# ANALYSIS OF INTERMEDIATE BAND MATERIALS USING THEORETICAL METHODS

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ABSTRACT: A new kind of photovoltaic material, Intermediate Band Material (MIB), has been proposed in previous works. This new photovoltaic materials is principally characterized by an intermediate band, isolated from the valence and conduction bands of the host semiconductors and is partially occupied. Therefore, this material can absorb photons with a lower energy than the bandgap energy of the original host semiconductor, and thus increasing significantly the limiting efficiency of conventional solar cells. However, although the operation of this solar cell has been proposed, it is necessary to use some method to be able to propose a material with this property. In this work, a theoretical study of the electronic and optoelectronic properties using quantum mechanics calculations is presented.

## 1 INTRODUCTION

In previous works, the importance of intermediate band materials in the field of the solar energy have been stressed [1]. The model of this solar cell and a scheme of their operation is shown in Fig.1.

The solar cells based on this intermediate band material has several characteristics. Between them, the presence of an intermediate band (IB), isolated from the conduction (CB) and valence (VB) bands stands out. If this requirement is not fulfilled, the electron-phonon interaction can produce thermal relaxation due to the interaction between the electrons and the phonons coming from the lattice. Moreover, the IB must have a finite width to avoid, as much as possible, processes of non-radiative recombination. The IB has to be partially filled to be able to absorb photons of low energies that promote electrons from the VB to the half filled IB and from this one to the CB.

This kind the solar cell presents efficiencies higher than the ones established by the Shockley limit [2], as have been demonstrated in the previous work of Luque and Martí [1]. They show how the efficiency is increased based on thermodynamic arguments and the operation of this kind the cell.
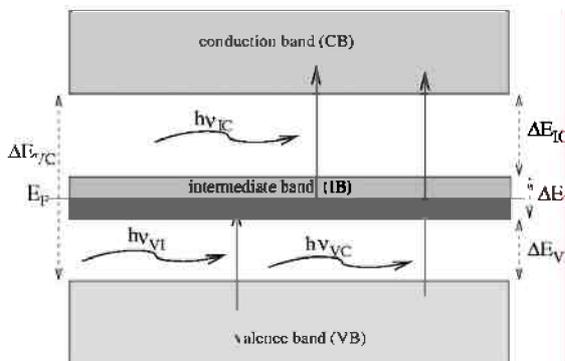


**Figure 1:** Model of the Intermediate band solar cell.

Our purpose in this work, is to describe, to implement and to apply the quantum mechanic methodology so that it can be used to study and to propose materials that present an intermediate band. Moreover, this methodology will be applied to determining some electronic and optical properties.

To achieve this task, first we will describe the approximations and methodology used in this work. In the second part we show some of the results obtained using these tools.

## 2 THEORETICAL ANALYSIS

In order to propose and subsequently determine the properties of this material it is necessary to use some type of methodology.

Because the chemical bonds in all kinds of materials are of quantum mechanical origin, the determination of the structure and properties can be realized using these tools. This implies the solution of the Schrodinger equation for the electrons and nuclei of the material. The first step in solving the problem is to use the Born-Oppenheimer approximation. Within this approximation the total energy can be expressed as the sum of the kinetic energy of the nuclei and the electronic energy. This electronic energy corresponds to a frozen nuclear configuration and acts as potential for the nuclear movement.

In spite of the simplification of the initial problem, we still have a many body problem: the interaction of all the electrons in the system. The following step is to use the Density Functional Theory (DFT) that allows us to map the interacting many-body problem onto a one-body problem using the Kohn-Sham (KS) method [3]. In this method the attention is focused on the electron density $\rho(\vec{r})$, defined as:

$$\rho(\vec{r}) = \sum_{\mu} |\psi_{\mu}(\vec{r})|^2 \qquad (1)$$

where $\psi_{\mu}$ are the wave functions of the system of non-interacting electrons whose electron density is $\rho$. These orbitals are the solution to the KS equation:

$$\left( -\frac{1}{2}\nabla^2 + V_{KS}[\rho] \right)\psi_n = \varepsilon_n \psi_n \qquad (2)$$

where $V_{KS}$ is the effective potential of the one electron problem.

$$V_{KS}[\rho] = V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{xc}[\rho] \qquad (3)$$

This potential is the sum of the ionic potential acting on the electrons, the average potential of the electron density, the so-called Hartree potential, is the exchange-correlation potential.

