

GENERAL EXPRESSION FOR OPTICAL TRANSITION PROBABILITIES WITHIN THE ENVELOPE-FUNCTION APPROXIMATION

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A general approach to the calculation of the momentum matrix elements within the envelope function approximation is presented. The contribution of anisotropy is shown for the first time to contribute to normal incidence absorption in *p*-type quantum wells. The present model also unifies the description of optical absorption in *n*- and *p*-type quantum wells.

I. Introduction

The possibility of normal-incidence absorption in *p*-type quantum wells was shown to be possible after Chang and James [1] (CJ) derived an expression for the momentum matrix elements for intrasubband transitions in *p*-type quantum wells (QW) on the basis of the envelope-function approximation (EFA). This expression is extended here to the case of transitions between states that penetrate strongly into the barrier and that involve strong conduction-valence band mixing, which are important for many small band gap and type-II superlattices. Finally, a very general expression for momentum matrix elements within the *k*·*p* theory is derived and then applied to obtain expressions for the momentum matrix elements for quantum wells.

In Section II, following the approach of CJ, the expression for momentum matrix elements is derived and nontrivially extended to the case of wave function penetration into the barrier. Section III shows that this expression can be derived from the second order *k*·*p* Hamiltonian itself.

II. EFA Theory of Momentum Matrix Elements

In the EFA, the total wave function for subband *N* as a function of parallel wave vector *k*_{||} can be written as a sum of the products of transformed Kohn-Luttinger wave functions [2] $|\mu\mathbf{k}\rangle$ and the corresponding envelope function amplitudes $\bar{F}_\mu(N\mathbf{k}_{||}, \mathbf{k}_z)$ as

$$|N, \mathbf{k}_{||}\rangle = \sum_{\mu, \mathbf{k}_z}^{\text{set A}} \bar{F}_\mu(N\mathbf{k}_{||}, \mathbf{k}_z) |\mu\mathbf{k}\rangle, \quad (1)$$

where the sum proceeds over the near-set of states A, in the Löwdin's sense [3]. The transformed Kohn-Luttinger wave function is given by [4]

$$\langle \mathbf{r} | \mu\mathbf{k} \rangle = e^{i\mathbf{k}\cdot\mathbf{r}} \left[u_\mu^0(\mathbf{r}) - \left(\frac{\hbar\mathbf{k}}{m_0} \right) \cdot \sum_{\gamma}^B \frac{\mathbf{P}_{\gamma\mu}}{E_\gamma - E_\mu} u_\gamma^0(\mathbf{r}) + \dots \right], \quad (2)$$

in terms of the Bloch wave functions $u_\mu^0(\mathbf{r})$ at the center of the Brillouin zone, where set B includes far-removed bands. For quantum wells, vector *k* in each

part of the structure (well or barrier) is given by $\mathbf{k} = \mathbf{k}_{\parallel} + k_z \hat{z}$, where k_z are the solutions of the $\mathbf{k} \cdot \mathbf{p}$ secular equation $|H(\mathbf{k}_{\parallel}, k_z) - E| = 0$, and H is the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian of order K . There are $2K$ solutions for coefficients $k_z(\mathbf{k}_{\parallel}, E)$, which are wave vector- and energy-dependent and, in general, complex [5]. A distinguishing feature of the present derivation is that coefficients $k_z(\mathbf{k}_{\parallel}, E)$ are treated as complex, which is the usual situation in the barrier material and for $\mathbf{k}_{\parallel} \neq 0$ in the well material.

The momentum matrix element between two states $|N\mathbf{k}_{\parallel}\rangle$ and $|M\mathbf{k}_{\parallel}\rangle$ is given by

$$\langle N\mathbf{k}_{\parallel} \left| \frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{p} \right| M\mathbf{k}_{\parallel} \rangle = \sum_{\nu, \nu'} \sum_{k_z, k'_z} \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, k_z)^* \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, k'_z) \langle \nu \mathbf{k} \left| \frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{p} \right| \nu' \mathbf{k}' \rangle, \quad (3)$$

where $\hat{\epsilon}$ gives the polarization of the incident light. Owing to the periodicity in the plane perpendicular to the growth direction and to the smallness of the photon momentum, the parallel wave vectors for the initial and final states are the same. As a result, k_z and k'_z are distinct because, in general, as the result of photon absorption, they refer to states at different energies, $E_N(\mathbf{k}_{\parallel}) \neq E_M(\mathbf{k}_{\parallel})$, that is, $\{k_z(\mathbf{k}_{\parallel}, E_N)\} \neq \{k_z(\mathbf{k}_{\parallel}, E_M)\}$, and because momentum in the growth direction is not conserved. Therefore, $\mathbf{k} \neq \mathbf{k}'$.

