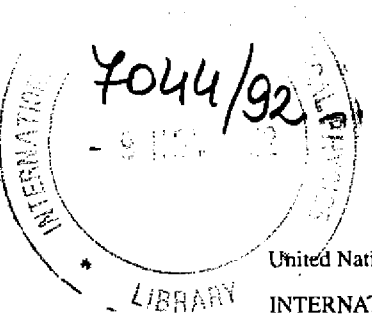


REF ID: A6



International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

**ON THE ESTIMATION OF MATRIX ELEMENTS
FOR OPTICAL TRANSITIONS IN SEMICONDUCTORS**

A.R. Hassan *

International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

A semi-empirical method is used to calculate the numerical values of the interband momentum matrix elements of the allowed optical transitions in semiconductors. This method is based on the evaluation of the ratio of the two-photon and one-photon absorption coefficients and the compare the result with the corresponding experimental values in a number of semiconductors both for direct and indirect transition processes. The numerical values of the momentum matrix elements are compared with the convenient theoretical calculations available. The result is found to agree fairly well with the corresponding values computed using the $\vec{k} \cdot \vec{p}$ perturbation theory.

MIRAMARE - TRIESTE

September 1992

* Permanent address: Department of Physics and Mathematics, Faculty of Engineering, Ain Shams University, 11517 Abassia, Cairo, Egypt.

1. INTRODUCTION

The direct and indirect interband transitions models are often used for the description of the optical properties of solids. These models require, in the dipole approximation, the calculation of the matrix elements for the electric dipole transitions between the initial and final states.

There are, in general, 16 different types of transition matrix elements depending on the specific transition concerned. In direct allowed transitions we have four interband (usually independent of \vec{k}) matrix elements, namely; band, exciton, exciton-exciton and biexciton-exciton momentum matrix elements. There are other four matrix elements corresponding to the indirect transitions. The remaining 8 (intraband) matrix elements are associated with the forbidden transitions in the direct and indirect processes. They couple states (band, exciton and biexciton) of the same band. We will concentrate, in this work, on the allowed band momentum matrix elements (MME) which is extensively studied and since the other matrix elements can be written in terms of it.

The computation of the MME is a crucial point in the calculation of optical properties because it depends very sensitively on the accuracy of the wave functions. There is a considerable amount of theoretical calculations concerning the MME which lack of a consistent with their approximate wave functions. Starace ¹ has differentiated between the alternative forms, so-called length, velocity and acceleration formulas for the MME. He showed that the MME is correctly given by the length formula for procedures involving a nonlocal Hamiltonian. In metal Petroff *et al.* ² and Gegusin *et al.* ³ using the APW functions have calculated the MME with ² and without ³ including the summation over the magnetic quantum number. Making use of the commutator relation of the Hamiltonian with the momentum operator the MME can be transformed into ∇V -matrix element (V is the crystal potential). Fritzsche ⁴ has proved that the MME should be preferred in numerical calculations of optical properties where ∇V -matrix element becomes inaccurate at low energies. The calculation of the MME in the Green's function method has been obtained by Chen ⁵. For zinc blende semiconductors the MME has been derived by Weiler ⁶ including the nonparabolic effect (i.e. at $\vec{k} \neq 0$).

In Section 3 the first four theoretical investigations ⁷⁻¹⁰ of the MME are analysed. These calculations are more reliable and usually treated when dealing with the one-photon and two-photon processes in semiconductors. The MME in these works are related to both band parameters and excitation energies in correspondence to a certain band model adopted in each process. We compare our numerical results of the MME with the values obtained from these calculations since our method depends on the type of band model and the specific transitions involved.