The main problem with this theory is that the exchange-correlation potential is unknown. If this potential were known, the solution would be exact. Unfortunately, we must make an approximation. Some of the more extensively used functionals are the local density approximation (LDA) and the generalized gradient approximation (GGA). In the LDA approximation the exchange-correlation energy can be expressed as

$$E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}(\rho)\rho(\vec{r})d\vec{r} \qquad (4)$$

where $\varepsilon_{xc}$ is the exchange-correlation energy of a uniform electron gas. The GGA approximation is similar, but it considers the possibility of the non-uniformity of the electronic density.

$$E_{xc}^{GGA}[\rho] = \int \varepsilon_{xc}(\rho, \vec{\nabla}\rho)\rho(\vec{r})d\vec{r} \qquad (5)$$

In spite of its approximations, this theory is one of the few that allows the study of large systems such as crystalline solids and allows us to obtain realistic results for many electron systems. However, LDA and GGA approximations have the problem of underestimating the band gaps. Nevertheless, some methods have been proposed to avoid this inconvenience.

Within these approximations the KS equations are solved using a basis set of plane waves or localized functions to represent the KS orbitals, in other words, to approximate the KS orbitals as a linear combination of plane waves or localized functions. In any case, it is convenient that this linear combination satisfies Bloch's theorem when used for solids. If the representation of the KS orbitals has translational symmetry, the orbitals will have a new index $\vec{k}$ to indicate a point in the Brillouin zone (BZ).

We have chosen to represent the KS orbitals as a linear combination of localized functions satisfying the symmetry requirements in order it provide us with a more feasible interpretation of the results and lower calculation costs than a plane wave. The intermediate band is better described with a localized basis set because it is more localized than the conduction band.

With this choice, the KS orbitals for the solid $\psi_{j,\vec{k}}(\vec{r})$ are built as a linear combination of localized orbitals adapted to the translational symmetry

$$\psi_{j,\vec{k}}(\vec{r}) = |j,\vec{k}\rangle = \sum_{u}\sum_{n_u} C_{u,n_u}^{j,\vec{k}} |\vec{k},u,n_u\rangle \qquad (6)$$

where the $j$ index labels the band and $\vec{k}$ represents a point in the BZ.

Each one of this adapted symmetry functions $|\vec{k},u,n_u>$ are formed by combinations of functions localized in different atomic positions $\phi_{n_u}(\vec{r})$ that satisfies Bloch's Theorem:

$$\left|\vec{k},u,n_u\right\rangle = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_{n_u}(\vec{r} - \vec{R} - \vec{\tau}_u) \qquad (7)$$

where, $u$ is an index that labels every atom contained in the unit cell of the solid, $n_u$ labels every basis function belonging to the atom $u$, $\vec{\tau}_u$ represents the position of the $u^{th}$ atom within the unit cell, $N$ is the number of cells under consideration, $C_{u,n_u}^{j,\vec{k}}$ is an expansion coefficient and $\vec{R}$ is a lattice vector representing the position of each cell within the solid:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \qquad (8)$$

In the last expression, $n$'s are integers and the $\vec{a}_i$'s are the lattice vectors. The functions $\phi_{n_u}$ are known as the basis set of the representation for the wave function.

Within the Born-Oppenheimer approximation the total energy, sum of the nuclei energy and the electronic energy in a frozen nuclear configuration, is minimized. The variables implied in this minimization are the coefficients $C_{u,n_u}^{j,\vec{k}}$.

The calculation will depend on the number of atoms of the crystalline cell, the number of basis functions localized in the atoms, the numbers of bands that we want obtain and the numbers of cells crystalline used to describe the finite crystal. The last parameter depends on the indices $(n_1, n_2, n_3)$ of the lattice vector $\vec{R}$. In others words, the numbers of times that we repeat the unit cell in each direction of $\vec{a}_i$ for building the finite crystal.