Substituting Eq. (2) into Eq. (3), the momentum matrix element becomes

$$\begin{aligned} \langle N\mathbf{k}_{\parallel} \left| \frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{p} \right| M\mathbf{k}_{\parallel} \rangle &= \left(\frac{\hbar^2}{m_0} \right) \hat{\epsilon} \cdot \sum_{\nu\nu'} \int dz \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z)^* P_{\nu\nu'}(\mathbf{k}_{\parallel}, z) \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) + \\ &+ \sum_i \epsilon_i \sum_{\nu\nu'} \int dz \left[-i \frac{d}{dz} \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z) \right]^* D_{\nu\nu'}^{zi}(z) \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) + \\ &+ \sum_i \epsilon_i \sum_{\nu\nu'} \int dz \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z)^* D_{\nu\nu'}^{iz}(z) \left[-i \frac{d}{dz} \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) \right], \end{aligned} \quad (4)$$

where D are the coefficients of the second-order terms in the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian [4]. Unless the envelope functions vanish at the well boundaries, the second and the third integrals above are not equal and, because $D_{\nu\nu'}^{iz} \neq D_{\nu\nu'}^{zi}$, the last two integrals cannot be simply combined. However, the second and third integrals in Eq. (4) can be done by parts and the two results added and then divided by two, yielding

$$\begin{aligned} \langle N\mathbf{k}_{\parallel} \left| \frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{p} \right| M\mathbf{k}_{\parallel} \rangle &= \left(\frac{\hbar^2}{m_0} \right) \hat{\epsilon} \cdot \sum_{\nu\nu'} \left\{ \int dz \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z)^* P_{\nu\nu'}(\mathbf{k}_{\parallel}, z) \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) + \right. \\ &+ \frac{1}{2} \int dz \left[-i \frac{d}{dz} \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z) \right]^* Q_{\nu\nu'}(\mathbf{k}_{\parallel}, z) \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) + \\ &\left. + \frac{1}{2} \int dz \bar{F}_{\nu}(N\mathbf{k}_{\parallel}, z)^* Q_{\nu\nu'}(\mathbf{k}_{\parallel}, z) \left[-i \frac{d}{dz} \bar{F}_{\nu'}(M\mathbf{k}_{\parallel}, z) \right] \right\}. \end{aligned} \quad (5)$$

in terms of band parameters P and Q defined in Ref. [1] for the 4×4 EFA model. Eq. (5) differs from the corresponding Eq. (A5) of CJ by the presence of two, and not one, terms multiplying quantity Q . Matrices $Q_{\nu\nu'}$ and $P_{\nu\nu'}$ for the 8×8 model are listed in another publication [6].

Note that for the 4×4 case treated by CJ, our respective results in [6] are different. In terms of CJ parameters A_1, A_2, B, C , the present results are as follows

$$\begin{array}{cccc}
 \hat{\epsilon} \cdot \mathbf{P} & \hat{\epsilon} \parallel \hat{x} & \hat{\epsilon} \parallel \hat{y} & \hat{\epsilon} \parallel \hat{z} \\
 A_1 & -\gamma_1 q_x & -\gamma_1 q_y & 0 \\
 A_2 & -\gamma_2 q_x & -\gamma_2 q_y & 0 \\
 B & 0 & 0 & \sqrt{3}\gamma_3(iq_x + q_y) \\
 C & -\sqrt{3}(\gamma_2 q_x - i\gamma_3 q_y) & \sqrt{3}(i\gamma_3 q_x + \gamma_2 q_y) & 0
 \end{array}$$

and

$$\begin{array}{cccc}
 \hat{\epsilon} \cdot \hat{\mathbf{Q}} & \hat{\epsilon} \parallel \hat{x} & \hat{\epsilon} \parallel \hat{y} & \hat{\epsilon} \parallel \hat{z} \\
 A_1 & 0 & 0 & -\gamma_1 \\
 A_2 & 0 & 0 & 2\gamma_2 \\
 B & i\sqrt{3}\gamma_3 & \sqrt{3}\gamma_3 & 0 \\
 C & 0 & 0 & 0
 \end{array}$$

Neglecting sign differences due to the different choices of the phase of the basis functions, the A_2 coefficient for $\hat{\epsilon} \cdot \hat{\mathbf{Q}}$ and $\hat{\epsilon} \parallel \hat{z}$ is $2\gamma_2$ and not γ_2 . Also, B and C in Table I of CJ are too large by a factor of 2.

In order to illustrate the difference between the present expression, Eq. (5), and Eq. (A5) of CJ, a numerical example is provided in Table. The differences for the selected example can be as much as 10%. Moreover, Eq. (A5) is seen to violate the principle of microscopic reversibility by as much as 20%.