The purpose of the present paper is to provide a new method to evaluate the MME between the initial valence, v , and the final conduction, c , bands

$$\langle c | \vec{\epsilon} \cdot \vec{p} | v \rangle \equiv | P_{cv} |$$

where $\vec{\epsilon}$ and \vec{p} are, respectively, the photon polarization and electron momentum operator. Nu-

numerical values of $|P_{cv}|^2$ are given for different classes of semiconductors such as the direct gap materials ZnO , GaN , $ZnSe$ and CdS and also for indirect gap ones GsP and GaS . The method is based on the theoretical estimation of the direct one-photon as well as two-photon absorption coefficients, $\alpha_d^{(1)}, \alpha_d^{(2)}$. The expression of $\alpha_d^{(1)}$ contains the square of MME while that of $\alpha_d^{(2)}$ includes the square of the product of two MME. Therefore, the square of the MME required can be deduced directly by comparing the ratios of $\alpha_d^{(2)}/\alpha_d^{(1)}$ from both the experimental and theoretical results provided that the same states are involved in the two processes. This occurs when $\hbar\omega \simeq (\hbar\omega_1 + \hbar\omega_2) \geq E_g$, where $\hbar\omega$ and $(\hbar\omega_1 + \hbar\omega_2)$ are the photon energies in the one-photon and two-photon processes, respectively and E_g is the band gap. We have also provided a calculation of the indirect one-photon and two-photon absorption coefficients $\alpha_i^{(1)}, \alpha_i^{(2)}$ for the application to the cases of GaP and GaS .

2. FORMALISM

2.1 Calculation of $\alpha_d^{(1)}$

Direct one-photon transition rate can be obtained from first order perturbation theory as ¹¹ (according to the 2-band model of Fig.1a)

$$W_{cv}^{(1)}(\omega) \sim |P_{cv}|^2 (\hbar\omega - E_g)^{1/2} \quad (1)$$

The absorption coefficient is therefore $(= 2nW^{(1)}/cN)$

$$\alpha_d^{(1)}(\omega) = C_1 |P_{cv}|^2 (\hbar\omega - E_g)^{1/2} \quad (2)$$

where $C_1 = \frac{ne^2 A_0^2 \mu_{cv}^{3/2}}{\sqrt{2} \pi^2 \hbar^4 m_0^2 c^3 N}$ where the parameters have their standard notations ¹¹.

2.2 Calculation of $\alpha_d^{(2)}$

From second order perturbation theory one obtains for the two-photon transition rate ¹² (adopting a 3-band model of Fig.1b)

$$W_{cv}^{(2)}(\omega_1, \omega_2) \sim |P_{cn} P_{nw}|^2 \left| \frac{1}{(E_n - E_v - \hbar\omega_1)} + \frac{1}{(E_n - E_v - \hbar\omega_2)} \right|^2 \times (\hbar\omega_1 + \hbar\omega_2 - E_g)^{1/2} \quad (3)$$

where E_n is the intermediate band energy. However, for some materials P_{cn} and P_{nw} give nearly the same numerical values as P_{cv} . As a result, the coefficient $\alpha_d^{(2)}$ for equal photon energies ($\hbar\omega_1 = \hbar\omega_2 = \hbar\omega'$) can be obtained from Eq.(3) as

$$\alpha_d^{(2)}(\omega') = C_2 \frac{|P_{cv}|^4}{(E_n - E_v - \hbar\omega')^2} (2\hbar\omega' - E_g)^{1/2} \quad (4)$$

where

$$C_2 = \frac{\sqrt{2} n e^4 A_0^4 \mu_{cv}^{3/2}}{\pi^2 \hbar^4 m_0^4 c^3 N}$$

Therefore, the required square MME is given by dividing Eq.(4) to Eq.(2) as

$$|P_{cv}|^2 = \frac{1}{2} \left(\frac{m_0 c}{e A_0} \right)^2 (E_n - E_v - \hbar\omega')^2 \left(\frac{\hbar\omega - E_g}{2\hbar\omega' - E_g} \right)^{1/2} \frac{\alpha_d^{(2)}}{\alpha_d^{(1)}} \quad (5)$$

2.3 Calculation of $\alpha_i^{(1)}$

From second order perturbation theory, concerning the 3-band model (Fig.2a), we obtained for the phonon-assisted one-photon absorption coefficient ¹¹

$$\alpha_i^{(1)}(\omega, \Omega) = C_3 |Q_{cn} P_{nw}|^2 \left(\frac{\hbar\omega \mp \hbar\Omega - E_g}{E_n - E_v - \hbar\omega} \right)^2 \quad (6)$$

where

$$C_3 = \frac{n e^2 m_c^{3/2} m_v^{3/2} A_0^2}{2^6 \pi^4 \hbar^7 m_0^2 c^3 N}$$

$\hbar\Omega$ is the phonon energy and Q_{cn} is the electron-phonon matrix element. (\mp) due to emission or absorption of phonons.