Moreover, other approximation used in solids is the pseudopotential approximation, based on the small contribution of core electrons in the bonds. This approximation has the advantage of reducing the computational cost, because the number of electrons is drastically reduced. Only the valence electrons are considered.

## 3 ELECTRONIC PROPERTIES

For determining electronic properties, we have used the SIESTA code [4] with pseudopotentials [5] to reproduce the core of the atoms. To introduce the exchange and correlation term we used the Perdew, Burke and Ernzerhof [6] parameterisation for GGA and the Ceperley-Alder [7] parameterisation for LDA.

Using the methodology described above, we have found several different materials that present the intermediate band. These compounds were found by substituting some transition metals in host III-V

semiconductors [8]. The resulting structure after the minimization of the total energy is almost cubic as shows Fig 2.
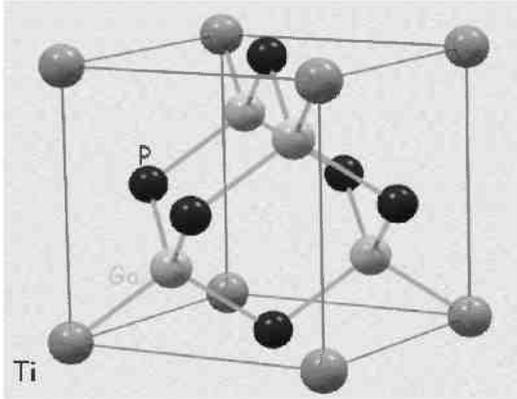


**Figure 2.** Crystalline structure of materials proposed.

The lattice parameter of the resulting alloy is higher than the original lattice parameter for the host semiconductor and the resulting atomic coordinates are slightly displaced from their original positions.
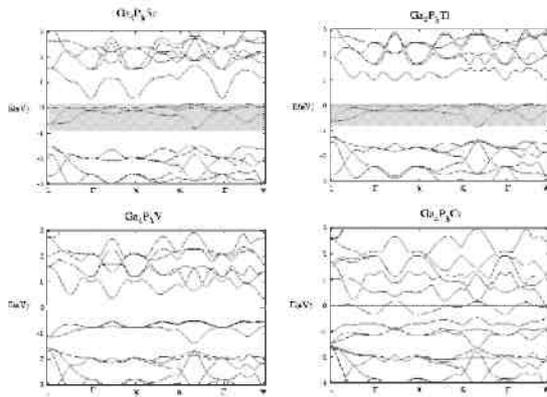


**Figure 3.** Band diagrams for some of the compounds analysed.

In Fig. 3, we present band diagrams for a series of $Ga_4P_3M$, compounds where M represents a transition metal atom. This figure shows a perfectly isolated intermediate band (stressed in the figure) for the situations where M is Ti or Sc. The Fermi level in these cases crosses the intermediate bands. When M is V the compound is a semiconductor and when is Cr we have a metallic material. An analysis of the projected density of states and the electronic density [9] reveals that the intermediate band for M=Ti and Sc is mainly made up of the $t_{2g}$ ($d_{xy}$, $d_{xz}$ and $d_{yz}$) orbitals belonging to the transition metal.

## 4 OPTICAL PROPERTIES

The optical properties, when the dipolar approximation for the interaction between matter and

radiation is used, are related to the electronic properties and the matrix element of the momentum operator. For example, the optical conductivity and others optoelectronic properties can be calculated using the Kubo formula [10]:

$$\sigma(\omega) = \frac{2e^2\Omega}{m^2 cn\omega} \sum_v \sum_c \int_{BZ} d\vec{k} \; |< v,\vec{k} \,| \, \hat{p} \,|\, c,\vec{k} >|^2 \times$$

$$\times [f_{v,\vec{k}} - f_{c,\vec{k}}] \delta(E_{c,\vec{k}} - E_{v,k} - \hbar\omega)$$

where $m$ and $e$ are the mass and charge of the electron respectively, $c$ is the speed of light in a vacuum, $n$ is the refraction index of the material, $\Omega$ is the volume of the Brillouin Zone (BZ), $f_{v,\vec{k}}$ are the occupation numbers and $\hbar\omega$ is the photon energy.
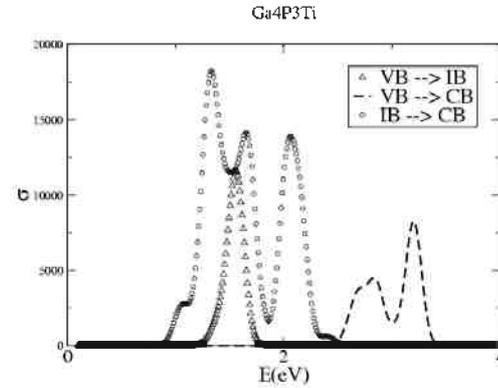


