Quasiparticle band structure of rocksalt-CdO determined using maximally localized Wannier functions

H Dixit, D Lamoen and B Partoens

CMT-group and EMAT, Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

E-mail: Hemant.Dixit@ua.ac.be

Received 30 August 2012, in final form 23 November 2012
Published 12 December 2012
Online at stacks.iop.org/JPhysCM/25/035501

Abstract

CdO in the rocksalt structure is an indirect band gap semiconductor. Thus, in order to determine its band gap one needs to calculate the complete band structure. However, in practice, the exact evaluation of the quasiparticle band structure for the large number of \( k \)-points which constitute the different symmetry lines in the Brillouin zone can be an extremely demanding task compared to the standard density functional theory (DFT) calculation. In this paper we report the full quasiparticle band structure of CdO using a plane-wave pseudopotential approach. In order to reduce the computational effort and time, we make use of maximally localized Wannier functions (MLWFs). The MLWFs offer a highly accurate method for interpolation of the DFT or \( GW \) band structure from a coarse \( k \)-point mesh in the irreducible Brillouin zone, resulting in a much reduced computational effort. The present paper discusses the technical details of the scheme along with the results obtained for the quasiparticle band gap and the electron effective mass.

1. Introduction

CdO is a transparent conducting oxide (TCO) with reported mobilities of the order of \( \sim 200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and conductivities as high as \( 42,000 \text{ S cm}^{-1} \) [3]. The ternary alloys \( \text{Cd}_x\text{Zn}_{1-x}\text{O} \) [4, 5] and \( \text{Cd}_x\text{In}_{1-x}\text{O} \) [6] are also of great experimental interest as regards finding novel and economic TCO materials.
with the conduction band minimum (CBM) located at \( \Gamma \). However, in practice, the exact evaluation of the GW band structure for the large number of \( k \)-points which constitute the different symmetry lines in the Brillouin zone can be an extremely demanding task compared to a DFT calculation. Moreover the situation is further complicated by the high value of the plane-wave cutoff required by the modified Cd pseudopotential (Cd\(^{20+}\) PP) that is essential for a correct treatment of the self-energy operator [13, 14]. Thus in order to reduce the computational effort, one can make use of maximally localized Wannier functions (MLWFs). The MLWFs offer a highly accurate method for the interpolation of the DFT or GW band structure from a coarse \( k \)-point mesh in the irreducible Brillouin zone, resulting in a much reduced computational effort.

This paper is further organized as follows. A brief introduction to the GW approximation and MLWFs along with the interpolation procedure is provided in section 2. The computational details are provided in section 3. Results and discussion follow in section 4.

2. Theory

2.1. The GW approximation

The GW approximation is based on the set of Hedin’s equations that, when solved self-consistently, yield the exact interacting single-particle Green function [11]. In the GW approximation, the vertex corrections are neglected, resulting in a simplified self-energy operator, i.e.,

\[
\Sigma^{GW} (\mathbf{r}, \mathbf{r}'; \epsilon) = \frac{i}{2\pi} \int d\epsilon' \epsilon^{(\alpha \beta)} G(\mathbf{r}, \mathbf{r}'; \epsilon + \epsilon') W(\mathbf{r}, \mathbf{r}'; \epsilon')
\]

(1)

where \( \delta \) is a positive infinitesimal number, and \( G \) and \( W \) are the electron Green function and dynamically screened Coulomb interaction, respectively. The quasiparticle equation

\[
[T + V_{\text{ext}} (\mathbf{r}) + V_{\text{H}} (\mathbf{r})] \psi (\mathbf{r}) + \int d\mathbf{r}' \Sigma (\mathbf{r}, \mathbf{r}'; \epsilon^{(\alpha \beta)} ) \psi (\mathbf{r}') = \epsilon_{\text{QP}} \psi (\mathbf{r}')
\]

