Ab initio Studies of the Band Parameters of III–V and II–VI Zinc-Blende Semiconductors

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Abstract—Electronic band-structure calculations are performed for zinc-blende III–V (AlP, AlAs, AlSb, GaP, GaAs, GaS, InP, InAs, and InSb) and II–VI (ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe) semiconductors using an ab initio pseudopotential method within a local-density approximation (LDA). Lattice parameters, band gaps, Luttinger parameters, momentum matrix elements and effective masses are studied in detail. It is shown that LDA calculations cannot systematically give accurate band parameters. It is found that LDA band parameters calculated using experimentally determined lattice constants are more accurate than those using LDA lattice parameters. We found that inclusion of the d electrons of Group-II atoms in the core gives more accurate band parameters. © 2005 Pleiades Publishing, Inc.

1. INTRODUCTION

Density-functional theory (DFT) is a powerful tool for studying the electronic structure of solids. It is well known that the band gaps of bulk solids calculated within the theory are systematically underestimated compared to experimentally determined ones [1] because of the theory’s failure to describe excited-state properties. Moreover, the problem rests with more than the local-density approximation (LDA). Following k · p theory (see, e.g., [2]), however, one can say that if fundamental excitation gaps are incorrect, then band dispersions should be as well. This realization has been used by Cardona et al. [3–6] in generating corrected band parameters (Luttinger parameters and spin splittings) for a number of semiconductors. Nevertheless, there remains some dispute regarding this issue [7]. For instance, in 1992, Fiorentini and Baldereshi [8, 9], using pseudopotential plane waves within the LDA, found that conduction-band masses (m_c) at point Γ were very close to experimental values for GaAs, AlAs, and Ge. However, the values of m_c found in [10] differ significantly from those determined experimentally for GaAs, GaSb, InP, and InAs. Similarly, the conduction-band effective masses calculated by Wang and Zunger [11] within the LDA agree well with experimental data for Si, while for CdSe the masses were not very accurate and a semiempirical modification led to somewhat better agreement. Kane [12], however, found that it was not possible to attain correct band gap and cyclotron masses in Si with a local static potential such as the LDA. Fairly good agreement with the experiment was obtained by Wang and Klein [13] for the conduction and valence band effective masses of GaP, GaAs, ZnS, and ZnSe using a linear combination of Gaussian orbitals within the LDA. A systematic study by Huang and Ching [14] of the effective masses for 32 semiconductors using a semi–ab initio technique shows much better agreement. Therefore, despite the importance of effective masses, the question of whether calculations within the LDA give correct effective masses is still open.

There is even less explicit research on the correctness of momentum matrix elements (E_p) calculated within the LDA, which are often claimed to be accurate. However, the validity of the statement has been less directly verified. The standard argument is that, in a pseudopotential approach, the pseudo–wave function has a very high overlap with the true wave function [11]. The value of E_p for GaAs calculated by Winkler [15], and Kageshima and Shiraishi [16] within the LDA is about ~1.7 times smaller than that determined experimentally [17, 18]. Kageshima and Shiraishi [16] concluded that wave functions calculated by the pseudopotential method lack a precise description around the atomic core regions. Furthermore, they suggested that momentum matrix elements cannot be directly estimated from these wave functions because the functions are smoother around the atomic cores, while the actual wave functions oscillate greatly. To fix the error, a core-repair term was added. By including the correction, significant improvement was indeed achieved for zinc-blende and wurtzite GaN. However, momentum matrix elements for polysilane, siloxene, and GaAs calculated with the correction and without it differ from each other by only 5.43, 3.0, and 1.8%, respectively. Wang and Zunger [11], however, had previously found a larger increase in the momentum matrix elements. To complicate matters further, Levine and Allan [19] found that, even within a scissors approximation, the velocity operator becomes renormalized.

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It should be noted that the correctness of the calculated and experimentally determined values of \( E_p \) is also being debated. Efros and Rosen [20], for example, concluded that Fu, Wang, and Zunger’s calculation result of \( E_p = 14.98 \) eV for bulk InP using a direct diagonalization method [21] is smaller than the measured value 20.6 eV, which indicates an underestimation of the coupling between the conduction and valence bands and an overestimation of the influence of the remote bands. However, even the values of \( E_p \) extracted from the experiments have an intrinsic scatter. For bulk InP, for example, experimental values of \( E_p \) vary from 16.6 [22] to 20.7 eV [23]. Therefore, the question of whether the momentum matrix elements calculated by the LDA are correct is still open.

