The evaluation of the matrix element for interband optical transitions in quantum wells using envelope functions

1993 J. Phys.: Condens. Matter 5 4091

(http://iopscience.iop.org/0953-8984/5/24/010)

J. Phys.: Condens. Matter 5 (1993) 4091–4098. Printed in the UK

The evaluation of the matrix element for interband optical transitions in quantum wells using envelope functions

M G Burt

BT Laboratories, Martlesham Heath, Ipswich IP5 7RE, UK

Received 13 January 1993

Abstract. The expression for the matrix element of position for an interband transition in a wide deep quantum well is derived using the envelope function expansion. It is found that the matrix element is not determined by the intra-atomic-like matrix element evaluated using band-edge Bloch functions, the result one might be led to expect either on intuitive grounds or as the result of a supposedly approximate evaluation in which only the dominant term in the envelope function expansion of each wave function is used. To obtain the correct expression, terms in the envelope function expansion that become vanishingly small in the limit of wide wells must be retained. Usually the interband matrix element is comparable with that for allowed intersubband transitions. Some implications for the DC Stark effect for quantum wells and non-linear refraction in quantum dot structures are mentioned.

1. Introduction

Recently, there has been increasing interest in optical intersubband processes in quantum wells [1, 2] such as occur in infrared detection [3], second harmonic generation [4, 5] and non-linear refraction and absorption [6–8]. The interest in these processes is due, in part, to the large dipole matrix elements [1] for these transitions. In analysing the effect of interband transitions compared with intersubband transitions on non-linear refraction and absorption [6, 7], it is necessary to know the corresponding dipole matrix element for interband transitions. It is easy to suppose that the dipole matrix elements for the interband transitions, which superficially appear to be intra-atomic in character, to be of a similar size to atomic dipole matrix elements and, in general, much smaller than the dipole matrix elements for allowed intersubband transitions in quantum wells. The purpose of this paper is to investigate this assumption by evaluating the dipole matrix element for an interband transition in a deep wide quantum well. Contrary to the above supposition, we find that the dipole matrix element for an interband transition can be much larger than that for allowed intersubband transitions.

In the next section the two-band electronic structure approximation [9] used in the calculation of matrix elements for interband transitions is described with particular reference to the envelope function expansion [10–12] of the wave function in the quantum well. In section 3 the dipole and momentum matrix elements for the transition between band-edge states is evaluated and shown to be in accord with the textbook theorem [13] relating such matrix elements. The two-band approximation of the envelope function expansion of each wavefunction has been used merely for clarity in sections 2 and 3. It is shown in appendix A that, in the limit of a wide well, the inclusion of the other bands does not alter the results. Also, to avoid inessential detail, the mathematical arguments are presented for

0953-8984/93/244091+08$07.50

the one-dimensional case throughout. Section 4 summarizes the results with an illustrative numerical example, and discusses some of the implications.

2. The model

In the two-band approximation [9] to the envelope function expansion [10–12], the wave function, Ψ, is given by

$$\Psi(x) = F_c(x)U_c(x) + F_v(x)U_v(x) \tag{1}$$

where U_c and U_v are the zone-centre eigenfunctions for the conduction band minimum, of energy E_c, and valence band maximum, of energy E_v, and F_c and F_v are the envelope functions. The zone-centre eigenfunctions U_c and U_v are periodic in the lattice constant, a, and we chose to normalize them so that the squared modulus has mean value unity over a unit cell, i.e.

$$\frac{1}{a}\int_{x_0}^{x_0+a} |U_c|^2\,dx = \frac{1}{a}\int_{x_0}^{x_0+a} |U_v|^2\,dx = 1 \tag{2}$$

the integrals being independent of x_0. For low-lying conduction band states, $\Psi^{(c)}$, the conduction band envelope function, $F_c^{(c)}$, is dominant and obeys the effective-mass equation [10–12]. For a wide deep well of width L, $F_c^{(c)}$ for the ground conduction band state is given inside the well ($|x| < L/2$) by

$$F_c^{(c)} = \sqrt{2/L}\cos(\pi x/L) \tag{3}$$

and is zero outside. The valence band envelope function $F_v^{(c)}$ for this ground conduction band state is given approximately by

