Implementation of the modified Becke–Johnson meta-GGA functional in Quantum Espresso

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ABSTRACT

In this paper we present an implementation of the modified Becke–Johnson meta-GGA functional (TB09) in the PWSCF program of Quantum ESPRESSO package via the Libxc library. Using the functionals of TB09 we calculated the band gaps of some semiconductors and compared the results with previous calculations and experiments. We showed that combining GGA pseudo-potential with TB09 functionals would improve greatly the band gaps compared with the GGA calculations. The details of our implementation and code samples are also given.

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1. Introduction

Density functional theory (DFT) is one of the most popular theories in the field of computational materials science [1,2]. It fairly predicts structures and properties of atoms, molecules, and solids. DFT is based on the Hohenberg–Kohn theorem [3] that shows the knowledge of the electron density in the ground state can be equivalent to one of the wave function itself, and the Kohn–Sham ansatz [4] that says in the ground state, the density of an interacting electron system can be approximated by the density of a non-interacting electron system. The main ingredient of the Kohn–Sham method is the introduction of the so-called exchange–correlation (xc) energy that describes all non-trivial many-body effects but its exact form is unknown and must be approximated. It turns out that the precision of DFT calculations depends on the form of such an xc energy.

Practically, one needs to evaluate both xc energy $E_{xc}$ and xc potential $v_{xc}$. The derivative of $E_{xc}$ is required as well in order to compute response properties. Based on a set of almost two hundred exchange and correlation functionals the Libxc library [5] is already implemented in many DFT codes [5]. In this paper we present results of our implementation of this library in Quantum ESPRESSO (QE) [6–8], an integrated suite of open-source computer codes for electronic structure calculations and materials modeling at nanoscale based on plane waves and pseudo-potentials, and compare the results with those obtained using other common methods and the experimental data. Currently only TPSS [9,10] meta-GGA functional is available in QE (version 5.0). Our first motivation is to provide users the possibility of using more meta-GGA functionals.

Band gap is a crucial property of semiconducting materials for it is related to their optical and electronic characteristics. However precise determination of band gaps using DFT calculations is still challenging. It is well known that (semi)local functionals like LDA and GGA tend to underestimate the band gap. Although sophisticated methods including hybrid functionals or the use of GW [11,12] approach yield much better results, they require a very high computational cost, while meta-GGA functionals give the accuracy comparable to LDA+$U$ [13] or LDA+DMFT [14] schemes but with computational costs comparable to the LDA method.

The modified Becke–Johnson meta-GGA xc functional [15] (TB09) is a semi-empirical functional constructed for giving an accurate band structure of insulators and semiconductors. It is not possible to generate transferable pseudo-potentials since it only works for solids and not for atoms (it is not size consistent). In this work, we instead use regular GGA type pseudo-potentials. We show that even results from this approach diverge compared with all-electron results of Tran et al. [15], it improves significantly the quality of the GGA calculations.

We tested our implementation and method on structures of different groups of solids and compared band gap calculations with the data in Ref. [15], where a fair agreement was found. It should be remarked that this present work involves unpolarized calculations only.
2. Theory

The Kohn–Sham equation in Hartree atomic units\(^1\) is given by

\[
\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Br}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}),
\]

where the first term represents the kinetic energy of electrons, the second is the external potential, and the third is the Hartree potential that describes the classical electrostatic repulsion between the electrons. The xc potential \(v_{\text{xc}}[n]\) is defined by

\[
v_{\text{xc}}[n](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})},
\]

where \(E_{\text{xc}}[n]\) is the xc energy functional associated with the electronic density \(n\) defined by

\[
n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2,
\]

where the sum runs over the occupied states.

Over the years, hundreds of different xc energy forms were proposed [16]. They are ordered [17] such that each family adds a dependency on another quantity, thereby increasing the precision of functional, numerical complexity and therefore the expensiveness. The LDA depends on the local density only. The GGA involves the gradient of the density, \(\nabla n(\mathbf{r})\). The meta-GGAs are associated with the Laplacian of the density, \(\nabla^2 n(\mathbf{r})\), and the kinetic energy density, \(\tau(\mathbf{r})\). Note that the meta-GGAs are effectively orbital functionals due to the dependence on \(\tau(\mathbf{r})\). We have functionals that include the exact-exchange (EXX) contribution to the energy and the ones that are composed of functionals that depend on the empty Kohn–Sham orbitals.

