Electronic and Optical Properties in the Tight-Binding Method

F. Raouafi,¹ R. Ben Chamekh,²,³ J. Even,³ and J.-M Jancu³,*

¹Physico-Chimie, des Microstructures et des Microsystèmes, Institut Préparatoire aux Études Scientifiques et Techniques, Université de Carthage, BP51, 2070 La Marsa, Tunisia
²Laboratoire de Photonique et Nanostructures, CNRS, 91460 Marcoussis, France
³Université Européenne de Bretagne, INSA FOTON, UMR 6082, F-35708 Rennes, France

(Received August 31, 2013; Revised February 19, 2014)

We show how the extended-basis spds* tight-binding model can be used to compute accurately the physical properties of tetrahedrally bonded semiconductor structures. This approach is particular suited for investigating the nanoscale material properties lying at the interface of material science and engineering. Nonlinear optical simulations in III-V semiconductors are presented with accurate benchmark calculations of ultra-short period GaAs/AlAs superlattices.

DOI: 10.6122/CJP.52.1376 PACS numbers: 71.15.Ap, 73.21.Cd, 78.30.Fs

I. INTRODUCTION

Both ab initio and empirical methods within atomic-scale simulations provide detailed information about the global properties of materials [1]. While first principles techniques like density functional theory (DFT) in the local density approximation (LDA) are well suited to predict structural properties and thermodynamics [1], the calculation of excited-state properties is still unsatisfactory. The known LDA band gap problem for instance results from the difference between the local density single particle potential and the self-energy operator that describes the quasi-particle of the system. It can be overcome within the GW approximation for the self-energy [1]. However, the precision of the GW approach still remains insufficient for a prediction of the conduction band energies within typical experimental uncertainties achieved in optical measurements. In addition, GW, because of the heavy computational burden, remains limited to the study of a few atoms. The necessity to accurately interpret the excited-state properties of semiconductor nanostructures has led to the development of various empirical approaches, ranging from the empirical pseudopotentials [2, 3] over k · p theory [4, 5] to tight-binding (TB) models [6–9]. Tight binding has existed for many years as a convenient and transparent model for the description of the electronic structure in molecules and solids. It often provides the basis for the construction of many body theories, such as the Hubbard model and the Anderson impurity approximation. Slater and Koster called it the tight binding or “Bloch” method and their historic paper in 1954 [7] “Simplified LCAO-method for the Periodic Potential Problems”

*Electronic address: Jean-Marc.Jancu@insa-rennes.fr
provided the systematic procedure for formulating a tight binding Hamiltonian. In this method, the Hamiltonian eigenstates are expanded in a linear combination of atomic-like orbitals (LCAO) and the interaction parameters are treated as “disposable constants” chosen to reproduce the band parameters. In addition to the Slater-Koster work [7], a good account of TB theory can be found in the classical physics textbooks of Harrison [8] and Bassani [9].

Among the early applications with a strong impact until nowadays, was the calculation of the electronic structure of graphene by Bassani and Parravicini [10], which allowed the interpretation of the first spectroscopic experiments [11]. Since the Slater-Koster method uses only a few basis functions, the computational effort is much smaller than that of methods based on plane-waves basis sets. Over the last 40 years there have been numerous applications of this approach, which has been pursued in a variety of problems, following different philosophies and placing different levels of emphasis on the required level of accuracy. One of them is to determine the minimal basis of atomic orbitals suited for describing accurately the electronic band structure of semiconductors in the whole Brillouin zone. From the interpretation of pseudopotential wave functions in terms of atomic symmetries [2, 12, 13], it became obvious that $d$-symmetric contributions play a crucial role both for the valence band maximum at the $\Gamma$-point and for the conduction states at the $X$ and $L$ points. This has led to the extension of the minimal $sp^3$ basis [8] towards higher-lying atomic states, like the next s-shell in the $sp^3s^*$ basis [6] and $d$ empty states of the $\Gamma_3$ symmetry in the $sp^3d^2$ model [14]. Finally, it turned out that the inclusion of all five atomic $d$-states becomes necessary for a reliable description of the valence bands and the first two conduction bands [15], defining the empirical $sp^3d^5s^*$ TB method here considered.

