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Four-band Hamiltonian for fast calculations in intermediate-band solar cells

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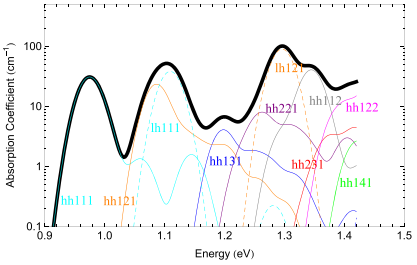
HIGHLIGHTS

- Four band Hamiltonian derived from ordinary 8 band LK-PB Hamiltonian.
- Allows for two orders-of-magnitude faster calculations.
- Reproduces reasonably well the quantum efficiency of a quantum dot solar cell.
- Produces detailed absorption coefficient information.
- Input for detailed balance analysis of nanostructured semiconductor devices.

GRAPHICAL ABSTRACT

Sub-bandgap absorption calculated with the LKPB (H_{uu}) (thick black line) and contribution of the transitions from all the bound states in the *hh* and *lh* bands to the *cb* states (including the IB states). In the legends each curve is labeled with two letters for the initial states and the quantum numbers of the *cb* final state.



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ABSTRACT

The 8-dimensional Luttinger–Kohn–Pikus–Bir Hamiltonian matrix may be made up of four 4-dimensional blocks. A 4-band Hamiltonian is presented, obtained from making the non-diagonal blocks zero. The parameters of the new Hamiltonian are adjusted to fit the calculated effective masses and strained QD bandgap with the measured ones. The 4-dimensional Hamiltonian thus obtained agrees well with measured quantum efficiency of a quantum dot intermediate band solar cell and the full absorption spectrum can be calculated in about two hours using Mathematica© and a notebook. This is a hundred times faster than with the commonly-used 8-band Hamiltonian and is considered suitable for helping design engineers in the development of nanostructured solar cells.

1. Introduction

The use of an intermediate band (IB), that is, a band within the energy gap of a semiconductor, can raise the detailed balance efficiency limit [1] of a solar cell from 41% to 63% [2]. This IB serves as a stepping stone permitting two low-energy photons to generate an electron-hole pair in the valence (VB) and conduction (CB) bands of the semiconductor. The voltage may be maintained approximately if the IB has a quasi Fermi level (or electrochemical potential) different from that of the CB and the VB. Thus, a higher efficiency may be achieved.

One way of producing an IB is by forming quantum dots (QDs)

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in a host semiconductor, [3] e.g. QDs of InAs in a GaAs host material. The InAs QDs produce potential wells in the GaAs CB; the wells confine the electrons with energies which are within the GaAs bandgap; these energy levels may act as an IB. Other material combinations may also behave like the InAs/GaAs.

Despite the concept's promise, only on very seldom occasions have efficiencies greater than the cell without QDs been achieved [4] and even then, merely marginally. The main reason is the weak absorption of the photons by the QDs. This absorption can be modeled using *ab initio*[5] or $\boldsymbol{k}\cdot\boldsymbol{p}$ [6] calculations. In both cases the calculation resources are huge. The so called Empiric $\boldsymbol{k}\cdot\boldsymbol{p}$ (EKP) Hamiltonian has been developed [7,8] to permit a much faster calculation, feasible on a laptop. This may greatly aid the device scientist in obtaining feedback from calculations in the task of improving IB solar cells. It is based on building a Hamiltonian whose eigenvalues are the experimental $E(\boldsymbol{k})$ dispersion functions.

However, the well-established method for studying the quantum characteristics of the nanostructure materials with a zincblende structure (those currently providing the greatest efficiency), including the absorption coefficients, is the use of the 8-band Luttinger Kohn (LK) [9,10] Hamiltonian modified by Pikus and Bir (PB) [11,12] to account for the strain in the lattice. This is a variety of the $\boldsymbol{k}\cdot\boldsymbol{p}$ methods introduced by Dresselhaus, Kip and Kittel [13] and extensively developed by Kane [14,15]. It has been found [16] that the LKPB Hamiltonian is about 100 times more time consuming than the EKP Hamiltonian for typical problem sizes and parameters

The most important reason for this time-consuming feature is that the LKPB Hamiltonian uses eight bands in the problems associated with photon absorption for solar cells in zincblende semiconductors. In this article we propose a four-band Hamiltonian derived from the LKPB one and we will see that the time-consumption is close to that of the EKP Hamiltonian and therefore almost 100 times faster than the 8-band LKPB Hamiltonian.

Among the approximations that we adopt for simplicity is the QD shape, which is considered a squat parallelepiped or box instead of the squat truncated quadrangular pyramid that dictates the theory [17]. Other authors have used different shapes such as full pyramids, [18,19] lenses [5] or, as we do, parallelepipeds [7,20–22].

The other approximation is the widely used concept of constant band offset, which considers the confining potential introduced by the QD as constant in all its volume, and zero outside it. We will describe the theoretical implications of this approximation.

