Local modified Becke-Johnson exchange-correlation potential for interfaces, surfaces, and two-dimensional materials

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The modified Becke-Johnson meta-GGA potential of density functional theory has been shown to be the best exchange-correlation functional to determine band gaps of crystalline solids. However, it cannot be consistently used for the electronic structure of non-periodic or nanostructured systems. We propose an extension of this potential that enables its use to study heterogeneous, finite and low-dimensional systems. This is achieved by using a coordinate-dependent expression for the parameter $c$ that weights the Becke-Russel exchange functional, in contrast to the original global formulation, where $c$ is just a fitted number. Our functional takes advantage of the excellent description of band gaps provided by the modified Becke-Johnson potential and preserves its modest computational effort. Furthermore, it yields with one single calculation band diagrams and band offsets of heterostructures and surfaces. We exemplify the usefulness and efficiency of our local meta-GGA functional by testing it for a series of interfaces (Si/SiO$_2$, AlAs/GaAs, AlP/GaP, and GaP/Si), a Si surface, and boron nitride monolayer.

INTRODUCTION

The world around us is inhomogeneous. Approximately homogeneous parts of matter are separated from each other and from the surrounding vacuum by interfaces and surfaces, and these regions are the origin of a vast number of fascinating and useful phenomena studied across different fields, ranging from biology, over soft matter, to solid-state physics [1]. Photoelectric effect, quantum Hall effect, symmetry-protected topological states, or electron flow in a transistor are well known examples of physics emerging at interfaces or surfaces [2]. Understanding electronic properties such as local band gaps, band alignments, energy levels of localized states at interfaces and surfaces is crucial to interpret and control the phenomena arising in these regions, opening the way to technological breakthroughs.

The most successful method for the theoretical study of surfaces and interfaces in unquestionably density-functional theory (DFT) [3, 4]. This theory combines an unparalleled accuracy with relatively mild computational requirements. In Kohn-Sham DFT all the complexities of the many-electron system are included in the so-called exchange-correlation (XC) functional. This is a rather complicated quantity that has to be approximated in any practical use of DFT, and that ultimately determines the quality of the results. Standard semilocal approximations to the XC functionals are quite successful in predicting many properties of solids, such as the atomic structure, phonon spectra or the qualitative band structure. Unfortunately, for an accurate description of band gaps and band alignments, it is necessary to use more advanced approximations, like hybrid functionals [5, 6] or even many-body $GW$ methods [7, 8]. These are computationally much more expensive and can be applied to small surface or interface models only. However, these small models are often not good enough to approximate the inhomogeneous regions of real systems.

A possible way out of this vicious circle are meta-GGA functionals. Here we will be interested in one such functional, the modified Becke-Johnson (MBJ) XC potential [9], which has been optimized for the description of electronic band gaps of homogeneous solids. Various comparisons [10–13] show that MBJ is the best semilocal approximation to determine band gaps, achieving on average an accuracy even better than the one of hybrid functionals [13], and at a much lower computational price.

The MBJ functional is built by combining a part of the Becke-Russel (BR) exchange potential [14] with a correction term proportional to the kinetic energy density $t (\mathbf{r}) = \sum_{i} N \vec{\nabla} \psi_{i}^{\ast} (\mathbf{r}) \cdot \vec{\nabla} \psi_{i} (\mathbf{r}) / 2$ and the electronic density $\rho (\mathbf{r}) = \sum_{i} |\psi_{i} (\mathbf{r})|^{2}$ (see the Supplemental Material [15] for more details). The weights of the two summands are proportional to a material dependent mixing parameter $c$. Led by the analogy with hybrid functionals [16], Tran and Blaha proposed $c$ to be given as

$$
e = \alpha + \beta \bar{g}^{\epsilon}$$

(1)

where $\bar{g}$ is the average of $g (\mathbf{r}) = |\vec{\nabla} \rho (\mathbf{r})| / \rho (\mathbf{r})$ in the unit cell

$$\bar{g} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d^{3} r \, g (\mathbf{r}) .$$

(2)

Originally [9], the exponent $\epsilon$ in Eq. (1) was fixed to 1/2 and the parameters $\alpha$ and $\beta$ were fitted to a set of materials, to minimize the error with respect to their experimental band gaps. Later, an improved fit was performed for $\epsilon = 1$ resulting in $\alpha = 0.488$ and $\beta = 0.5$ bohr [17].
We chose the latter parameters for this work, as they predict band gaps of semiconductors very close to their experimental values. Other parameters were also obtained recently for more specialized material sets [18, 19].