2.4 Calculation of $\alpha_i^{(2)}$

The indirect two-photon absorption coefficient can be derived ¹³ from third order perturbation theory as (adopting the 4-band model of Fig.2b and taking equal photon energies)

$$\alpha_i^{(2)}(\omega', \Omega) = C_4 |Q_{cm} P_{mn} P_{mw}|^2 \left| \frac{(2\hbar\omega' \mp \hbar\Omega - E_g)}{(E_m - E_v - 2\hbar\omega')(E_n - E_v - \hbar\omega')} \right|^2 \quad (7)$$

where

$$C_4 = \frac{n e^4 A_0^4 m_c^{3/2} m_v^{3/2}}{2^5 \pi^4 \hbar^7 m_0^4 c^3 N}$$

Since the magnitude of the matrix elements P_{mn} , P_{mw} and P_{mv} have nearly the same value as P_{cv} , therefore the square of the MME can be obtained from Eqs.(6) and (7) as

$$|P_{cv}|^2 = 2 \left(\frac{m_0 c}{e A_0} \right)^2 \left| \frac{(E_m - E_v - 2\hbar\omega')(E_n - E_v - \hbar\omega')}{(E_n - E_v - \hbar\omega')} \right|^2 \times \left| \frac{(\hbar\omega \mp \hbar\Omega - E_g)}{(2\hbar\omega' \mp \hbar\Omega - E_g)} \right|^2 \frac{\alpha_i^{(2)}}{\alpha_i^{(1)}} \quad (8)$$

3. REVIEW OF KANE, KELDYSH, BRAUNSTEIN AND BASOV CALCULATIONS

We provide, in this section, some theoretical derivations of the MME which relate it to the excitation energies and to a certain band model as we have done in the previous section. For the allowed one-photon process, the first approximation given by Kane ⁷ by means of the $\vec{k} \cdot \vec{p}$ perturbation theory in which he relates the energy gap, E_g the spin-orbit splitting of the valence band, Δ_{so} , and the conduction band effective mass, m_c to $|P_{cv}|^2$. In his non-perturbative approach to the problem of multiphoton absorption process Keldysh ⁸ has provided a new approximated expression to the MME relating its value to the band parameters of the material.

For the two-photon process there are two approximations considered in the calculation of MME. The first one is given by Braunstein ⁹ considering a 3-band model like that of Fig.1b. Two MME have occurred in his expression of the allowed two-photon transition rate. These MME are related to the oscillator strengths f_{cv} , f_{mv} which couple the valence and the conduction bands to the intermediate band. After evaluating the oscillator strengths from the f sumrule and $\vec{k} \cdot \vec{p}$ approximation, the two MME take the forms given in Table 1. The second approximation is due to Basov ¹⁰ in which a 2-band model consisting of only the valence and the conduction bands is adopted. The intermediate state, in this case, could be a state of the same valence or conduction bands. As a result one has a product of two MME, an interband allowed MME of constant magnitude and an intraband forbidden MME of magnitude proportional to the wave vector \vec{k} . In Table 1 we summarize the different approximate expressions for the MME and the corresponding band model adopted for each process.

4. NUMERICAL RESULTS AND CONCLUSION

We have performed numerical calculations of the square of magnitude of MME in different classes of semiconductors such as *ZnO*, *ZnSe*, *GaN*, *CdS* and *GaP*, *GaS* whose band structures and physical parameters are well known. These samples have been chosen because they are representatives of different band structures and consequently of different transition processes. The values of $\alpha_d^{(1)}$, $\alpha_d^{(2)}$, $\alpha_i^{(1)}$ and $\alpha_i^{(2)}$ have been taken from the available experimental data. The results together with the corresponding values from Kane, Keldysh, Braunstein and Basov works are summarized in Table 2.