The outline of the paper is as follows. In Section II, we discuss the general features of the $spds$ basis, including original calculations on the second-order optical response of III-V cubic semiconductors. Short-period GaAs/AlAs superlattices (SLs) are investigated in Section III, and the paper is concluded in the last section.

II. THE EMPIRICAL SPDS TIGHT-BINDING MODEL

II-1. Two-center approximation.

The central point of the Slater-Koster approach [7] is the two-center approximation. This name derives from an approximation for the crystal potential as a sum of spherically symmetrical potentials around each atom and matrix elements, between the orbitals on two different sites can involve the potential from either of the orbital sites. If all are on the same site, this is a one center, or on-site matrix element. If the orbitals are on different sites and are “neighbors” while the potential is on one of these sites, we have a two center matrix element, or “hopping integral”. All other possibilities, namely three center terms and the overlap of orbitals on distant sites are neglected. The two center approximation is more than just a convenient rejection of certain terms. It allows for expressing the dependence of the hopping integrals upon distance analytically, which is a perquisite in the calculation of strained nanostructures and the total energy and related properties.
II-2. Define a basis of atomic orbitals

In free atoms of group III and V, the $sp^3$ basis is physically complete for the valence shell. However, when a cubic III-V semiconductor is formed (a crystal with an inversion-asymmetric zinc blende structure and the point group $Td$), these atomic states can interact with those of adjacent sites from the potential matrix elements whose values are not so much smaller than the atomic level spacing [8]. Consequently, one cannot expect that the $sp^3$ basis remains close to complete for the electronic bands and interactions of the same magnitude between valence orbitals, and higher-lying atomic states cannot be excluded. Completeness of the tight-binding basis can be approached in term of the irreducible representations $\Gamma_i$ of the point group $T_d$ coupled with the analysis of the lowest reciprocal lattice vectors [15].

While for the $\Gamma_1$ conduction-band states the inclusion of a second $s$-symmetric basis state (called $s^*$ in Ref. [6]) is the obvious issue, the $\Gamma_4$-symmetric valence band maximum can be built either from the $(p, p^*)$ or $(p, d)$ basis. The orbital decomposition into irreducible representations of the reciprocal-lattice vectors $<111> \rightarrow 2\Gamma_1 + 2\Gamma_4$ and $<200> \rightarrow \Gamma_1 + \Gamma_3 + \Gamma_4$ demonstrates that the inclusion of a full set of five atomic d-states ($\Gamma_3$ and $\Gamma_4$ symmetries) is the better choice for the numerical completion of the Hamiltonian. This leads to the 40-band tight-binding model characteristic of the $spds^*$ basis.

II-3. How to find the tight-binding parameters

While the above considerations provide arguments for a reasonable basis choice, they give no indication concerning the values of the on-site energies and interaction matrix elements of the Hamiltonian. Therefore, a starting parameterization for the $sp^3d^5s^*$ model is required. Usually in tight-binding, the nearest neighbor approximation is used and hopping matrix elements are different from zero only between neighboring atoms. This is suited for semiconductors and insulators where atoms share the stability of a full valence shell and weakly interact with remote sites [8, 9]. It was illustrated in Ref. [15] how the universal TB parameters can be obtained from an analysis of the free-electron energy bands of the face-centered cubic lattice. Based on the empty lattice, the TB parameterizations of zinc-blende semiconductors including the spin-orbit interaction are interpolated as follows: the splitting between the on-site $p$ and $s$ energies is fixed to the difference of atomic energies while the on-site $d$ and $s$ energies are taken from the values derived for free electrons. The hopping integrals are modified in order to achieve the correct band ordering and symmetry of the crystal states. Finally, the deviations between the theoretical and experimental band positions are minimized within a numerical procedure based on the nonlinear conjugate gradient method acting on the whole parameterization. When comparing the TB parameters of a given semiconductor with those of the free electron reference, e.g., for germanium, the average change is only 1/3 of their absolute mean. This indicates that the order of magnitude for electronic interactions is correctly reproduced and agrees with a pseudopotential picture, where semiconductor band structures always display a free-electron character [2].
II-4. Comparison of different basis sizes