(2)

has then to be solved to obtain the quasiparticle energies \( \epsilon_{\text{QP}} \) and wavefunctions \( \psi \). In the above expression, \( T \) is the kinetic energy operator, and \( V_{\text{ext}} \) and \( V_{\text{H}} \) are the external potential and the Hartree potential, respectively. In practice, both the \( G \) and \( W \) operators are constructed within the quasiparticle approximation by using the Kohn–Sham wavefunctions \( \psi _{\text{i}} \) and energies \( \epsilon _{i} \) obtained from the DFT based calculations. In our work, the self-energy is calculated with the now well known non-self-consistent GW or single-step \( G_0W_0 \) approximation [11] and hereafter will be referred to as the GW approximation for simplicity.

2.2. Wannier functions

The electronic ground state of a periodic solid is represented with Bloch functions \( \psi _{nk} \) at each band \( n \) and \( k \)-point with norm-conserving PPs. An alternative representation of Bloch functions can be given in terms of spatially localized functions known as Wannier functions (WFs) [15]. The WF centered on a lattice site \( \mathbf{R} \), \( \psi _{nk} (\mathbf{r}) \), is written in terms of the set of Bloch states as

\[
\psi _{nk} (\mathbf{r}) = \frac{V}{(2\pi)^3} \int _{BZ} \left[ \sum _{m} t_{mn}^{(k)} \psi _{mk} (\mathbf{r}) \right] e^{-i \mathbf{k} \cdot \mathbf{R}} d\mathbf{k}
\]

(3)

where \( V \) is the unit cell volume, the integral is over the Brillouin zone, and \( U^{(k)} \) is a unitary matrix that mixes the Bloch states at each \( k \). \( U^{(k)} \) is not uniquely defined and different choices will lead to WFs with varying spatial localizations. WFs are the solid-state equivalent of localized molecular orbitals [16, 17], and thus provide a chemical picture of the system. Following the method of Marzari and Vanderbilt [18], the MLWFs can be constructed by minimizing the spread, \( \Omega \), of the \( N \) generalized WFs defined as

\[
\Omega = \sum _{n=1}^{N} \left[ (|\psi _{n0} (\mathbf{r})|^2 - |\psi _{n0} (\mathbf{r})|\psi _{n0} (\mathbf{r})|^2 \right] (4)
\]

where we refer to the unit cell at the origin, since all sets of Wannier functions are equivalent within a lattice-vector translation, \( \psi _{n0} (\mathbf{r} - \mathbf{R}) = \psi _{n0} (\mathbf{r}) \).

2.3. The interpolation procedure

GW or DFT band structure interpolation based on MLWFs is a highly accurate method because it preserves valuable information about the band connectivity. Hence, band crossings, avoided crossings and degeneracies are treated correctly at much lower computational cost [19, 20]. On the basis of a ground-state DFT calculation, performed using ABINIT [21–24] code, MLWFs are constructed by passing the DFT wavefunctions \( \psi _{nk} ^{\text{DFT}} \) and the DFT eigenvalues \( \epsilon _{nk} ^{\text{DFT}} \) in the full irreducible Brillouin zone to the Wannier90 [25] code. Then, one uses the post-processing tools of Wannier90 to interpolate the band structure. The details of this procedure are discussed in [24]. In the GW case, the procedure is equivalent; one has to pass to Wannier90 the GW quantities instead of the DFT ones. It should be noted that since we perform the \( G_0W_0 \) calculations, only the DFT eigenvalues are replaced by the GW eigenvalues. Thus to construct the quasiparticle band structure we just calculate the GW corrections at a reduced set of \( k \)-points of the irreducible Brillouin zone. ABINIT further uses symmetry operations to obtain the corrections corresponding to the full irreducible Brillouin zone. Finally the post-processing tools of the Wannier90 code lead to the interpolated quasiparticle band structure.