It should also be noted that the above-mentioned problems are relatively less studied in II–VI semiconductors, which have a cation \( d \) band inside the main valence band playing a significant role in their electronic structures [24–29]. In III–V semiconductors the \( d \) levels are several eV lower in their energy than the lowest \( sp \) valence band states [30]. So the effect of the \( d \) states on the electronic structure of III–V compounds can be disregarded. In earlier research, the strong \( p–d \) coupling in II–VI semiconductors has usually been taken into account by including the \( d \) electrons (i) in the core, but also including nonlinear core corrections for exchange and correlation, and (ii) in the valence complex [24–26], but keeping the \( s \) and \( p \) semicore electrons in the core. Currently, the description of \( p–d \) coupling is still being improved. Despite numerous studies, the question as to which of the approaches related to \( p–d \) coupling is correct and consistent with \( k \cdot p \) band parameters is still open.

In this paper we provide the first systematic study of eigenvalues at \( \Gamma, X, \) and \( L \); the Kane momentum matrix elements \( E_p \) and \( E'_p \) (defined as \( 2P^2/m_0 \) in eV) corresponding to the fundamental direct \( p–s \) energy gap \( E_g \) and the \( p–p \) gap \( E'_g \) at point \( \Gamma \); the conduction-band effective masses \( m_{c,1}^{001}, m_{c,1}^{011}, \) and \( m_{c,1}^{111} \); the heavy-hole effective masses \( m_{hh,1}^{001}, m_{hh,1}^{011}, \) and \( m_{hh,1}^{111} \); the light-hole effective masses \( m_{lh,1}^{001}, m_{lh,1}^{011}, \) and \( m_{lh,1}^{111} \); and the Luttinger parameters \( \gamma_1^f, \gamma_2^f, \) and \( \gamma_3^f \). Furthermore, we answer the question as to whether band parameters calculated within the framework of the LDA are correct.

### 2. COMPUTATIONAL DETAILS

#### 2.1. Local-Density Approximation

Ab initio calculations were performed for III–V (AlP, AlAs, AlSb, GaP, GaAs, GaP, InP, InAs, and InSb) and some II–VI (ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe) semiconductors with a zinc-blende structure. We did not study the II–VI compounds HgS, HgSe, and HgTe, because it is well known that spin–orbit coupling (which is not accounted for in this work) plays a significant role [24]. The unit cell considered consists of two atoms of Group-III (II) at \((0, 0, 0)\) and an atom of Group-V (VI) at \((a/4, a/4, a/4)\), where \( a \) is the lattice constant.

Ab initio pseudopotentials were generated using the Troullier–Martins method [31]. We have considered \( s, p \) and \( d \) as valence states in order to build the pseudopotential for the atoms of Group-III and V using the \( p \) potential as the local potential, while \( s \) and \( d \) are taken as the nonlocal parts. We determined \( E_{\text{cut}} \) by requiring convergence of the total energy \( E_{\text{tot}} \). For all the III–V semiconductors considered, \( E_{\text{cut}} = 60 \) Ry was used.

To study the II–VI compounds, \( s, p \), and \( d \) states were considered as valence states. Pseudopotentials for Group-II atoms were generated in two ways: (i) including the \( d \) electrons, which are inside the valence shell, in the valence complex while keeping the semicore \( s \) and \( p \) states in the core, and (ii) including the \( d \) electrons in the core. For the latter case, we used \( E_{\text{cut}} = 30 \) Ry, and a nonlinear exchange correlation was added, which is known to give better agreement with experimental data [25]. For the former case, convergent results were obtained for \( E_{\text{cut}} = 70 \) Ry. The semicore \( d \) electrons of the III–V compounds were included in the core because, as discussed in Section 1, the energy level of the electrons arc far below the outermost \( sp \) levels [30] and the electrons are not expected to significantly affect the band structure of the compounds.

Band-structure calculations were performed using the PEtot code developed by L.-W. Wang [32], which uses the ab initio pseudopotential method within the LDA and neglects spin–orbit coupling. The Pulay–Kerker scheme was used for self-consistent potential processing. In addition, \( g \)-space Kleinman–Bylander nonlocal pseudopotential implementations were used with a mask function scheme, without the need for preprocessing the pseudopotentials. The LDA exchange-correlation contribution was accounted for by means of Perdew and Zunger’s parametrization [33] of the calculations by Ceperley and Alder [34]. The self-consistent solution of the one-electron Kohn–Sham equation was performed using a planewave pseudopotential algorithm [35].

The potential for the unit cell under consideration was found by performing self-consistent calculations using 10 special \( k \) points in the Brillouin zone. Then, using this potential, eigenenergies at the special \( k \) points were found by nonconsistent calculations.

#### 2.2. Band Parameters

Carrier effective masses are defined as

\[
\frac{1}{m_c(k_0)} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} \right|_{k = k_0}
\]