From Table 2 we show that the numerical values for the square of magnitude of MME have nearly the same order of magnitude as the values obtained using other theoretical approximations. It is of interest to remark that the present values of $|P_{cv}|^2$ agree fairly well with the values computed using the $\vec{k} \cdot \vec{p}$ perturbation approach ⁷. One could have used the theoretical values without much difference in the results.

In conclusion, we have introduced a new semi-empirical method for the calculation of the MME. In the previous theoretical estimations of the MME different approximations have been used

in order to obtain an analytical form of the MME. On the other hand, the present method is simply based on comparing the numerical values of the ratios $\alpha^{(2)}/\alpha^{(1)}$ calculated from perturbation theory and the corresponding experimental values for a number of semiconductors. The results agree with the different theoretical approximations.

Acknowledgments

The author would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

REFERENCES

1. A.F. Starace, Phys. Rev. **A3**, 1242 (1971).
2. I. Petroff and C.R. Viswanathan, Phys. Rev. **B4**, 799 (1971).
3. I.I. Gegusin and V.N. Datsyuk, Phys. Stat. Sol. (b) **118**, K121 (1983).
4. V. Fritzsche, Phys. Stat. Sol. (b) **148**, 395 (1988).
5. A.B. Chen, Phys. Rev. **B14**, 2384 (1976).
6. M.H. Weiler, Solid State Commun. **39**, 937 (1981).
7. E.O. Kane, J. Phys. Chem. Solids **112**, 82 (1956); **1**, 249 (1957).
8. L.V. Keldysh, Sov. Phys. JETP **18**, 253 (1964).
9. R. Braunstein, Phys. Rev. **125**, 475 (1962);
R. Braunstein and Ockman, Phys. Rev. **134**, A499 (1964).
10. N.G. Basov, A.Z. Grazyuk, I.G. Zubarev, V.A. Katulin and O.N. Krokhin, Sov. Phys. JETP **23**, 366 (1966).
11. F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions of Solids*, ed. R.A. Ballinger (Pergamon Press, Oxford, 1975).
12. A.R. Hassan, Il Nuovo Cimento **70B**, 21 (1970).
13. F. Bassani and A.R. Hassan, Il Nuovo Cimento **7B**, 313 (1972).
14. I.M. Catalano, A. Cingolani and M. Lepore, Solid State Commun. **55**, 155 (1985).
15. V.V. Arsenev, V.A. Dneproskii, D.N. Klysho and A.N. Penin, Sov. Phys. JETP **29**, 413 (1969).
16. J.C. Phillips, Solid State Phys. **18**, 56 (1966).
17. M.S. Bepalov, L.A. Kuleuskii, V.P. Makarov, A.M. Prokhorov and A.A. Tikhanov, Sov. Phys. JETP **28**, 77 (1969).
18. E. Kauev and A. Rabenau, Z. Naturforsch **120**, 942 (1957).
19. S.A. Abagyan and V.K. Subashiev, Sov. Phys. Solid State **6**, 2529 (1965).

TABLE CAPTIONS

Table 1 Different forms for the square of the MME obtained by means of different authors and their corresponding band models.

Table 2 Experimental values of $\alpha_d^{(2)}/\alpha_d^{(1)}$ (for ZnSe, ZnO, GaN and CdS) or $\alpha_i^{(2)}/\alpha_i^{(1)}$ (for GaP and GaS) and the numerical values of $|P_{cv}|^2$ (erg gm) from present work and the other calculations ⁷⁻¹⁰.