3. Computational details

The electronic structure and the quasiparticle correction to the band gap have been calculated using the plane-wave pseudopotential code ABINIT. For the electronic structure the plane-wave cutoff is chosen using the total energy
convergence criterion of $2 \times 10^{-2}$ eV. The atomic positions and structural parameters have been optimized by calculating the Hellmann–Feynman forces. The stresses are optimized with the criterion of $2 \times 10^{-5}$ eV Å$^{-3}$. We choose a $4 \times 4 \times 4$ Monkhorst–Pack [26] $k$-point mesh which yields eight $k$-points in the irreducible Brillouin zone.

The Cd$^{20+}$ PP used is generated with the OPIUM [27] code according to the Troullier–Martins [28] method with Perdew–Zunger local density approximation (LDA) [29]. The electronic configuration of the Cd atom is [Ar]4s$^2$4p$^6$4d$^{10}$5s$^2$. The standard DFT PP treats the 4d and 5s electrons as valence ones, and the result is the Cd$^{12+}$ PP. In this work we construct the 20-electron PP (Cd$^{20+}$ PP); a radius cutoff of 0.52 Å for 4s, 4p and 4d is chosen. It should be noted that we do not construct our 20-electron PP for the neutral Cd atom, but rather for the Cd ion with the 4s state unoccupied. This radius cutoff shows the smallest transferability error for ionic configurations of Cd (neutral, +1 and +2), at the cost of an increased plane-wave cutoff. We have used 125 Ha as the energy cutoff for plane waves, when Cd$^{20+}$ PP is used.

The parameters used within ABINIT to calculate the self-energy are optimized with the convergence criterion of 0.1 eV for the band gap at Γ. We have found that, for both the screening and the self-energy calculation, 400 bands are sufficient to converge the GW band gap. The dielectric matrix is calculated with the Godby–Needs [30] plasmon-pole model [11] and is used to calculate the screening.

4. Results and discussion

Let us first consider the LDA band structure, as shown in figure 1(a), calculated with the modified Cd$^{20+}$ PP at the optimized lattice constant of 4.65 Å. The optimized lattice constant shows good agreement with the experimental value of 4.70 Å. The Cd$^{20+}$ PP leads to a marginal opening of the band gap in contrast to the all-electron calculation [10], where the CBM crosses the Fermi energy indicating semi-metallic nature. The LDA band gap at the Γ point is 1.47 eV, which is larger than the all-electron result of 1.1 eV, and we obtain an indirect band gap of 0.13 eV with the Cd$^{20+}$ PP. The Cd d energy levels lie around $\sim$7 eV and are at a higher binding energy compared to the experimental result of $\sim$8.8 eV [31] below the VBM.

Now we move on to the Wannier interpolation scheme. In order to determine the number of $k$-points needed to realize a converged band structure using MLWFs, we first apply the technique to the LDA results. We have used a regular $4 \times 4 \times 4$ Monkhorst–Pack $k$-point mesh which yields eight $k$-points in the irreducible Brillouin zone and 64 $k$-points in the complete Brillouin zone. The MLWFs are constructed from Cd-centered s, p, d and O-centered s, p guiding functions and further, using the post-processing tools of the Wannier90 code, the Wannier-interpolated band structure is calculated. We exclude the deep lying semi-core bands corresponding to Cd 4s and 4p orbitals in the computation of the band structure. The Wannier-interpolated LDA band structure is presented in figure 1(b). The interpolated band structure is virtually indistinguishable from the LDA counterpart for all the valence bands and the lowest conduction band. Thus the $4 \times 4 \times 4$ Monkhorst–Pack $k$-point mesh, i.e. computation at eight $k$-points in the irreducible Brillouin zone, is sufficient for reconstructing the band structure using the Wannier interpolation scheme.