In spite of its many virtues, analyzed in detail in Ref. [11], the MBJ potential also suffers from drawbacks. For example, it is not a functional derivative of any density functional [20, 21], and therefore it violates a few exact conditions [22] and it cannot be used to calculate total energies. Yet another, more practical, problem originates from the form of Eq. (2). Since \( g \) is averaged over the whole periodic unit cell, the functional cannot be consistently used for inhomogeneous systems. This is better explained with a couple of examples. Let us consider a heterostructure made of two materials with very different values of \( c \). In this case, the MBJ potential would use a value of \( c \) averaged over the whole supercell, leading to an incorrect description of the local band gaps of both constituents. Another example are low-dimensional systems, such as surfaces or molecules. In these cases, \( \bar{g} \) converges with the size of the unit cell to a completely inadequate value, that depends on the ionization potential of the system. Some groups tried to solve this problem either by fixing the value of \( c \) to the one of the bulk [23], or by constraining the size of the vacuum region to the value that yields the bulk \( c \) parameter [24]. These procedures might in some cases result in good band gaps in bulk-like regions, but the quality of the description of surfaces is highly questionable.

The impossibility to reliably describe the electronic structure of heterostructures or finite systems is a serious drawback, that hampers the systematic application of this meta-GGA functional to evaluate band gaps or band diagrams in high-throughput calculations for computational materials design. For such calculations, the state-of-the-art for band structures remains the more expensive screened hybrid functional HSE06 [25, 26], despite its significantly higher computational cost and larger mean average error [13]. Here, we propose an effective solution to enable the use of the MBJ potential in automated calculations of nanostructured systems, through an inexpensive local reformulation of the parameter \( c \).

**FORMULATION OF THE LOCAL MBJ FUNCTIONAL**

We extend the scheme that we had originally applied to obtain a local hybrid functional for interfaces [27, 28] and we define the locally averaged, but spatially varying, function

\[
\bar{g}(r) = \frac{1}{(2\pi\sigma^2)^{3/2}} \int d^3r' g(r') e^{-\frac{|r-r'|^2}{2\sigma^2}}, \tag{3}
\]

that depends on a smearing parameter \( \sigma \). We will discuss in the following how \( \sigma \) can be determined once for all, and set as a parameter that defines the functional. The possibility to use a smeared local estimator was suggested by Marques et al. [27] and mentioned as a promising perspective in Refs. [17, 29], but no realization had been attempted yet. The form of \( \bar{g} \) in Eq. (3) is particularly convenient because it can be easily implemented into DFT codes using fast-Fourier transforms via a convolution of \( g(r) \) and the Gaussian in the reciprocal space. We thus introduce the local MBJ (LMBJ) exchange potential with the local parameter \( c(r) \) given by

\[
c(r) = \alpha + \beta \bar{g}(r) \tag{4}
\]

with \( \bar{g}(r) \) as in Eq. (3) and \( \alpha = 0.488 \) and \( \beta = 0.5 \) bohr.

In principle, the LMBJ potential with the local estimator (Eq. 3) could be already used for surfaces and other systems with vacuum. However, a few problems remain. To recover the correct asymptotic behavior of the XC potential, it is necessary that \( c \to 1 \) in the vacuum region. Furthermore, at the matter-vacuum boundary \( g(r) = |\nabla \rho(r)|/\rho(r) \) takes values ranging up to \( \sim 1000 \) bohr\(^{-1}\), leading to extremely large values of the XC potential and thus hindering the calculation from converging. Another complication arises from the fact that \( \rho(r) \) becomes vanishingly small far from the nuclei, leading to numerical instabilities. We solve all these problems by enforcing \( c(r) \to 1 \) for regions of low density through the modification

\[
g(r) = \frac{1-\alpha}{\beta} \left[ 1 - \text{erf} \left( \frac{\rho(r)}{\rho_{th}} \right) \right] + \frac{|\nabla \rho(r)|}{\rho(r)} \text{erf} \left( \frac{\rho(r)}{\rho_{th}} \right) \tag{5}
\]

and by introducing a threshold density \( \rho_{th} \). For \( \rho(r) \gg \rho_{th} \), we obtain the previous limit \( g(r) = |\nabla \rho(r)|/\rho(r) \), while in the opposite case \( g(r) = (1-\alpha)/\beta \) and \( c(r) = 1 \).

