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Abstract - In this work we are going to exploit k.p perturbation theory for calculation of momentum matrix elements and energy eigenvalue of semiconductors in general, and calculate the \( E_c \) & \( E_v \) the energy on conduction band and valence band respectively. Finally, we formulate the energy spectrum energy for II-VI material using the relation between the reduce mass \( \mu^* \) and the unperturbed band gap \( E_g \).

Keywords- II–VI materials; Narrow gap semiconductor; The k.p perturbation theory.

I. INTRODUCTION

Optical transitions in atoms and molecules occur between discrete levels. Semiconductors (bulk) are however characterized by bands and the study of optical processes in semiconductors invariably requires complete knowledge of band structure [1]. The band theory of solids, including semiconductors, is a many-particle theory involving all electrons and ions and their mutual interactions. This many-body problem may be reduced under various approximations to a single-electron problem that predicts most of the important features. In the one electron theory an electron is assumed to exist in a periodic potential and the solution of the time-independent Schrödinger’s equation,

\[
\left( \frac{\hbar^2}{2m_0} \right) \nabla^2 \psi + \left[ E - V(r) \right] \psi = 0
\]

where \( V(r) \) is the potential energy of an electron due to the potential produced by the nuclei of the atoms and other electrons) with periodic boundary conditions yields different bands that are separated from each other by a forbidden band gap.

We note that in optical transitions from the valence band to the conduction band the electrons involved cover an energy interval of a small fraction of an electron Volt (eV). Therefore, it is sufficient to know the band structure within a few \( k_B T \) from the conduction and valence band extrema. For most of the common semiconductors the wave functions of the electrons at the band edges are readily describable by atomic \( s \) and \( p \) functions. For states slightly away from the extrema the k.p perturbation theory proves to be a very useful approximation.

A solid consists of many atoms and electrons. The total energy of the system is the sum of the kinetic energies of all the nuclei and the electrons, the potential energies due to internuclear forces, the potential forces, the potential of the nuclei, the magnetic energy associated with the spin and the orbit.

The total Hamiltonian of the system may be constructed accordingly.

The formidable problem of solving the resultant Schrödinger equation is bypassed invoking several approximations. Since the motion of the nuclei is sluggish, the electrons instantaneously adjust their motion to that of the ions.

The k.p perturbation method [2,3] is based on the fact that the cell periodic functions for the electrons for any \( k \) but different bands from a complete set and the expression of the wave functions for electrons are in terms of the functions for the minima and maxima(i.e HOMO-LUMO bands).

In this work we try to calculate \( E_c \) and \( E_v \) by solving Schrödinger equation and finally calculate \( E_g \) pending on the result that we got it and finally use it to calculate the electron energy spectrum in II-VI material.

II. THE K.P PERTURBATION THEORY

NEGLECTING SPIN

Let us consider the wave function for the electrons having a value \( k \) near the minima in the \( n^{th} \) band.

For simplicity we assume that the minima are located at \( k=0 \). The theory is applicable also within the minima that are located at \( k = k_0 \). The wave function is given by

\[
\psi = u_{n0}(r) \exp(ikr) = \sum C_n u_{n0}(r) \exp(ikr)
\]  

Replacing \( \psi \) by (1) in the Schrödinger equation we get

\[
- \left[ \frac{\hbar^2}{2m_0} \nabla^2 + \frac{\hbar^2}{2m_0} k_p + \frac{\hbar^2}{2m_0} + V(r) \right] u_{n0}(r) = E_{n0}(k) u_{n0}(r)
\]  

However \( u_{n0} \) is the wave function for \( k=0 \) in the \( n^{th} \) band satisfying the equation

\[
- \left[ \frac{\hbar^2}{2m_0} \nabla^2 + V(r) \right] u_{n0}(r) = E_{n0}(0) u_{n0}(r)
\]  

We now put eq.(1) in eq.(2) and use eq.(3) to obtain potential energy due to the electron-electron Interaction

\[
\sum C_n \left[ E_{n0}(0) + \frac{\hbar^2}{2m_0} k^2 + \frac{\hbar^2}{m_0} k_p \right] u_{n0}(r) = \sum C_n E_n(k) u_{n0}(r)
\]
Multiplying both sides of eq.(4) by \( u_i^* (r) \) and integrating over the unit cell \((V)\), then the following set of linear homogeneous equation is obtained
\[
C_i \left[ E_n (k) - E_i (0) \right] \frac{h^2 k^2}{2m_0} \sum_j C_{ij} \frac{h}{m_0} (kP_{ij}) = 0
\]
(5)

Where
\[
P_{ij} = \int v^* (r) P_{ij} \, u_j (r) \, dr.
\]
(6)

By giving \( l \) successive integer values one obtains the full set of equations.