Table. Comparison of the matrix elements using the formalism of equation (5) in the text and Eq.(A5) of Chang and James [1] for important interband transitions for the case of a 50Å GaAs/Al_{0.5}Ga_{0.5}As, $x = 0.30$, quantum well. The calculation uses a 60:40 conduction-valence band offset ratio. Our 8×8 EFA model yields four bands at the center of the Brillouin zone (actually, $k_x = 10^{-7}$ inverse Bohr radii): $HH1 = -23.06$ meV, $LH1 = -51.71$ meV, $HH2 = -88.45$ meV, and $LH2 = -148.24$ meV. The matrix elements are given in the units of Rydberg.

Matrix Element	Present Formalism, Eq.(5)	Eq. A5 of Chang and James
$\frac{2}{m_0} P_{x,y}(HH1 \rightarrow LH2) ^2$	$1.71 \cdot 10^{-2}$	$1.64 \cdot 10^{-2}$
$\frac{2}{m_0} P_{x,y}(LH2 \rightarrow HH1) ^2$	$1.71 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$
$\frac{2}{m_0} P_x(HH1 \rightarrow HH2) ^2$	$2.76 \cdot 10^{-2}$	$3.00 \cdot 10^{-2}$
$\frac{2}{m_0} P_x(HH2 \rightarrow HH1) ^2$	$2.76 \cdot 10^{-2}$	$2.56 \cdot 10^{-2}$
$\frac{2}{m_0} P_{x,y}(LH1 \rightarrow HH2) ^2$	$2.20 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$
$\frac{2}{m_0} P_{x,y}(HH2 \rightarrow LH1) ^2$	$2.20 \cdot 10^{-2}$	$2.42 \cdot 10^{-2}$
$\frac{2}{m_0} P_x(LH1 \rightarrow LH2) ^2$	$6.68 \cdot 10^{-2}$	$6.36 \cdot 10^{-2}$
$\frac{2}{m_0} P_x(LH2 \rightarrow LH1) ^2$	$6.68 \cdot 10^{-2}$	$7.42 \cdot 10^{-2}$

Lastly, it is possible to unify the description of light absorption in p - and n -type quantum wells. Since \mathbf{P} and \mathbf{Q} ultimately derive from the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, Eq. (5) can be rewritten in the following transparent fashion:

$$\begin{aligned}
 \langle Nk_{\parallel} \left| \frac{\hbar}{m} \hat{\epsilon} \cdot \mathbf{P} \right| M\mathbf{k}_{\parallel} \rangle &= \hat{\epsilon} \cdot \sum_{\mu\nu} \langle F_{\mu}(Nk_{\parallel}, z) \left| \frac{\partial^2 \hat{H}_{\mu\nu}}{\partial \mathbf{k} \partial \mathbf{k}} \cdot \mathbf{k}_{\parallel} + \frac{\hbar}{m} \mathbf{P}_{\mu\nu} + \right. \\
 &\quad \left. + \frac{1}{2} \left[\left(\frac{1}{i} \frac{\vec{d}}{dz} \right)^* \frac{\partial^2 \hat{H}_{\mu\nu}}{\partial \mathbf{k} \partial k_z} + \frac{\partial^2 \hat{H}_{\mu\nu}}{\partial \mathbf{k} \partial k_z} \left(\frac{1}{i} \frac{\vec{d}}{dz} \right) \right] \right| F_{\nu}(M\mathbf{k}_{\parallel}, z) \rangle \quad (6)
 \end{aligned}$$

where the arrows indicate the direction in which the derivatives should be taken. The second term is the dominant term in valence-to-conduction band transitions. In the single band case ($\mu = \nu = 1$), the first two terms lead to an overlap integral between orthogonal final and initial envelope functions and, thus, yield zero. The last term is proportional to the inverse effective-mass tensor m_{iz}^{-1} , which can be exploited with a proper orientation of the incident light with respect to the crystal axes. For valence intersubband transitions in the 8×8 model, in normal incidence ($\epsilon_z = 0$) and $k_{\parallel} = 0$, the last term couples light and heavy-hole components of the initial and final states. This contribution is made possible by the presence of mixed $k_x k_z$ and $k_y k_z$ terms in the Hamiltonian, which points to the importance of anisotropy in optical transitions. The second term is important only if the initial and final hole states have a significant admixture of conduction-band states. The first term couples same-parity components of the initial and final states away from the center of the Brillouin zone, which is important for heavier-doped MQWs. The above argument unifies the description of optical absorption in n - and p -type heterostructures and points to the dominant effect of anisotropy in both intervalence and interconduction subband transitions.

III. General Derivation of the EFA Momentum Matrix Element

Here a conceptually simpler way of deriving the expressions for momentum matrix elements within the envelope function approximation will be derived. The final expression can be used to easily obtain the momentum matrix elements for quantum wires and dots.