In Fig. 1, the quality of the \( sp^3d^5s^* \) Hamiltonian is illustrated by comparing the electronic structure of cubic GaAs with previous TB models. In the smallest \( sp^3 \) basis, the valence-band dispersion is quite reasonable, in contrast to the conduction bands where only the direct surroundings of \( \Gamma_6c \) are reliable [8]. The nearest-neighbor \( sp^3s^* \) model gives the correct positions of the \( L_6c, X_6c, \) and \( X_7c \) conduction-band minima, but the transverse masses at the \( L \) and \( X \) points are not reproduced [6]. Even though some improvement of the band dispersion can be achieved with interaction parameters between more distant atoms, the erroneous projection on the atomic symmetries cannot be corrected. In addition, the difference between the electron and light-hole effective masses is not correctly reproduced in the \( sp^3s^* \) calculations, whereas the nearest-neighbor \( sp^3d^5s^* \) Hamiltonian corrects this deficiency. Concerning the transverse mass at the \( X \) point, it was shown in Ref. [15] that the \( pd \) interactions are required for the correct energy dispersion of the conduction bands along the \( X - W \) pathway. In conclusion, the extended-basis \( spds^* \) TB model allows for a reliable description of the band structure of cubic GaAs up to 5 eV above the valence-band maximum, corresponding to the energetic region of interest for optics. The same trends are found for other zinc-blende semiconductors also in the wurtzite phase, as was recently demonstrated [16, 17].

![Comparison of GaAs TB band structures](image)

**FIG. 1:** Comparison of GaAs TB band structures obtained for different basis sizes: \( sp^3 \) (left) [7], \( sp^3s^* \) (middle) [5], and \( sp^3d^5s^* \) (right) [15]. The energy reference is the valence band maximum. Green and red circles indicate the correct and incorrect energy-band dispersion.

II-5. Strain effects

Intraband deformation potentials describe the shift of each individual energy state with respect to an absolute energy in a crystal under deformation [8]. These parameters are of crucial importance in order to evaluate the quantum confinement effect for holes and electrons in strained nanostructures. Their experimental values are accurately reproduced
in the \( sp^3d^5s^* \) basis including a distance dependence for the on-site orbital energies and hopping integrals which can be modeled in different ways [15, 19, 20]. It was shown in detail [15] that the erroneous sign for the uniaxial and hydrostatic deformation potentials of the \( \Gamma_{4c} \) states and the \( X \) conduction-band valleys in smaller TB models is corrected due to the large bonding d-component of the corresponding wave functions. As seen in Section III, even though the strain in GaAs/AlAs superlattices (SL) is quite small, some details of the SL band positions could not be reproduced without reasonable values of the bulk deformation potentials. Finally, TB models were also found suited for describing very large strain effects [21], which is a prerequisite in today’s research, for instance, for semiconductor quantum wires.