Equations 3 and 5 define our LMBJ functional and have been implemented in the VASP code [30]. Since the projector-augmented-waves (PAW) method is used [31], the implementation includes a careful treatment of the PAW spheres in addition to the plane-wave part. We give technical details on the implementation in the Supplemental Material [15].

Before applying the LMBJ potential to realistic systems, we have to choose appropriate values for the parameters \( \sigma \) and \( \rho_{th} \). We set \( \sigma = 3.78 \) bohr = 2 Å, which means that \( g(r) \) is averaged over a region which covers typical interatomic distances. We remark that a similar value was selected for the corresponding \( \sigma \) parameter in Ref. 28 and that we have checked that, with this choice of the smearing, we recover the bulk band gaps calculated with the original MBJ potential (see Supplemental Material [15]). Concerning the threshold density \( \rho_{th} \), we chose a value corresponding to the threshold Wigner-Seitz radius \( r_s^{th} = (3/4\pi\rho_{th})^{1/3} \) = 5 bohr. This value lies well above the \( r_s \) value of most of the metals listed in Ref. [32] and our tests show that we obtain again bulk band gaps of common semiconductors very close to those
yielded by the MBJ potential (see Supplemental Material [15]). Clearly, a different choice should be made if one is interested in simulating materials with extremely low electronic densities. Setting either $\sigma$ and $\rho_{th}$ to smaller values than the chosen ones leads to a clear underestimation of the bulk band gaps.

**APPLICATION OF THE LMBJ FUNCTIONAL**

We are going to apply now the LMBJ functional to study band diagrams of electronic systems in which the crystal periodicity is broken in one direction (e.g., $z$): we therefore consider the local value of $c(r)$ averaged in the $x$-$y$-plane, $\tau_{xy}(z)$, and we calculate the local band structure along the $z$ axis.

To evaluate the local band structure, we calculate the local density of states (LDOS) $D_i(c)$, where we divided the unit cell into slices $\Omega_i$ parallel to the interface with thickness $\Delta z$. The LDOS is then obtained as [28, 33]

$$D_i(c) = \frac{1}{V_{BZ}} \sum \int_{BZ} \omega_{kn}^i \delta(c - \epsilon_{kn})d^3k$$

(6)

with the weight function

$$\omega_{kn}^i = \int_{\Omega_i} |\tilde{\varphi}_{kn}(r)|^2 d^3r,$$

(7)

where $\tilde{\varphi}_{kn}(r)$ are the Kohn-Sham wave functions at wave vector $k$ of band $n$ with eigenvalue $\epsilon_{kn}$.

An important test of our functional is the Si/SiO$_2$ interface, since the bulk $c$ values and the bulk band gaps of the two constituents differ significantly. For this system, we expect that the standard MBJ potential, that used an averaged $c$ value, leads to a poor description of the band gaps of both Si and SiO$_2$. To make a direct comparison with calculations in literature possible, we use the same supercell generated by Giustino and Pasquarello [34], already used in Refs. 28 and 35. The interface model consists of 11 Si atomic layers along the (001) direction and 10 layers of SiO$_2$ in the $\beta$-cristabolite form. We adopted an $8 \times 8 \times 2$ $k$-point grid and a cut-off energy of 400 eV. As in all other calculations in this work, we used PAW pseudopotentials [31] and a spin unpolarized formalism.

We first preconverged the calculation using the Perdew-Burke-Ernzerhof (PBE) functional [36] and used the result as a starting point for the subsequent LMBJ calculation.