Table 1

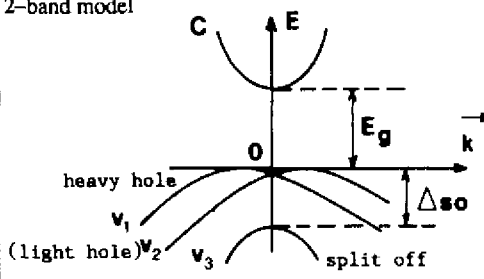
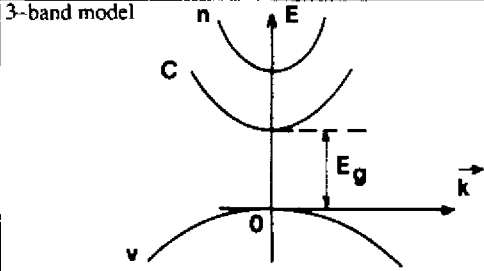
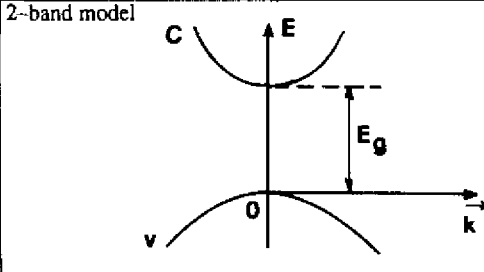
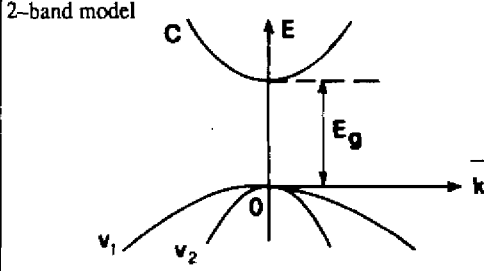
| Source | Square of MME | Band Model |
|---|---|--|
| Kane ⁷ allowed transitions | $ P_{cv} ^2 = \frac{3}{2} \left(\frac{m_0^2}{m_c} - m_0 \right) \times$ $\frac{E_g(E_g + \Delta_{s0})}{(3E_g + \Delta_{s0})}$ | 2-band model  |
| Braunstein ⁹ allowed- allowed transitions | $ P_{cn} ^2 = \frac{1}{2} m_0 \hbar \omega_{cn} \left(\frac{m_0}{m_c} - 1 \right)$ $ P_{nv} ^2 = \frac{1}{4} m_0 \hbar \omega_{nv} \left(\frac{m_0}{m_{cv}} \right)$ | 3-band model  |
| Keldysh ⁸ allowed transitions | $ P_{cv} ^2 = 3 \frac{m_0^2 E_g}{m_{cv}}$ | 2-band model  |
| Basov ¹⁰ allowed forbidden transitions | $ P_{cn} P_{nv} ^2 = P_{cv} ^2 \times$ $\hbar^2 (\vec{\epsilon} \cdot \vec{k})^2$ | 2-band model  |

Table 2

| Crystal | $\alpha^{(2)}/\alpha^{(1)}$ exp. | $ P_{cv} ^2$ present work | $ P_{cv} ^2$ Kane | $ P_{cv} ^2$ Braunstein | $ P_{cv} ^2$ Keldysh | $ P_{cv} ^2$ Basov |
|---------|-------------------------------------|------------------------------|------------------------|----------------------------|-------------------------|------------------------|
| ZnSe | $0.72 \times 10^{-5a,b}$ | 3.56×10^{-38} | 2.28×10^{-38} | 1.52×10^{-38} | 0.97×10^{-38} | 0.98×10^{-38} |
| ZnO | $0.73 \times 10^{-5a,c}$ | 3.23×10^{-38} | 2.58×10^{-38} | 1.81×10^{-38} | 1.21×10^{-38} | 0.64×10^{-38} |
| GaN | $0.43 \times 10^{-5a,d}$ | 3.12×10^{-38} | 3.9×10^{-38} | 2.6×10^{-38} | 1.81×10^{-38} | 1.52×10^{-38} |
| CdS | $0.21 \times 10^{-5a,e}$ | 2.92×10^{-38} | 0.87×10^{-38} | 1.43×10^{-38} | 0.95×10^{-38} | 0.73×10^{-38} |
| GaP | $0.41 \times 10^{-5f,a}$ | 2.68×10^{-38} | 0.22×10^{-38} | 1.42×10^{-38} | 0.94×10^{-38} | 0.34×10^{-38} |
| GaS | $0.56 \times 10^{-5a,c}$ | 3.32×10^{-39} | 3.9×10^{-39} | 2.53×10^{-39} | 1.86×10^{-39} | 1.66×10^{-39} |