In a code, subroutines basically take \(n(\mathbf{r})\), \(\nabla n(\mathbf{r})\), \(\nabla^2 n(\mathbf{r})\), and \(\tau(\mathbf{r})\) and return the corresponding xc energy density \(e_{\text{xc}}(\mathbf{r})\) and all its relevant partial derivatives. We have implemented the xc functions of Libxc library in QE in order to be capable of using this family of functionals along with the possibility of adding a rich and consistent number of functionals.

It has been shown that TB09 can generate a fairly accurate band gap with the expensiveness of GGA functionals [15, 18, 19]. The resulting band gaps are of the same order of magnitude as expensive methods and are globally close to experiments. TB09 does not have any expression for the exchange energy and does not have correlation terms. Its exchange potential is given by

\[
V^{\text{TB09}}_x(r) = c V^{\text{Br}}_x(r) + (3c - 2) - \frac{1}{\pi} \frac{\sqrt{2\pi r}}{n(r)},
\]

where \(V^{\text{Br}}_x(r)\) is the Becke–Roussel potential (BR) [20], and \(c\) stands for

\[
c = \alpha + \beta \frac{1}{V_{\text{cell}}} \left( \int d^3r \left| \nabla n(r) \right| n(r) \right)^{1/2},
\]

with \(\alpha\) and \(\beta\) the free parameters, and \(V_{\text{cell}}\) the volume of a unit cell. Because there is no energy expression, it is impossible to define derivatives of energy. For this reason, the total energy and the forces are not well correlated, which is required for geometric optimization. For it is not possible to generate transferable pseudopotentials, our approach is first to perform a PBE optimization or use an experimental structure, followed by a band structure calculation which combines the TB09 potential and a PBE pseudopotential. Moreover, the calculation including the TPSS correlation term was also performed. We found that such an inclusion of correlation term slightly improves our results.

1 \(\hbar = m_e = 1\).

3. Implementation details

3.1. Program flow

Like all DFT codes, PWSCF program in QE is very complex. It is the result of years of extensive collaboration and sharing. Fig. 1 represents the diagram of the part of our interest. Basically, \(v_{\text{of}, \rho}\) subroutine calls either \(v_{\text{xc}}\) or \(v_{\text{xc, meta}}\) depending on whether a non-meta-GGA or a meta-GGA calculation is performed. Then the subroutine \(v_{\text{xc, meta}}\) calls either \(v_{\text{xc, tpss}}\) or \(v_{\text{xc, tb09}}\) subroutine. Right now, the subroutine \(v_{\text{xc, tpss}}\) can call either \(\text{tbsscxc}\) or \(\text{tbsscxc, lxc}\) subroutine. The former is the original TPSS implementation of QE, while the latter is based on Libxc. The subroutine \(v_{\text{xc, tb09}}\) calls \(\text{tb09cxc, lxc}\) only. So, the way subroutines are called remains unchanged and new subroutines contain a "lxc" at the end of their names. A convenient feature of Libxc is that it provides an interface in C and Fortran90. Another nice feature of Libxc is that it allows us to build our own functionals. Since QE is written in Fortran90, this language is also used in our implementation. Fig. 2 shows how Libxc subroutines are called and how the TPSS correlation term is added.

The major change is that QE expects the Slater term to be calculated separately, whereas Libxc includes it in its output. This should only matter when the density and the gradient go to zero.

3.2. Procedure

This subsection describes how to use TB09 potential in QE. The information which determines what functional to be used for a calculation is basically provided by the pseudo-potential files. In QE, xc functionals are defined by keywords. For instance we have

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>tpss</td>
<td>sla+pw+tpss+tpss</td>
</tr>
<tr>
<td>tb09</td>
<td>sla+pw+tb09+tb09</td>
</tr>
</tbody>
</table>

for meta-GGA TPSS and TB09 functionals. One can provide in the pseudo-potential file either four keywords or the corresponding special names. Note that, in the current version (version 5.0), QE only uses norm-conservative pseudo-potential type files with meta-GGA functionals. In order to use GGA pseudo-potential one has to change the keywords related to the functional type information. In the case of TB09 potential, we have changed the label that defines the GGA functional by “TB09”.