II-6. Linear and second-order optical response

We demonstrate the quality of the \( sp^3d^5s^* \) model with the calculation of the spectral functions of cubic GaAs, AlAs, and InAs. The optical response of semiconductors is usually described by a series of optical susceptibilities, characterizing the linear and nonlinear responses of the crystal under the electromagnetic field [22]. The resulting theoretical modeling represents one of the strongest challenges in computational physics, because it requires a good representation of the excited states and dipole matrix elements as well as the inclusion of the excitonic and local-field corrections [8, 18, 22, 23]. Empirical and \textit{ab initio} calculations can be envisioned for this purpose. Semi-empirical approaches give more easily a satisfactory description of excited states and are much more efficient from a computational point of view when applied to nanostructures. Nevertheless, they are sensitive to the parameterization issue. In the Slater-Koster approximation, the electronic wave functions are developed onto an orbital basis set where the spatial dependence is unknown. These orbitals are however characterized by symmetry, orthogonality, and the Hamiltonian eigenstates (envelope function). Very interestingly, these characteristics allow for the electromagnetic fields to be built-in without any ambiguity from the point of view of the gauge invariance with a derivation of the Hamiltonian matrix elements in momentum space [24, 25]. Optical properties in the tight-binding method can be then be calculated without adding empirical parameters in the Hamiltonian. Figure 2 shows the \( sp^3d^5s^* \) complex dielectric function (imaginary and real part) of c-GaAs compared to the experimental spectrum [26]. We used a mesh of 10000 points to sample the Brillouin zone, and the resulting discrete transitions are dressed with a 0.001 eV Gaussian broadening in order to get a smooth spectra. The overall agreement is satisfactory, especially in the static limit (Table I), whereas the electron – hole interactions account for the small discrepancies at the \( E1 \) and \( E2 \) critical points [27]. Conversely, atomistic pseudopotentials [3], suited for the simulation of electronic states in low-dimensional systems, fail for dielectric constants [28]. This is mainly due to a poor description of the surface of the Brillouin zone and the limitation of the parameterization scheme [3]. The good agreement found in the literature for the refractive index of GaAs [29] stems from a compensation of errors in the band structure and dipole moments [28]. Fig. 3 shows the calculated nonlinear susceptibility \( \chi^{(2)} \) of GaAs in an \( sp^3d^5s^* \) basis with the experimental result [23]. In the simulation we included both the virtual-electron and virtual-hole contributions, although the latter is found to be much
smaller than the former in the same way as the $\mathbf{k} \cdot \mathbf{p}$ calculations [22]. Peaks in $\chi^{(2)}$ can be identified to be coming from the 2W and W resonances in the surrounding of the $E_1$ and $E_2$ critical points [22]. They are found to be sensitive to the value of the dipole matrix elements between the two first conduction-band states, and their modeling is obviously beyond the abilities of the smaller TB basis [30]. Finally, the optical susceptibility in the static limit is presented in Table I, and it agrees with experiment and the phenomenological calculations [31].

![Graph showing the dielectric function of GaAs](image)

**FIG. 2**: Real and imaginary parts of the GaAs dielectric function calculated using the *spds* tight binding model and compared with the experimental spectrum [26].

**TABLE I**: High frequency dielectric constant $\varepsilon(\infty)$ and nonlinear susceptibility $\chi^{(2)}$ for cubic semiconductors calculated with the *spds* tight-binding model and compared to the experimental data [26].

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>AlAs</th>
<th>InAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon(\infty)$</td>
<td>10.5(10.9)</td>
<td>8.1(8.1)</td>
<td>12(12.3)</td>
</tr>
<tr>
<td>$\chi^{(2)}$</td>
<td>170 (170)</td>
<td>300(320)</td>
<td>70(74)</td>
</tr>
</tbody>
</table>

**III. BENCHMARK CALCULATIONS OF GAAS/ALAS SUPERLATTICES**

$(\text{GaAs})_{n}/(\text{AlAs})_{n}$ [001] superlattices grown lattice-matched on GaAs substrate provide a stringent test for evaluating the performance of the *ab initio* and empirical approaches, because the conduction-band minimum (CBM) occurs at different $k$-points other
FIG. 3: Second-order susceptibility of GaAs calculated using the $spds^*$ tight binding model compared with experiment [23].