^a Ref.14, ^b Ref.15, ^c Ref.16, ^d Ref.18, ^e Ref.17, ^f Ref.19

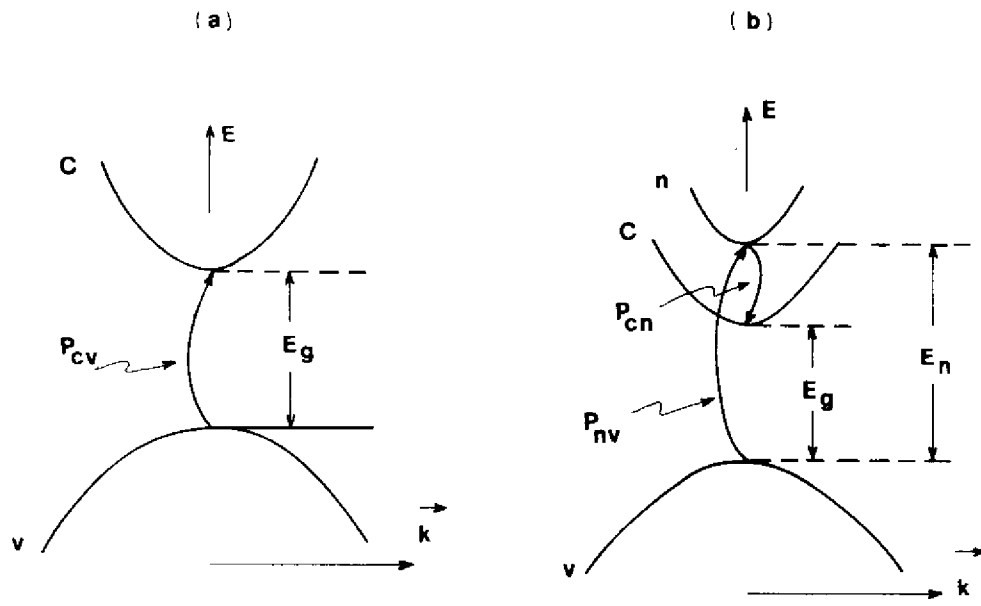


Fig.1 Schematic diagrams of a 2-band (a) and 3-band (b) models used for the calculation of the direct one-photon and two-photon absorption coefficients. The MME are indicated by the arrows.

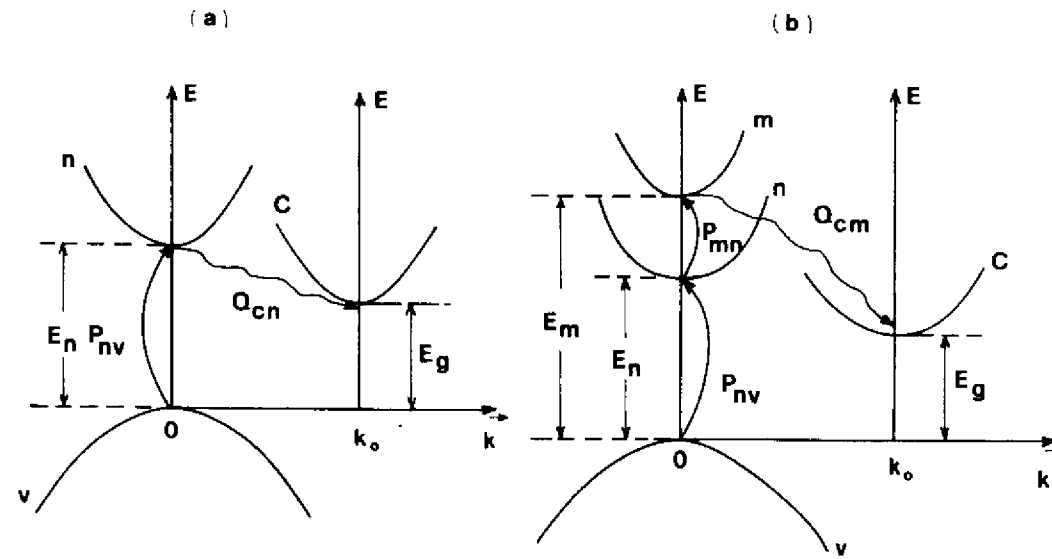


Fig.2 Schematic diagrams of the 3-band (a) and 4-band (b) models needed for the calculation of the indirect one-photon and two-photon absorption coefficients. The MME and the electron-phonon matrix elements are indicated by arrows.