In the general case, the set of equations has a non-trivial solution if the determinant of the coefficients \( C_i \) is zero. This condition gives the energy eigenvalues \( E_n (k) \) in terms of the quantities \( E_n (0) \) and \( P_{ij} \). The relative values of the expansion co-efficient \( C_i \) are then obtained by using the values \( E_n (k) \). The absolute values of \( C_i \) are obtained by imposing normalization condition on \( u_i \). Therefore, the energy eigenvalues near a characteristic point \( k = 0 \) can be expressed as
\[
E_n (k) = E_n (0) + \frac{h^2 k^2}{2m_0} + \frac{\hbar^2}{m_0} \sum_j \left[ kP_{ij} \right] (0) \right] \right]^2
\]
where the prime at the sum indicates summation overall \( n \) and \( l \) with \( n \neq l \).

The second and third terms in eq.(2) can be developed as small perturbations in the vicinity of the minima \( k = k_0 \neq 0 \). Therefore, eq.(2) can be written as
\[
\left[ \frac{-\hbar^2 \nabla^2 + \hbar^2 (k-k_0)^2}{2m_0} + \frac{\hbar^2}{m_0} \sum_j [kP_{ij} (0)] \right] u_i (r) = E_n u_i (r)
\]
(8)

and the energy eigenvalue in eq.(7) near a characteristic point \( k_0 \) can be expressed as
\[
E_n (k) = E_n (0) + \frac{\hbar^2 (k-k_0)^2}{2m_0} + \frac{\hbar^2}{m_0} \sum_i \left[ (k-k_0) \right] P_{ij} (0) \right] \right]^2
\]
(9)

Eq.(9) can be simplified when interactions between only two bands are of interest (e.g., the valence and conduction bands) and the energy difference between these is small compared to the difference with all other bands. Then we can write
\[
E_n (k) = E_n (0) + \frac{\hbar^2}{2m_i^*} \sum_i \left[ (k-k_0)^2 \right]
\]
(10)

where \( i = x, y, z \) and the effective mass can be expressed as
\[
\frac{1}{m^*} = \frac{1}{m_0} \pm \frac{2}{m_0} \left[ E_n (k_0) - E_i (k_0) \right]^2
\]
(11)

with +ve or -ve for the upper or lower band, respectively.

Then we can use eq.(9) for the deviations of \( E(k) \) from the parabolicity expression [4,5] near a critical point \( k_0 \) as following
\[
E(k-k_0) = \frac{E_n}{2} + \frac{\hbar^2 (k-k_0)^2}{2m_0} + \frac{\hbar^2}{m_0} \left[ \frac{1}{E_n} \left( \frac{1}{m^*} \right) \right]
\]
(12)

From eq.(11), and eq.(12) we can write
\[
E(k-k_0) = \frac{E_n}{2} + \frac{\hbar^2 (k-k_0)^2}{2m_0} + \frac{\hbar^2}{m_0} \left[ \frac{1}{E_n} \left( \frac{1}{m^*} \right) \right]
\]
(13)

with \( m^* \) as the effective mass in the conduction (+) or valence (-) band. \( E_g = E_n (k=0) - E_i (k=0) \) is the band gap energy. This illustrates the usefulness of the \( k.p \) method in a simple example.

If we write eq. (13) in terms of reduce mass \( \mu^* \) where \( [(\mu^*)^2 = (m_e)^2 + (m_i)^2] \) and \( m_e \) is the effective electron mass at the edge of the CB in the absence of any field and \( m_i \) is the effective mass of the heavy hole at the top of the VB in the absence of any field, and assuming that the conduction band minimum and the valence band maximum are at the zone center, then we can write
\[
E_n (k) = \frac{E_g}{2} + \frac{\hbar^2 k^2}{2\mu^*} + \frac{E_g}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_g}}
\]
(14)

and
\[
E_i (k) = \frac{E_g}{2} + \frac{\hbar^2 k^2}{2\mu^*} - \frac{E_g}{2} \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_g}}
\]
(15)

where \( E_g \) is the unperturbed band gap. From eq. (14) & eq. (15) we can estimate the following
\[
E_n (k) - E_i (k) = E_g \sqrt{1 + \frac{\hbar^2 k^2}{\mu^* E_g}}
\]
(16)
If we write \( k=(2\pi/D) \) where \( D \) is the crystallite diameter, so we can write

\[
E_g = E_c(k) - E_v(k) = E_{g_0} + \frac{2\hbar^2\pi^2}{D^2}\mu^* \tag{17}
\]