$$(E_c - E_v)F_v^{(c)} \approx -(i\hbar/m)p_{vc}\,dF_c^{(c)}/dx \tag{4}$$

where p_{vc} is the interband momentum matrix element

$$p_{vc} = \int_{x_0}^{x_0+a} \frac{dx}{a} U_v^* p U_c \tag{5}$$

which is also independent of x_0. Hence

$$F_v^{(c)} \simeq (i\hbar p_{vc}/mE_g)(\pi/L)\sqrt{2/L}\sin(\pi x/L) \tag{6}$$

with $E_g = E_c - E_v$. Similarly for the highest valence band state, $\Psi^{(v)}$,

$$F_v^{(v)} = \sqrt{2/L}\cos(\pi x/L) \tag{7}$$

$$F_c^{(v)} \simeq -(i\hbar p_{cv}/mE_g)(\pi/L)\sqrt{2/L}\sin(\pi x/L). \tag{8}$$

It is by no means essential for the discussion in the next section to be restricted to the two-band expansion given here. As is shown in appendix A, the remaining bands do not contribute to the matrix elements in the limit of a wide well.

3. Evaluation of interband matrix elements

3.1. Dipole matrix element

To evaluate the dipole matrix element between the band-edge quantum well states $\Psi^{(c)}$ and $\Psi^{(v)}$, we use the envelope function expansion given in the previous section:

$$\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle = \int_{-\infty}^{+\infty} \Psi^{(c)*} x \Psi^{(v)}\,dx = \int_{-\infty}^{+\infty} (F_c^{(c)}U_c + F_v^{(c)}U_v)^* x (F_c^{(v)}U_c + F_v^{(v)}U_v)\,dx. \tag{9}$$

It is tempting to argue as follows. The dominant term in $\Psi^{(c)}$ is $F_c^{(c)}U_c$ and that in $\Psi^{(v)}$ is $F_v^{(v)}U_v$ (indeed, the neglected terms become vanishingly small in comparison in the limit of wide wells), so as an approximation

$$\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle \approx \int_{-\infty}^{+\infty} (F_c^{(c)}U_c)^* x (F_v^{(v)}U_v)\,dx = I_{cv}. \tag{10}$$

To evaluate the integral in the limit of slowly varying Fs one uses the standard argument that the rapidly varying part of the integrand, $U_c^* x U_v$, can be replaced by its mean value, $\overline{U_c^* x U_v}$, over a unit cell, say that between x_0 and $x_0 + a$. The orthogonality of the Us ensures that this mean value is the same for all unit cells regardless of their positions, so

$$\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle \approx \overline{U_c^* x U_v} \int_{-\infty}^{+\infty} F_c^{(c)*} F_v^{(v)}\,dx. \tag{11}$$

Since $F_c^{(c)}$ and $F_v^{(v)}$ are one and the same normalized function, $\sqrt{2/L}\cos(\pi x/L)$ inside the well and zero outside, the integral is just unity. Therefore

$$\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle \simeq \overline{U_c^* x U_v} = \int_{x_0}^{x_0+a} \frac{dx}{a} U_c^* x U_v. \tag{12}$$

Since U_c and U_v are orthogonal, the integral is independent of the point about which the dipole moment is taken; we could replace x by $x - x_1$. Choosing x_1 somewhere between x_0 and $x_0 + a$ we easily see that integral is of the order of a. This is what we would expect because of the intra-atomic nature of the transition across the gap. However, there is a disturbing aspect to this result: it depends on the choice of x_0. A simple example will show this. Take two-band model approximations to U_c and U_v, e.g.

$$U_c = \sqrt{2}\sin(\pi x/a) \qquad U_v = \sqrt{2}\cos(\pi x/a). \tag{13}$$

Then the integral turns out to be $-(a/2\pi)\cos(2\pi x_0/a)$; it oscillates with mean value zero. As is shown in appendix B, this is not a quirk of the two-band approximation, but a general feature. The fact that our answer depends on the choice of x_0, i.e. the way we decide how to divide the range of integration into unit cells of length a, suggests that our factorization of the integrand into slowly varying and rapidly varying parts has been misguided. A better factorization is $F_c^{(c)*} x F_v^{(v)}$ as the slowly varying part and $U_c^* U_v$ as the rapidly varying part. The mean value, $\overline{U_c^* U_v}$, of the rapidly varying part is now zero, independently of the choice of x_0. This gives zero for the whole integral in the limit of slowly varying envelope functions regardless of how the infinite range of integration is divided into unit cells; this

result does not depend on the specific form of $F_c^{(c)}$ and $F_v^{(v)}$ chosen above. (The reader may object that one cannot put x with $F_c^{(c)*}$ and $F_v^{(v)}$ because it is not slowly varying; its derivative is always unity. However, its logarithmic derivative, $1/x$, is the more appropriate quantity to consider and this is small except in a small fraction of the integration range near $x = 0$.) A proof that the integral on the RHS of (10) is indeed zero, as one might expect from the oscillatory nature of the RHS of (12), for bound states with slowly varying envelope functions is given in appendix C.

