General expression for optical transition probabilities in the envelope-function approximation

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A general approach to the calculation of the momentum matrix elements in the envelope function approximation is presented. The contribution of the anisotropy is shown for the first time to contribute to the normal incidence absorption in the p-type quantum wells. The present model also unifies the description of optical absorption in the n- and p-type quantum wells. © *1994 American Institute of Physics.*

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 the p-type quantum wells (QW) on the basis of the envelope-function approximation (EFA). This expression is extended here to the case of the transitions between states which penetrate strongly into the barrier and which involve strong conduction-valence band mixing. These transitions are important for many small band gap and type-II superlattices. Finally, a very general expression for momentum matrix elements in the $\mathbf{k}\cdot\mathbf{p}$ theory is derived and then applied to obtain expressions for the momentum matrix elements for quantum wells.

In Sec. II, following the approach of CJ, we derive the expression for the momentum matrix elements and nontrivially extend to the case of the wave function penetration into the barrier. In Sec. III we show that this expression can be derived from the second-order $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian itself.

II. EFA THEORY OF MOMENTUM MATRIX ELEMENTS

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

$$|N,\mathbf{k}_\parallel\rangle=\sum_{\mu,k_z}^{\text{setA}}\tilde{F}_\mu(N\mathbf{k}_\parallel,\mathbf{k}_z)|\mu\mathbf{k}\rangle, \tag{1}$$

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

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

in terms of the Bloch wave functions $u_\mu^0(\mathbf{r})$ at the center of the Brillouin zone, where the set B includes the far-removed bands. For the quantum wells, the vector $\mathbf{k}$ in each part of the structure (the well or the barrier) is given by $\mathbf{k}=\mathbf{k}_\parallel+k_z\hat{z}$, where k_z are the solutions of the $\mathbf{k}\cdot\mathbf{p}$ the 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 the coefficient $k_z(\mathbf{k}_\parallel,E)$, which are wave vector- and energy-dependent and, in general, complex.[5] A distinguishing feature of the present derivation is that the coefficients $k_z(\mathbf{k}_\parallel,E)$ are treated as complex coefficients, 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

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

where $\hat{\epsilon}$ is the polarization of the incident light. Because of 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' differ from each other because, in general as a result of photon absorption, they refer to states at different energies, $E_N(\mathbf{k}_\parallel)\neq E_M(\mathbf{k}_\parallel)$, i.e., $\{\mathbf{k}_z(k_\parallel,E_N)\}\neq\{k_z(\mathbf{k}_\parallel,E_M)\}$, and because the momentum in the growth direction is not conserved. Therefore $\mathbf{k}\neq\mathbf{k}'$.

Substituting Eq. (2) into Eq. (3), we can write the momentum matrix element in the form

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

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 third integrals given above *are not equal* and, because $D^{iz}_{\nu\nu'}\neq D^{zi}_{\nu\nu'}$, the last two integrals cannot be simply combined. However, the second and third integrals in Eq. (4) can be integrated by parts and the two results added and then divided by two, yielding

$$\left\langle N\mathbf{k}_{\|}\left|\frac{\hbar}{m_0}\,\hat{\epsilon}\cdot\mathbf{p}\right|M\mathbf{k}_{\|}\right\rangle=\left(\frac{\hbar^2}{m_0}\right)\hat{\epsilon}\cdot\sum_{\nu\nu'}\left\{\int dz\bar{F}_{\nu}(N\mathbf{k}_{\|},z)^{*}\mathbf{P}_{\nu\nu'}(\mathbf{k}_{\|},z)\bar{F}_{\nu'}(M\mathbf{k}_{\|},z)\right.$$

$$+\frac{1}{2}\int dz\left[-i-\frac{d}{dz}\,\bar{F}_{\nu}(N\mathbf{k}_{\|},z)\right]^{*}Q_{\nu\nu'}(\mathbf{k}_{\|},z)\bar{F}_{\nu}(M\mathbf{k}_{\nu},z)$$

$$\left.+\frac{1}{2}\int dz\bar{F}_{\nu}(N\mathbf{k}_{\|},,z)^{*}\mathbf{Q}_{\nu\nu'}(\mathbf{k}_{\|},z)\left[-i\,\frac{d}{dz}\,\bar{F}_{\nu'}(M\mathbf{k}_{\|},z)\right]\right\}. \quad (5)$$

In terms of the 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 because of the presence of two, rather than one, terms multiplying the quantity **Q**. The matrices $\mathbf{Q}_{\nu\nu'}$ and $\mathbf{P}_{\nu\nu}$ for the 8×8 model are listed in another publication.[6]

Note that for the 4×4 case treated as CJ, our respective results in Ref. 6 are different. In terms of the CJ parameters A_1, A_2, B, and C, these results are as follows:

$\hat{\epsilon}\cdot\mathbf{P}$	$\hat{\epsilon}\|\hat{\mathbf{x}}$	$\hat{\epsilon}\|\hat{\mathbf{y}}$	$\hat{\epsilon}\|\hat{\mathbf{z}}$
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

and

$\hat{\epsilon}\cdot\hat{\mathbf{Q}}$	$\hat{\epsilon}\|\hat{\mathbf{x}}$	$\hat{\epsilon}\|\hat{\mathbf{y}}$	$\hat{\epsilon}\|\hat{\mathbf{z}}$
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.