In a bulk semiconductor, the momentum matrix element between states $|Nk\rangle$ and $|Mk\rangle$ can be written in terms of the derivative of the $k \cdot p$ Hamiltonian as

$$\frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{P}_{NM} = \sum_{\nu\nu'}^{all} F_{\nu}(Nk)^* \left[\hat{\epsilon} \cdot \frac{\partial H_{\nu\nu'}(\mathbf{k})}{\partial \mathbf{k}} \right] F_{\nu'}(Mk), \quad (7)$$

which is simply an application of the Hellman-Feynman theorem [7-9]. In principle, the sum in Eq. (7) proceeds over all the bands at a band extremum, which is why wave function amplitudes F have no bar over them. In order for the wave function to be expressible in terms of Kohn-Luttinger functions for set A only, as in Eq.(1), one must perform a unitary transformation of the basis [10] which eliminates the coupling between sets A and B in the infinite dimensional $k \cdot p$ Hamiltonian H . After performing the indicated transformation [6], it is nontrivial to show that the momentum matrix element up to terms of order k is given by

$$\langle Nk \left| \frac{\hbar}{m_0} \hat{\epsilon} \cdot \mathbf{p} \right| Mk \rangle = \sum_{\mu\mu'}^A \bar{F}_{\mu}(Nk)^* \hat{\epsilon} \cdot \frac{\partial \bar{H}_{\mu\mu'}(\mathbf{k})}{\partial \mathbf{k}} \bar{F}_{\mu'}(Mk). \quad (8)$$

where \bar{H} denotes the transformed $k \cdot p$ Hamiltonian.

In the case of a quantum well, the wave functions are eigenstates of the parallel momentum, k_{\parallel} , which is conserved in an optical transition. In analogy to Eq. (7), for a QW, the momentum matrix element becomes

$$\sum_{\nu\nu'}^{all} \int dz F_{\nu}(Nk_{\parallel}, z)^* \left[\hat{\epsilon} \cdot \frac{\partial H_{\nu\nu'}(\mathbf{k})}{\partial \mathbf{k}} \right]_{k_z = -i \frac{\partial}{\partial z}} F_{\nu'}(Nk_{\parallel}, z). \quad (9)$$

Employing the unitary transformation of the basis functions, one finally arrives at the momentum operator of the form

$$\left(\frac{\hbar^2}{m_0}\right) \hat{\epsilon} \cdot \mathbf{P} + \left(\frac{\hbar^2}{m_0}\right) \hat{\epsilon} \cdot \frac{1}{2} \left[\mathbf{Q} \left(\frac{1}{i} \frac{\vec{d}}{dz} \right) + \left(\frac{1}{i} \frac{\vec{d}}{dz} \right)^* \mathbf{Q} \right], \quad (10)$$

which agrees with Eq.(5) and validates the newly derived Eq.(8) as well as gives credence to the revision of the entries in CJ's table of results. Analogously, this technique can be applied to quantum wires and dots. The resulting expressions add new insights into the selection rules that are operative in those structures. The complete treatment is the subject of another paper [6].

The expression of Chang and James for the EFA momentum matrix elements for intersubband transitions in *p*-type quantum wells was extended to the case of envelope function penetration into the barrier in a way that satisfies the principle of microscopic reversibility. Anisotropy was shown to be important for valence intersubband transitions.

Another approach to the problem of calculating momentum matrix elements was then developed by showing that to order *k* these matrix elements can be obtained by differentiating the *transformed* EFA Hamiltonian with respect to momentum. To my knowledge, this result has not been proved before or applied to the problem of calculating the momentum matrix elements in band-gap engineered structures.

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1. Yia-Chung Chang and R.B.James, *Phys. Rev.* **B39**, 12672 (1989).
 2. J.M.Luttinger and W.Kohn, *Phys. Rev.* **97**, 869 (1955).
 3. P.Löwdin, *J.Chem. Phys.* **19**, 1396 (1961).
 4. M.Altarelli, in *Heterojunctions and Semiconductor Superlattices*, Eds. G.Allan, et al., Springer-Verlag, Berlin, 1986, pp.12-37.
 5. D.L.Smith and C.Mailhot, *Phys. Rev.* **B33**, 8345 (1986).
 6. F.Szmulowicz, *Phys. Rev. B* (1994), to be published.
 7. R.B.Feynman, *Phys. Rev.* **56**, 340 (1939).
 8. H.Hellman, *Einführung in die Quantenchemie*, Deuticke, Leipzig, 1937.
 9. S.T.Epstein, in *Force Concepts in Chemistry*, Ed. R.M.Deb, Van Nostrand Reinhold, New York, 1981, pp.1-38; *Am. J. Phys.* **22**, 613 (1954).
 10. G.L.Bir and G.E.Pikus, *Symmetry and Strain-Induced Effects in Semiconductors*, Wiley, New York, 1974.