Now that we have found that retaining only the dominant parts, $F_c^{(c)}U_c$ and $F_v^{(v)}U_v$, of $\Psi^{(c)}$ and $\Psi^{(v)}$ leads to zero contribution to $\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle$, we are forced to consider the effects of the second term in the envelope expansion even though it becomes vanishingly small compared with the first term in the limit of wide wells. Consider

$$I_{cc} = \int_{-\infty}^{+\infty} (F_c^{(c)}U_c)^* x (F_c^{(v)}U_c)\,dx \tag{14}$$

i.e. the integral having two conduction band envelope functions in the integrand. Using the fact that $|U_c|^2$ is rapidly varying and has mean value unity over a unit cell, the integral is approximately

$$\int_{-\infty}^{+\infty} F_c^{(c)*} x F_c^{(v)}\,dx. \tag{15}$$

In a similar way, for the integral involving two valence band envelope functions,

$$I_{vv} = \int_{-\infty}^{+\infty} (F_v^{(c)}U_v)^* x (F_v^{(v)}U_v)\,dx \simeq \int_{-\infty}^{+\infty} F_v^{(c)*} x F_v^{(v)}\,dx. \tag{16}$$

Using the explicit forms of the Fs given in section 2 one sees that I_{cc} and I_{vv} are equal and together contribute

$$I_{cc} + I_{vv} = p_{cv}/im\omega_g \tag{17}$$

to the dipole matrix element where $\hbar\omega_g = E_g$. The final integral $\int_{-\infty}^{+\infty}(F_v^{(c)}U_v)^* x (F_c^{(v)}U_c)\,dx$ can easily be seen to vanish in the limit of a wide well, because $\overline{U_v^* U_c} = 0$. Taking all these results together we have, in the limit of a wide deep well,

$$\langle\Psi^{(c)}|x|\Psi^{(v)}\rangle = p_{cv}/im\omega_g. \tag{18}$$

As is discussed in appendix A, these results hold even when the complete envelope expansion is used.

3.2. Momentum matrix element

The evaluation of the momentum matrix element, $\langle\Psi^{(c)}|p|\Psi^{(v)}\rangle$, proceeds in a similar manner to that for the dipole matrix element. However, the evaluation is much simpler for the momentum matrix element case, even though the action of the derivative on the FU-type products doubles the number of terms, because only one term contributes in the limit of a wide well. The terms involving the derivative of an envelope function can be dropped immediately because they contribute, at most, terms of order $1/L$ to the matrix element. (Indeed, the contributions of order $1/L$ vanish by symmetry and orthogonality

arguments, but we do not need this stronger result.) So only terms involving derivatives of the periodic functions U_c and U_v survive. Since U_c and U_v are Bloch functions for stationary points in the band structure, $\overline{U_c^* p U_c}$ and $\overline{U_v^* p U_v}$ both vanish. We are left then with integrals involving $U_c^* p U_v$ and $U_v^* p U_c$. The latter integral vanishes in the limit of a large well because the envelope function factor $F_v^{(c)*} F_c^{(v)} \sim 1/L^3$ which gives an integral $\sim 1/L^2$ so we are left with

$$\langle \Psi^{(c)} | p | \Psi^{(v)} \rangle = \int_{-\infty}^{+\infty} F_c^{(c)*} F_v^{(v)} U_c^* p U_v \, dx = \overline{U_c^* p U_v} \int_{-\infty}^{+\infty} F_c^{(c)*} F_v^{(v)} \, dx = p_{cv}. \tag{19}$$

This is the interband bulk matrix element, as expected. Taking (18) and (19) together we have

$$\langle \Psi^{(c)} | p | \Psi^{(v)} \rangle = im\omega_g \langle \Psi^{(c)} | x | \Psi^{(v)} \rangle \tag{20}$$

in accordance with the standard textbook result [13] relating matrix elements of position and momentum for bound states.

