo.}} - E_g^{\text{Expt.}}) * 100 / E_g^{\text{Expt.}}$ .

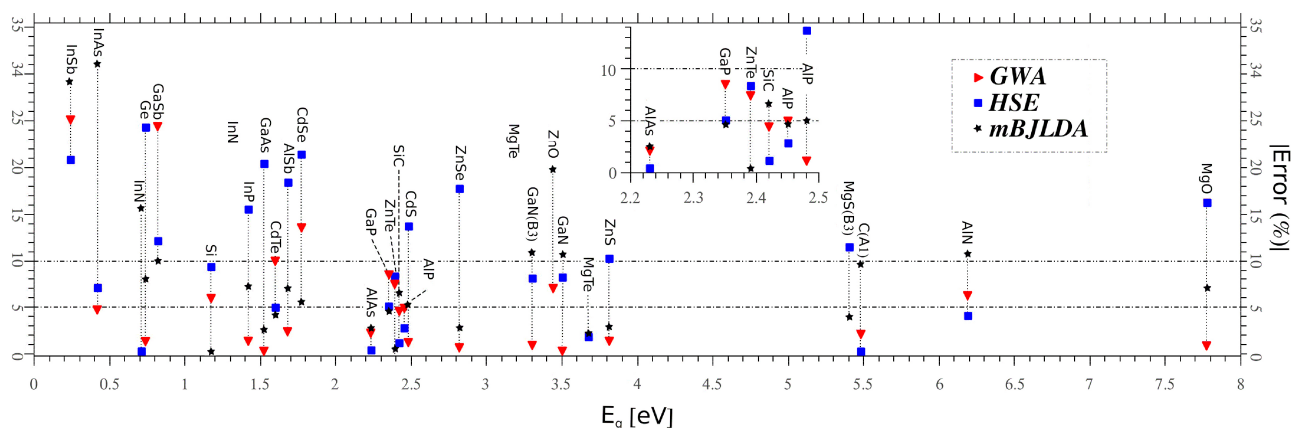


FIGURE 1. The vertical axis is the absolute percent error ( $|\text{Error}(\%)|$ ). Each vertical line is drawn at the low-temperature experimental band gap value for each semiconductor. It compares, the three best results (GWA, mBJLDA, and HSE) according to our analysis. The inset shows in more detail the semiconductors with a gap between 2.2 to 2.5 eV for clarity (see Table I and text).

HISS (35%). On the other hand, more than a 20% deviation from experiment occurs when using mBJLDA in 7% of the cases, and with the GWA in 8% of the semiconductors studied, which is to be compared with HSE (15%), HISS (46%). All together, the best results are obtained when using the GWA; mBJLDA is next, but also HSE gives results with acceptable accuracy. A special case is the very-low-gap InSb. In this case none of the methods give less than a 20% error although it would be more reasonable to judge these results from the absolute deviation in electron-volts rather than from the percent deviation (see Table I). It is important for the overall picture to stress that the GWA and our calculations with the mBJLDA potential present deviations less than 5% in 15 of the 27 semiconductors considered. When the HSE potential is considered, 12 of the 27 present less than a 5% deviation.

One more observation. In the previous analysis we took into account only low temperature band gap data. In Table I, we also present some calculations for which we did not found experimental reports at low temperature. Since the calculations are done at 0K, room-temperature measurements require extrapolation either using Varshni's law or a quadratic fit or any other suitable method which, in any case, generates an extra uncertainty in the obtained 0K data. If we rather use the high temperature data, the HSE potentials give a better agreement with experiment.

Recently the mBJLDA potential has presented very good results in the study of complex systems. Is the case of the electronic, and magnetic features of the metal-insulator transition phase of VO<sub>2</sub>, which are well reproduced using the mBJ potential [51]. This result does not reproduce correctly using the hybrid functional HSE [52].

## 7. Conclusions

The accurate calculation of the band gap of semiconductors is a difficult task that has been the object of intense research

with the result of important progress during the last approximately ten years. As a continuation of our previous work (PRB) where we performed a detailed analysis of the performance of the recently published modified Becke-Johnson potential presented in this work our analysis of some different solutions and compare their results among them to pinpoint the actual accuracy of this empirical potential as compared to other methods. A group of 27 semiconductors (see Table I) for which we found low temperature data on the band gap value were considered. The results of the GWA, the Wien2k implemented with the mBJLDA potential, and codes using a hybrid functional, HSE, and HISS were taken into consideration. The results reported by Marques *et al.* [28] were found to be less accurate than the ones of the GWA, the mBJLDA potential and the HSE functional (see text above for the precise definition used here). The GWA was found to give, all together the best results. The mBJLDA potential produces results slightly less accurate and HSE comes next. The two first methods give quite good results (prediction better than 5% for 15 of the 27 semiconductors studied). In Fig. 1, we compare the performance of the three best methods found in this analysis for each of the 27 semiconductors separately. It is important to stress the empirical character of the mBJLDA potential because it prevents the consistent definition of the optimization procedure which contrasts with the sound bases of the GWA. Even with the several theoretical non-properly solved issues, the mBJLDA potential gives rise to acceptable predictions of the band gap value as compared to experiment. An extra factor to be taken into account is the computational cost. If one would seek for precision without taking this factor into account, the GWA is the method to use. If one would prefer to sacrifice a little the precision obtained against the savings in computational cost, the mBJLDA potential seems the appropriate method. In conclusion, we can typify the state of matters with respect to the calculation of the band gap of semiconductors as follows. A quite precise method does exist, the GWA approximation. It's computational cost

is higher. A relatively quicker code, the Wien2k implemented with the mBJLDA potential, gives somehow less accurate results but quite acceptable at lower computational cost. Other methods do exist but are less accurate. Very recently, the new approximation announced in the Ref. [53] was implemented in the Wien2k 12.1 code for public use. The new hybrid functional YS-PBE0 is “equivalent” to the HSE one, according to the authors. We will study this new functional in future work.

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