than $\Gamma$ as a function of the period $n$. In a tight-binding context, the direct applicability of bulk parameters to heterostructures are obviously restricted to the nearest-neighbor approximation, because the next-nearest neighbor interaction parameters, needed for instance to reproduce the correct transverse mass at the $X$ point in the $sp^3$ and $sp^3*$ basis, are not transferable to interfacial bonds between chemical species. In an $spds^*$ calculation, the deformations in the AlAs region can be treated within classical elasticity, resulting in homogeneous tetragonal strain, and the modifications of the TB parameters are accounted for the inclusion of distance dependencies derived from the deformation potentials. Except for the atomic positions in the supercell, the only further input required is the valence band offset (VBO), chosen in accordance with experimental data of 0.55 eV [32]. For all atoms not on the interface, the on-site energies are shifted in accordance with the VBO, and for the As layer forming the interface, half this shift is applied. The average is justified since the As on-site integrals possess similar energy values in the GaAs and AlAs parameterizations. Except for small strain corrections, all SL interactions are parameterized as in the corresponding bulk materials. Figure 4 shows the calculated band structure for the monolayer superlattice with the $spds^*$ basis. The CBM is characterized by a $L$-derived state with nearly half of the wave function localized on the Ga sublattice, in agreement with $ab$ initio calculations [33]. The TB gap energies of $(GaAs)_n/(AlAs)_n$ SL are displayed in the right-hand side panel of Fig. 5, together with the experimental and pseudopotential results [3]. The calculated interband transitions correspond to the free electron - hole recombination, neglecting any excitonic effects. As these corrections are rather small compared to the magnitude of the quantization energies, the main results displayed in Fig. 5
are not affected. Both in the pseudopotential and tight-binding simulations, the $L$-derived energy states strongly oscillate with the SL period $n$. In the $spds^*$ model, the CBM derives from the $X_{xy}$-like AlAs bands for $n = 2–3$, whereas the second conduction subband evolves from the $X_z$ folded states in the center of the tetragonal Brillouin zone. This is a direct consequence of the tetragonal strain in the AlAs layer that shifts the $X_z$ valleys above the $X_{xy}$ valleys of about 25 meV. The crossover between the $X_{xy}$ and $X_z$ subbands occurs for $n = 4$, according to the large longitudinal mass at the $X$ point. For $n = 5–14$, the CBM derives from the $X_z$-like AlAs band in the TB model. Since the valence-band maximum (VBM) occurs at $\Gamma$ localized in the GaAs well whatever $n$, the interband transition is pseudo-direct in momentum space and indirect in real space (type-II). The quantum size effects, associated with $n$ and the reduced masses at the $X$ and $\Gamma$ points induce a type-II $\rightarrow$ type-I transition for $n = 15$, and the CBM corresponds to a $\Gamma$-like GaAs band. All results for each period $n$ are in full agreement with the experimental data at low temperature [32]. The accuracy of the $spds^*$ model in the GaAs/AlAs superlattices evidences transferability of the bulk TB parameters to quantum structures with an energy offset at the interface region. Interestingly, atomistic pseudopotentials use As parameters depending on the number of neighboring Ga and Al sites [3], in qualitative correspondence with the TB parameterization model at interfaces. However, the advantage of tight-binding is to better distinguish the bonds towards the Ga and Al sites: they are parameterized as in the corresponding strained bulks. As one can see in Fig. 5, TB results are in an excellent agreement with experiment, and most of the improvements can be related to a more precise parameterization of the electronic band structures. In particular, the low type I $\rightarrow$ type II crossover found for $n = 6–7$ in Ref. [3] results from the small electronic confinement scaling with the effective mass of GaAs of 0.099 m$_0$ instead of 0.067 m$_0$ [26].

**FIG. 4:** Electronic band structure of the (GaAs)$_1$/ (AlAs)$_1$ superlattice calculated with the $spds^*$ TB model.
IV. CONCLUSION AND OUTLOOK

The success of the extended extended-basis $sp^3d^5s^*$ tight binding model relies on the availability of correct approximations and the unique ability to describe with the same precision any region of the Brillouin zone of semiconductors. It has been effective in accurately calculating physical properties for different configurations: short period superlattices [34], surfaces [35], SI photonics [26], quantum dot nanostructures [37, 38], and spin effects [39], where other computational methods are known to show some limitations. The major part of the tight binding community has now adopted this model, and is still exploring the limits of its applicability. New developments of interest concern the exact representation of the local wave function real space. This would allow for modeling the many-body corrections, specifically, the Coulomb direct and exchange interactions in semiconductor nanostructures.

References