In the top panel of Fig. 1 we show the in-plane averaged local mixing for different values of the smearing $\sigma$. For very large $\sigma = 37.8$ bohr, i.e., a smearing over the whole heterostructure, we obtain as expected a constant mixing $\tau_{xy}(z) = 1.32$. In this limit, our LMBJ potential restores the original MBJ (a reference calculation with the MBJ potential yields $c = 1.30$). This calculation thus overestimates, underestimates the $c$-parameter for Si, SiO$_2$ respectively, and consequently the band gaps. Decreasing the smearing leads to a variation of $c$ across the slab. We find $\sigma = 3.78$ bohr to be optimal, since it reproduces the bulk mixing of both Si (heterostructure: $c = 1.13$, bulk: $c = 1.11$) and SiO$_2$ (heterostructure: $c = 1.56$, bulk: $c = 1.58$) well. Interestingly, our optimal smearing value agrees with the one obtained in Ref. [28] for local hybrids using the same Gaussian smearing of the local mixing parameter applied to the same interface model.

In the bottom panel of Fig. 1 we present the LDOS calculated with the optimal $\sigma = 3.78$ bohr. The local band gaps of Si and SiO$_2$ in the middle of the slab using LMBJ ($E_g(Si) = 1.39$ eV, $E_g(SiO_2) = 8.09$ eV) compare well with the MBJ bulk values ($E_g(Si) = 1.20$ eV, $E_g(SiO_2) = 8.79$ eV), even we can clearly see that the SiO$_2$ layer is too thin to allow the saturation of the local band gap to the correct bulk value. In fact, we can clearly observe in Fig. 1 that the interface states extend much more inside SiO$_2$ than in Si. In addition to the local band gaps, we can deduce the band offsets at the
interface directly from our calculation. We obtain ΔEV = 1.98 eV and ΔEC = 4.72 eV for the valence and conduction band offset, respectively. We should compare these numbers with experimental (ΔEVexp = 4.44 eV and ΔECexp = 3.38 eV [38]) and theoretical GW (ΔE\text{GW} = 4.1 eV and ΔE\text{GW} = 2.9 eV [35]) and local hybrid values (ΔE\text{LH} = 4.27 eV and ΔE\text{LH} = 3.05 eV [28]), the latter obtained for the same interface model as in our calculation. The comparison shows that LMBJ gives the correct type of band alignment, with both electrons and holes confined in the SiO2 layer, however the bands of SiO2 are placed ~ 2 eV too high in energy. This is a direct consequence of the fact that, for the Si/SiO2 interface, the LMBJ potential gives basically the same valence band offset as PBE (ΔEV\text{PBE} = 2.13 eV). Finally, from the local band edges we obtain for the width of the interface ~16.6 bohr, which is slightly larger than previous experimental [39] and theoretical [33] results.

We complement the results for the Si/SiO2 interface with band diagrams of other well studied semiconductor interfaces, presented in the Supplementary Material [15] in comparison with other theoretical and experimental results. For all considered systems, we obtain local band gaps which agree well with bulk counterparts. The band offsets we obtain are typically better than those obtained by PBE or MBJ potentials and they are comparable with those obtained with hybrid functionals [40]. We find that the results are sensitive to the size of the supercell used to model the interface, as we are extracting band gaps from the value of the local band gap in the middle of the layer. Here we used interface models from the literature to enable comparisons with previous calculations. Those supercells were used originally in two steps calculations, where only the valence band offset was extracted from a supercell calculation, while band gaps were calculated for bulk crystals. We can conclude that one has to pay attention to include more atomic layers to extract accurate band diagrams from a single supercell calculation. In this respect, the use of LMBJ becomes particularly advantageous when the supercell is large, due to its reduced computational cost in comparison with hybrid functionals or GW.

As a next step we consider the application of the LMBJ potential to a crystal with a surface. We chose as a test system the clean (001) surface of silicon with the 2 × 1 reconstruction resulting from numerical optimization [41]. This model agrees well with both experimental measurements [42] and recent calculations [43]. We conducted the LMBJ calculation for a slab consisting of 32 atomic layers and the width of vacuum between periodic slabs was set to 79.4 bohr. The energy cut-off was set to 245.3 eV and we used an 8 × 8 × 1 k-point grid. As for the Si/SiO2 interface, we chose for the smearing σ = 3.78 bohr, and a threshold density \( \rho_{th} \) corresponding to \( r_{th} = 5 \) bohr as justified above.