**Figure 4.** Partial and total conductivity $\left(eV.\Omega^{-1}\right)$ for the $Ga_4P_3Ti$ system using the VB, IB and CB.

It has to be noted that it is necessary to previously obtain the electronic properties, characterized principally by the energies ($E_{b,\vec{k}}$) of the different bands in the BZ and the corresponding occupations numbers ($f_{b,\vec{k}}$).

Using the description of the KS orbitals in terms of the linear combinations of the localized functions, the matrix elements of the momentum operator $< v,\vec{k} \,|\, \hat{p} \,|\, c,\vec{k} >$ [11] between the $|\, v,\vec{k} >$ and $|\, v,\vec{k} >$ states take the form:

$$< v,\vec{k} \,|\, p \,|\, c,\vec{k} >= \sum_{\vec{R}} e^{i\vec{R}\vec{k}} \sum_u \sum_{n_u} \sum_q \sum_{n_q} C_{u,n_u}^{v,\vec{k}} C_{q,n_q}^{c,\vec{k}} \times$$

$$(9)$$

$$\times \int \phi_{n_u}^*(\vec{r} + \vec{\tau}_u) \hat{p} \phi_{n_q}^*(\vec{r} + \vec{\tau}_q - \vec{R}) \, d\vec{r}$$

From this expression, it is possible to see that the matrix elements depend on several factors: the atomic basis of the functions used ($\phi_{nu}$), the expansion

coefficients of the band in the chosen $\vec{k}$ point ($C_{u\,n}^{v,\vec{+}}$), the number of cells used in the calculation and the integral containing the product of two basis functions. Each basis function is located in different atom within different cells placed $\vec{R}$ with respect to the reference cell.

One advantage in using localized functions is the rapid convergence because the integral connecting two different basis functions quite distant from each other will be negligible.

The results of calculating the optical conductivity are shown in Fig.5. In reaching this figure, we have only considered the states on the top of the VB, on the bottom of the CB and the states on the IB. It can be seen that the energy at which the material begins to absorb photons, corresponding to the transition of the intermediate band (IB) to the conduction band (CB), is smaller than that corresponding to the transitions from the valence band (VB) to CB. In fact, the absorptions of the VB to the IB also correspond to lower energy than the VB to the CB. Therefore, this compound is able to absorb photons of lower energy than the traditional the VB to the CB to promote electrons from the IB to the CB and the VB to the IB. For this reason, the total conductivity is higher to lower energies than the semiconductor host (GaP).

## 5 CONCLUSIONS

We have analysed some theoretical methods used to study the electronic and optical properties of solids. The application has focused in the intermediate-band materials, because of its importance in solar cells. Based on the Born-Oppenheimer approximation and minimizing the total energy we have obtained the relaxed nuclei positions and the KS orbitals using a basis set as the localized functions adapted to the symmetry.

From these methods we have used the application to various materials, some of them exhibiting a partially full intermediate band. After obtaining the electronic properties, we have analysed them to calculate some of their optoelectronic properties, such as the optical conductivity. We have applied this methods to the $Ga_4P_3Ti$ system, one the materials which presents an intermediate band.

One of the problems of the methodology used (DFT) is that the electronic exchange and correlation terms have to be approximated as has been previously explained. We have developed and implemented [12] new theoretical methodologies. In the first place we have to mention the development and implementation of the Exact Exchange (EXX) in order to substitute the usual LDA and GGA exchange terms. The use of the EXX in the calculation of the properties of several III-V semiconductors yields results very close to the experimental values.

## 6 ACKNOWLEDGMENTS

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