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Fig. 2. A sample of the tb09xc.lxc subroutine. One can see how the Libxc library is called. The first part concerns the TB09 potential, whereas the second part compute the TPSS correlation term.

4. Results and discussion

In Table 1 and Fig. 3, we compare the band gaps of solids of groups A1, A4, B1, B3, and B4, obtained by different computational schemes and experiments. Unlike Tran et al. [15] who performed full-potential (linearized) augmented plane-wave and local orbitals [FP-(L)APW+lo] calculations, our work is based on plane waves and pseudo-potentials. Although these calculations were carried out on experimental geometries, we compared the band gaps at both experimental and optimized lattices. Structural optimizations were performed using the BFGS quasi-newton algorithm where both total energy and atomic forces were minimized using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA). Band gap calculations were performed using GGA-pseudo-potential and TB09 potential with and without TPSS correlation terms. For comparison we also include experimental data and all-electron calculations TB09 taken from Ref. [15], as well as some TPSS results taken from Ref. [18].

First of all, structural optimizations do not improve the results compared with the calculations with experimental geometries and even make things worse like in the LiF case. We also carried out calculations using the TPSS meta-GGA functional correlation term and found that it improves slightly the results compared with experiments. For example, we obtained an average error of about 21% and 25% with and without this term, respectively. A comparison between theoretical methods shows that the TPSS meta-GGA functional leads to the results similar to PBE. For instance, both approaches tend to model Ge as a metal. In the case of MgO, its band gap is even more underestimated. Tran et al. [15] found that the semi-local TB09 potential leads to the results that are of similar accuracy as more sophisticated and expensive approaches. We show that this is also the case using the PBE pseudo-potential based approximation instead of all-electron calculations.

Overall, we can see that our calculations are in good agreement with the data found in the literature although still globally underestimate band gaps. However, all the TB09 calculations significantly improve the calculations based on PBE functionals. Qualitatively, the difference of the original TB09 results compared with the experimental data is in average about 8% (with a maximum of 22% for ZnO). Our PBE calculations lead to a difference from experimental data of about 42% and therefore confirm the quality of the TB09 potential for band gap calculations. Although our approach does not give the same accuracy than the all-electron calculation [15], PBE results are still significantly improved since the difference between calculations at optimized and experimental geometries and experimental data are in average 22% (25% without correlation) and 21% (26% without correlation), respectively. We note that there is a small difference between computations at optimized and experimental structures, the latter giving better results. We also compared our results with TB09 published data and found that our computations with experimental geometries lead to a difference of 18% (21% without correlation) whereas with optimized geometries it is of 24% (28% without correlation).

Our calculation with experimental geometries using the TPSS correlation term gives, for instance, for BN and Kr, the band gap of
Fig. 3. (Color online). Calculated versus experimental band gaps, where GGA and TB09 calculations with optimized geometries and experimental structures from this present work, and the calculated band gaps with TB09.

Source: Taken from Ref. [15] are shown as references.

5.85 and 11.17 eV, respectively, in very good agreement with the results of Tran et al. (5.85 and 10.83 eV). Good agreement was also observed for LiF that has a very large band gap. For Ar, LiCl, and Ge, we found the errors between our calculations and the results in Ref. [15] are of about 5%.

5. Conclusion

In this work we presented our implementation of the xc functionals of Linx library in QE (version 5.0) which allows us to use a broad varieties of functionals, including the modified Becke–Johnson meta-GGA functionals. With the help of several solids of group A1, A4, B1, B3 and B4, we showed that it is possible to improve band gap calculations by combining GGA pseudo-potential with the semi-local TB09 potential. With such a modification we obtained a good accuracy compared with PBE calculations. It was also observed that by adding the TPSS correlation term the results were improved slightly. A patch based on Quantum ESPRESSO (version 5.0) and Libxc (version 1.2.0) has been generated and is available upon request.

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References