Ignoring the sign differences due to the different choices of the phase of the basis functions, the A_2 coefficient for $\hat{\epsilon}\cdot\mathbf{Q}$ and $\hat{\epsilon}\|\hat{\mathbf{z}}$ is $2\gamma_2$, rather than γ_2. In addition, B and C in Table I of CJ are larger 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 given in Table I. The differences for the selected example can be as high as 10%. Moreover, Eq. (A5) violates the principle of microscopic reversibility by as much as 20%. Lastly, it is possible to unify the description of light absorption p- and n-type quantum wells. Since **P** and **Q** are ultimately derived from the **k·p** Hamiltonian, Eq. (5) can be rewritten in transparent fashion

TABLE I. 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 50 Å $GaAs/Al_xGa_{1-x}As$, $x=0.30$, 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
$\frac{2}{m_o}\lvert P_{x,y}(HH1 \rightarrow LH2)\rvert^2$	$1.71 \cdot 10^{-2}$	$1.64 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_{x,y}(LH2 \rightarrow HH1)\rvert^2$	$1.71 \cdot 10^{-2}$	$1.79 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_z(HH1 \rightarrow HH2)\rvert^2$	$2.76 \cdot 10^{-2}$	$3.00 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_z(HH2 \rightarrow HH1)\rvert^2$	$2.76 \cdot 10^{-2}$	$2.56 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_{x,y}(LH1 \rightarrow HH2)\rvert^2$	$2.20 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_{x,y}(HH2 \rightarrow LH1)\rvert^2$	$2.20 \cdot 10^{-2}$	$2.42 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_z(LH1 \rightarrow LH2)\rvert^2$	$6.68 \cdot 10^{-2}$	$6.36 \cdot 10^{-2}$
$\frac{2}{m_o}\lvert P_z(LH2 \rightarrow LH1)\rvert^2$	$6.68 \cdot 10^{-2}$	$7.42 \cdot 10^{-2}$

$$\left\langle N\mathbf{k}_{\parallel}\left|\frac{\hbar}{m}\hat{\varepsilon}\cdot\mathbf{p}\right|M\mathbf{k}_{\parallel}\right\rangle=\hat{\varepsilon}\cdot\sum_{\mu\nu}\left\langle F_{\mu}(N\mathbf{k}_{\parallel},z)\left|\frac{\partial^2\bar{H}_{\mu\nu}}{\partial\mathbf{k}\partial\mathbf{k}}\cdot\mathbf{k}_{\parallel}+\frac{\hbar}{m}\mathbf{p}_{\mu\nu}\right.\right.$$
$$\left.\left.+\frac{1}{2}\left[\left(\frac{1}{i}\frac{\bar{d}}{dz}\right)^{*}\frac{\partial^2\bar{H}_{\mu\nu}}{\partial\mathbf{k}\partial k_z}+\frac{\partial^2\bar{H}_{\mu\nu}}{\partial\mathbf{k}\partial k_z}\left(\frac{1}{i}\frac{\bar{d}}{dz}\right)\right]\right|F\nu(M\mathbf{k}_{\parallel},z)\right\rangle \qquad (6)$$

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 the orthogonal final function and the initial envelope function, 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 the normal incidence ($\epsilon_z=0$) and $\mathbf{k}_{\parallel}=0$, the last term couples light- and heavy-hole components of the initial and final states. This contribution is possible cause of the presence of mixed k_xk_z and k_yk_z terms in the Hamiltonian, which points to the importance of anisotropy in the optical transitions. The second term is important only if the initial and final hole states haves 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 the 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 we will show a conceptually simpler way of deriving the expressions for momentum matrix elements in the envelop function approximation. The final expression can be used to easily obtain the momentum matrix elements for quantum wires and quantum dots.

In a bulk semiconductor the momentum matrix element between the states $|N\mathbf{k}\rangle$ and $|M\mathbf{k}\rangle$ can be written in terms of the derivative of the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian as follows:

$$\frac{\hbar}{m_0}\,\hat{\epsilon}\cdot\mathbf{P}_{NM}=\sum_{\nu\nu'}^{\text{all}} F_\nu(N\mathbf{k})^*\left[\hat{\epsilon}\cdot\frac{\partial H_{\nu\nu'}(\mathbf{k})}{\mathbf{K}}\right]F_{\nu'}(M\mathbf{k}). \tag{7}$$

This 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 the wave function amplitudes F have no bar over them. In order to express the wave function in terms of Kohn–Luttinger functions for set A only, as in Eq. (1), we must perform a unitary transformation of the basis,[10] which eliminates the coupling between sets A and B in the infinite-dimensional $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian H. After performing the indicated transformation,[6] it is easy to show that the momentum matrix element up to terms of order $\mathbf{k}$ is given by

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

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

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

$$\sum_{\nu\nu'}^{\text{all}}\int dz F_\nu(N\mathbf{k}_\parallel,z)^*\left[\hat{\epsilon}\cdot\frac{\partial H_{\nu\nu'}(\mathbf{k})}{\partial\mathbf{k}}\right]_{k_x=-(d/dx)} f_{\nu'}(n\mathbf{k}_\parallel,z). \tag{9}$$

Employing the unitary transformation of the basis functions, we finally obtain a momentum operator of the form

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

which agrees with Eq. (5), validates the newly derived Eq. (8), and gives credence to the revision of the entries in the CJ's table of results. Analogously, this technique can be applied to quantum wires and quantum dots. The expressions thus obtained give 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 the best of 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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