In Fig. 2 (left) we show the converged average \( \tau_{xy}(z) \) along the direction perpendicular to the slab surface. We obtained \( \tau_{xy}(z) \approx 1.11 \) for \( z \) in the middle of the slab and \( \tau_{xy}(z) \approx 1.0 \) for \( z \) in the vacuum region. The former agrees well with the bulk mixing of Si (\( c = 1.13 \)) and the latter is the desired property of LMBJ in the vacuum. We observe a small peak exactly at the surface, which originates from the large gradient of the density and it is thus of a physical origin. Even if varying \( \rho_{th} \) leads to a different size of this peak, these changes have no significant influence on the local potential, and thus on the electronic structure. This may be different in other materials and should be subject of further investigations.

In Figs. 2 (middle) and (right) we present the LDOS and band structure of the Si slab. For the local band gap in the middle of the slab we obtained \( E_g = 1.26 \) eV, which agrees well with bulk calculation. Finally, the two surface states visible in both the LDOS and band structure match with those calculated in Ref. [43] using hybrid functionals, including their dispersion and distance from the bulk edges.

In our final test we turned to two-dimensional materials. We chose hexagonal boron-nitride (h-BN), since there is a renewed interest in its electronic structure [44, 45] and the band gap of its parent bulk (three-
dimensional) structure is described very well by the MBJ potential [17]. Bulk h-BN consists of layered honeycomb monolayers with in-plane lattice constant \(a = 4.72\) bohr and interlayer distance of 6.29 bohr (for the AA' stacking which was predicted to be most stable [46, 47]).

We first calculated the electronic structure of bulk h-BN using PBE, MBJ and LMBJ (with \(\sigma = 7.56\) bohr) potentials with an energy cut-off of 400 eV and a \(21 \times 21 \times 17\) k-point grid. We obtained band gaps \(E_{g}^{PBE} = 3.88\) eV, \(E_{g}^{MBJ} = 5.64\) eV and \(E_{g}^{LMBJ} = 5.55\) eV. The local mixing of the LMBJ calculation is basically constant in the bulk crystal: \(c = 1.31\). This value is very close to the mixing \(c = 1.33\) of a bulk MBJ calculation. Both the MBJ and LMBJ band gaps agree well with HSE and experimental results of \(E_{g}^{HSE} = 5.95\) eV [47] and \(E_{g}^{exp} = 6.08\) eV [48], respectively. For the h-BN monolayer we kept the lattice constant \(a = 4.72\) bohr. The width of vacuum between periodic replicas of the monolayers was set to 56.7 bohr, the energy cut-off was 400 eV and we used a \(21 \times 21 \times 1\) k-point grid. The smearing and threshold Wigner-Seitz radius were set to \(\sigma = 7.56\) bohr and \(r_{th}^{s\text{th}} = 5\) bohr, respectively.

In the top part of Fig. 3 we show the band structure calculated using the PBE and LMBJ potentials. The indirect and direct (at \(K\)) band gaps we obtained with PBE were \(E_{g}^{PBE} = 4.68\) eV and \(E_{d}^{PBE} = 4.70\) eV, respectively. This result is improved by the use of the LMBJ potential, which yields \(E_{g}^{LMBJ} = 5.25\) eV and \(E_{d}^{LMBJ} = 6.70\) eV. These values improve over PBE and differ by \(\sim 10\%\) from values obtained by hybrid functional calculations (\(E_{g}^{HSE} = 5.68\) eV, \(E_{d}^{HSE} = 6.13\) eV [49]). Other theoretical and experimental works obtained a direct (indirect) band gap of 6.47 eV [47] and 6.1 eV [50], respectively.

CONCLUSIONS

We proposed a generalization of the successful MBJ potential introduced by Tran and Blaha [9] to calculate bulk band structures. Our local MBJ functional enables the calculation of band diagrams of heterostructures and the evaluation of energy levels of finite systems. To this end, we have defined a position dependent parameter \(c(r)\), averaged over a region of approximately a unit cell, that replaces the constant parameter \(c\) of the MBJ functional. We have demonstrated that our LMBJ potential allows to obtain band diagrams at interfaces with other materials or with the vacuum in a single calculation, reproducing well both surface states and bulk band states inside the layers. We discussed examples of application of the LMBJ functional to semiconductor interfaces, a Si surface and a h-BN monolayer, proving that we can obtain band gaps of the quality of hybrid functionals even for a 2D material. Thanks to its computational efficiency, the LMBJ potential allows for reliable band structure calculations of large inhomogeneous systems, also when hybrid functional and GW approaches are computationally too expensive.

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