Next, we calculate the quasiparticle corrections in the full irreducible Brillouin zone selected using the same $4 \times 4 \times 4$ Monkhorst–Pack $k$-point mesh. For a quantitative comparison, in table 1 we give the LDA and GW direct gaps at two high symmetry points in the first Brillouin zone—Γ and X. With the Cd$^{20+}$ PP we obtain significant quasiparticle corrections to the LDA eigenvalues. The GW band gap at the Γ point is 2.88 eV. It should be noted that the quasiparticle corrections depend on the $k$-point. Again, the MLWFs are constructed from Cd-centered s, p, d and O-centered s, p guiding functions and the Wannier-interpolated GW band structure is calculated further, using the post-processing tools of the Wannier90 code. We only supply the GW eigenvalues at eight $k$-points in the irreducible Brillouin zone for this computation.

The full Wannier-interpolated LDA and GW band structures are compared in figure 2. The LDA valence bands are shown with green lines while the GW valence bands are shown by purple lines. Also, the conduction bands are

![Figure 1.](image-url) (a) LDA and (b) Wannier-interpolated LDA band structure (using a $4 \times 4 \times 4$ Monkhorst–Pack $k$-point mesh) of CdO.

<table>
<thead>
<tr>
<th>$k$ point</th>
<th>Γ</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>1.47</td>
<td>7.12</td>
</tr>
<tr>
<td>GW</td>
<td>2.88</td>
<td>9.21</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>1.41</td>
<td>2.09</td>
</tr>
</tbody>
</table>
The calculated band mass (along $0^\circ$ and $\sim 1.07$ eV [31]. The direct gap at $0^\circ$ (electronic mass, Table 2.) Wannier-interpolated LDA (green lines) and GW curves show the depicted using green curves for the LDA part while purple curves show the GW counterpart. The shaded green part represents the band gap for the LDA part and the shaded purple area represents the quasiparticle correction to the CBM. The band dispersions for the LDA and GW cases are similar for the upper part of the valence band. The Cd d energy levels, however, are shifted downwards and positioned at $\sim -9$ eV in the GW band structure. These levels show a good agreement with the reported experimental value of $-8.8$ eV. The conduction band dispersions in the LDA and GW band structures are quantitatively different at high symmetry points, such as X, L, reflecting the k-point dependence of the quasiparticle energy corrections. The indirect band gap obtained using the Wannier-interpolated GW band structure is 1.68 eV and is in agreement with the reported range of 1.2–2 eV in the experiments [32]. Our calculations show a significant improvement for the indirect gap of CdO compared to previous quasiparticle corrections which report 0.68 eV [33] (the HSE03 + GW approach) and 1.07 eV [31]. The direct gap at $\Gamma$ (2.88 eV) is, however, overestimated compared to the experimental counterpart of $\sim 2.2$ eV. We have also calculated the electron effective mass along the $\Gamma$–X direction for the Wannier-interpolated CBM. The calculated band mass (along $\Gamma$–X), for both the LDA and GW band structures, is $0.22 m_e$ and this is also in good agreement with the experimental value of $0.21 m_e$ [34]. Table 2 summarizes the results obtained for the band gap, band mass and positioning of the Cd d energy levels in the LDA and GW band structures.

5. Conclusions
In conclusion, we present the complete quasiparticle band structure of rocksalt-CdO using the maximally localized Wannier functions. The calculated band gaps and electron effective mass are in agreement with the experiment. The Wannier functions prove to be a useful tool for interpolating the quasiparticle band structure and only a coarse mesh of k-points is sufficient for reproducing the band dispersion accurately. The computational cost can be drastically reduced with the help of a Wannier interpolation scheme in a standard plane-wave pseudopotential calculation.

Acknowledgments
We gratefully acknowledge financial support from the IWT-Vlaanderen through the ISIMADE project, the FWO-Vlaanderen through project G.0191.08 and BOF-NOI of the University of Antwerp. This work was carried out using the HPC infrastructure of the University of Antwerp (CalcUA), a division of the Flemish Supercomputer Center (VSC), which is funded by the Hercules foundation.

References