Besides this Introduction, Section 2 contains the theoretical background where the basic aspects of the LKPB Hamiltonian are explained, in a big extent with the purpose of fixing the paper's nomenclature; it also explains the strain model that produces constant offsets and which is used in this paper for simplicity. Section 3 introduces the concepts in which the 4-band Hamiltonian is based. Section 4 presents results of this Hamiltonian concerning the energy spectrum, eigenstates and absorption coefficients, always in comparison with the EKP Hamiltonian and the 8-band LKPB Hamiltonian; the reasonable agreement achieved with the measured data constitute the main justification of this method. Section 5 comprises an estimate of the calculation time of the 4-band Hamiltonian as compared to that of the 8 band. Finally a conclusions Section 6 is added. The paper also contains an Appendix A in which the formulas for calculating the LKPB Hamiltonian are described. An on-line Supplementary data file accompanies the paper and includes Section 1, on the choice of parameters, Section 2, on the determination of the strain function, Section 3, on the strained material fitting of the effective masses and finally, Section 4 in which some of the properties of the Fourier transforms are set out.

2. Theoretical background

$\boldsymbol{k}\cdot\boldsymbol{p}$ methods are based on developing a one-electron Hamiltonian into an orthonormal basis $|0,\nu,\boldsymbol{k}\rangle = |0,\nu\rangle\exp(i\boldsymbol{k}\cdot\boldsymbol{r})/\sqrt{\Omega}$ where $|0,\nu\rangle$ is a the Γ-point Bloch function (GBF), which has the periodicity of the lattice, ν is the band index, $\boldsymbol{k}$ is an arbitrary wavevector of the first Brillouin zone and Ω is the volume of calculation (in this paper, a cube of $60\times60\times60$ nm^3), which must be large with respect to the nanostructure studied here (a box of $16\times16\times6$ nm^3). The 0 index refers to the Γ point ($\boldsymbol{k}=0$). We call this basis the standard basis. This standard basis is usually limited to a small number, n_B, of bands of interest. The matrix elements relating basis vectors of different $\boldsymbol{k}$ are automatically zero, so that the Hamiltonian is represented as a matrix of dimension n_B whose elements are functions of $\boldsymbol{k}$. The matrix usually undergoes the process known as renormalization [23] to account for the neglected bands.

For zincblende semiconductors, it is very common to use the conduction band (*cb*), and three valence bands (VBs): the heavy hole (*hh*) the light hole (*lh*) and the spilt off (*so*) bands. Disregarding the spin for the moment, the zincblende lattice belongs to the T_d symmetry group. The *cb* GBF is often called $|S\rangle$ and has spherical symmetry (it is an *s*-function). At $\boldsymbol{k}=0$, the three VBs degenerate and the eigenfunctions are linear combinations of three GBFs called $|X\rangle$, $|Y\rangle$ and $|Z\rangle$ with the symmetry of *x*, *y* and *z* (see, e.g. Datta [23]) respectively (they are *p*-functions). However each of these functions may be considered with spin up or down and denoted as $|S\uparrow\rangle\ldots|Y\downarrow\rangle$ etc.

In the EKP Hamiltonian we neglect the spin and use $|S\rangle$, $|X\rangle$, $|Y\rangle$ and $|Z\rangle$ to form the standard basis. This leads to a 4-band Hamiltonian. Furthermore, we use a simple Hamiltonian (H_0) that neglects the important spin–orbit coupling and any strain effect. The eigenvalues of a $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian are the $E(\boldsymbol{k})$ dispersion functions, whose details can be seen in e.g., Datta [23]. These dispersion functions are replaced in the EKP Hamiltonian by parabolic experimental ones, characterized by the band edges and effective masses, but the eigenvectors of (H_0) are retained. See [8,20] for details.

In contrast, the spin is taken into account in the LK Hamiltonian and when the origin of energy is set at the VB top, eigenvalues are E_g, E_g, 0, 0, 0, 0, $-\Delta$, $-\Delta$, where E_g and $-\Delta$ are experimental data characteristic of the material. The eigenvectors are linear combinations of the states $|S\uparrow\rangle\ldots|Y\downarrow\rangle$ etc. and in this paper they are labeled as $|cb+\rangle$, $|hh+\rangle$, $|lh+\rangle$, $|so+\rangle$, $|cb-\rangle$, $|hh-\rangle$, $|lh-\rangle$, $|so-\rangle$. For details see reference [23].

As the number of eigenvalues is 8, the LK Hamiltonian is represented by an 8-dimension (8D) matrix. If the eigenvectors are ordered as indicated above, the 8D matrix may be divided into four blocks [19].

$$(H)=\begin{pmatrix}(H_{uu}) & (H_{ul})\\ (H_{lu}) & (H_{ll})\end{pmatrix} \tag{1}$$

The interesting aspect of this block separation is that is $(H_{lu})=(H_{ul}^{+})$ (hermitical conjugate) and $(H_{ll})=(H_{uu}^{*})$ (complex conjugate); therefore, only two of the four matrices have to be determined.

Each one of the block matrices may be considered the sum of a kinetic matrix (the LK part), which applies to non-strained materials, and a strained material matrix (the PB part). Auxiliary functions are defined to write the matrix elements, and are presented in the Appendix A. For different materials they depend of a set of parameters that can be found in the literature [24].

All the LK matrix elements are functions of $\boldsymbol{k}$; the PB matrix elements depend on elements of the strain tensor. The strain tensor elements are multiplied by material-dependant factors