By using following assumption, given in appendix

\[\frac{\mu^*}{m_e} = 0.3375 \ln 0.5622 E_{g_0} \tag{18}\]

So we can write eq. (16) as

\[
E_c(k) - E_v(k) = E_{g_0}\left(1 + \frac{\hbar^2 k^2}{\mu^* E_{g_0}}\right)^{\frac{1}{2}}
\]

\[
= E_{g_0}\left(1 + 2\left(\frac{m}{\mu^*}\right) \frac{\hbar^2 k^2}{2m_e E_{g_0}}\right)^{\frac{1}{2}} \tag{19}\]

\[
= E_{g_0}\left(1 + 2\left(\frac{1}{0.3375 \ln 0.5622 E_{g_0}}\right) \frac{\hbar^2 k^2}{2m_e E_{g_0}}\right)^{\frac{1}{2}}
\]

\(E_c(k) - E_v(k)\) is the band gap denoted by \(E_g\).

Calculations in eq.(19), and comparing with literature [7] is in good agreement.

### III. FORMULATION OF THE ELECTRON ENERGY SPECTRUM IN II-VI MATERIALS

Ghatak et. al [6] expressed the energy equation for the conduction electron as

\[
\gamma(E) = \left(\frac{\hbar^2 k^2}{2m_e} + \frac{(e A_0/2m)^2}{E_c(k) - E_v(k)}\right)^{\frac{1}{2}} \tag{20}
\]

where \(\gamma(E)=E\) in the case of relatively wide band gap semiconductor, and \(A_0\) is the amplitude of the light wave, \(e_\epsilon\) is the polarization vector, \(e\) the magnitude of the carrier charge, \(m\) is the free electron mass, \(\left\langle \left| e_\epsilon \cdot P_{cv}(k)\right|^2 \right\rangle_{av}\) is the average of the square of the optical matrix element (OME).

He introduce the electron energy spectrum for II-VI material as

\[
\rho(E) = E - \frac{\epsilon^2 I \lambda^2}{96\pi c m_e \epsilon_\epsilon_0} \left[1 + \frac{2m_e}{\mu^*} \frac{E}{E_{g_0}}\right]^{\frac{3}{2}} \tag{21}\]

Eq.(22) gives the electron energy spectrum for II-VI materials, in particular \(ZnS_xSe_{1-x}\) (0<x<1) as an example.

### REFERENCE


Appendix

The following data in Table I were obtained from Abo-Hassan et al.[7].

TABLE I. Shift in band gap \( \Delta E_g \) caused by grain size effect and reduce effective mass \( \mu^* \) for ZnS\(_x\)Se\(_{1-x}\) (0\(<x<1\)) thin films

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \mu^*/m_e )</th>
<th>( E_g(eV) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.14</td>
<td>2.5816</td>
</tr>
<tr>
<td>0.34</td>
<td>0.17</td>
<td>2.9514</td>
</tr>
<tr>
<td>0.35</td>
<td>0.17</td>
<td>2.9565</td>
</tr>
<tr>
<td>0.37</td>
<td>0.17</td>
<td>2.9573</td>
</tr>
<tr>
<td>0.41</td>
<td>0.17</td>
<td>2.9865</td>
</tr>
<tr>
<td>0.48</td>
<td>0.18</td>
<td>3.0521</td>
</tr>
<tr>
<td>0.78</td>
<td>0.22</td>
<td>3.2910</td>
</tr>
<tr>
<td>0.80</td>
<td>0.22</td>
<td>3.3023</td>
</tr>
<tr>
<td>0.82</td>
<td>0.22</td>
<td>3.3531</td>
</tr>
<tr>
<td>0.90</td>
<td>0.23</td>
<td>3.5469</td>
</tr>
<tr>
<td>0.96</td>
<td>0.24</td>
<td>3.5197</td>
</tr>
<tr>
<td>0.99</td>
<td>0.24</td>
<td>3.7351</td>
</tr>
</tbody>
</table>

From the results presented in Table I, the relationship between \( \mu^*/m_e \) and the stress-free energy gap \( E_{gc} \) can be written as

\[
\frac{\mu^*}{m_e} = 0.3375 \ln 0.5622 E_{gc}
\]

Figure 1. \( E_g \) vs \( x \) with reference to Abo Hassan[7] (dash line). The solid line represents results from the present work.