4. Summary and discussion

The dipole and momentum matrix elements have been evaluated for the interband transition between the band-edge states of a wide deep quantum well using the envelope function expansion for the wave functions. The textbook relation between these matrix elements is regained after taking into account apparently insignificant terms in the envelope function expansion. The relation ensures that the interband optical absorption rates obtained for a quantum well using the $\boldsymbol{E} \cdot \boldsymbol{r}$ and $\boldsymbol{A} \cdot \boldsymbol{p}$ forms of the interaction are the same. The dipole matrix element is independent of the intra-atomic-like matrix element of the dipole operator with respect to the band-edge states, with the integral taken over a unit cell, which we have shown to be an ill-defined quantity in any case. Neither is the dipole matrix element related to well width as in the case of allowed intersubband transitions. Rather, the dipole matrix element is determined by the matrix element of momentum between the band-edge states and the band gap. It can easily exceed the dipole matrix element for allowed intersubband transitions. For instance, the dipole matrix element between the ground and first excited state of a deep quantum well is about 0.18 of the well width, 18 Å for a 100 Å wide well. Taking the energy E_p related to the interband momentum matrix element as 20 eV, a typical value for a III–V semiconductor [14], and a band gap of 0.2 eV, the interband dipole matrix element is 44 Å.

The size of the interband dipole matrix element raises an interesting question concerning the DC Stark effect in quantum wells. The narrowing of the gap is usually understood using a particle in a box model. The ground state and the first excited states repel each other in an electric field because of the dipole matrix element; the ground state falls. This happens for both electrons and holes and the band gap shrinks. However, the presence of a large interband dipole moment suggests that the band gap will increase in the presence of an electric field. This would tend to decrease if not reverse the shrinking of the band gap that would occur in its absence. However, we should note that the model used here is only really applicable to the conduction band and light-hole band in a zincblende semiconductor (light-hole-like, that is, in the direction perpendicular to the interfaces). We would only expect to see such competition between the intersubband and interband effects for conduction-band–light-hole-band Stark shifts in low-band-gap semiconductors. For the conduction and heavy-hole bands (heavy-hole-like, that is, in the direction perpendicular to the interfaces), the

strong coupling via the $k \cdot p$ interaction will not be present for zero wave vector component parallel to the interfaces, and a large dipole matrix element and the consequent competition between the intersubband and interband effects on the Stark shift are not expected. In quantum dots light- and heavy-hole band states become coupled [15]. One would therefore expect a substantial interband dipole matrix element from the component bulk volume states that are light-hole-like in the direction of the light polarization. For non-linear refraction in quantum dots this suggests that both intraband and interband processes have to be considered, and that it does not necessarily follow that the two-photon absorption contribution (which involves both interband and intraband transitions) will necessarily dominate over the optical Stark effect (which involves only interband transitions) contribution in the mid-gap region as is the case in bulk samples [16]. Indeed both experimental and theoretical evidence for this view has been found [17].

To summarize the main point of this paper, the author can do no better than paraphrase remarks made by Ridley [18]. In matrix elements, the momentum operator will always emphasize the spatial rate of change of the wave functions while the position operator will emphasize their spatial extent. So, if the wave functions are each approximated by just one term of the type FU with slowly varying F independent of the rapidly varying periodic U, then a paradox arises: the matrix elements of position are determined by the Fs while those of momentum by the Us and would appear independent of each other, yet the matrix elements are related by a standard textbook theorem. It is clear, then, that a more accurate expression for the wave function must be used, as in this paper, to get the correct result.

Acknowledgments

The author is grateful to Professor C Flytzanis for a stimulating discussion that prompted this investigation, to Dr R A Abram for a discussion that improved the original version of appendix C, and Professor B K Ridley for enlightening correspondence.

Appendix A. Contribution of the remaining bands to $\langle \Psi^{(c)} | x | \Psi^{(v)} \rangle$

The full envelope function expansion of the wave function $\Psi^{(s)}$ (s = c or v) is

$$\Psi^{(s)} = F_c^{(s)} U_c + F_v^{(s)} U_v + \sum_r F_r^{(s)} U_r. \tag{A1}$$

In the slowly varying envelope function approximation

$$F_r^{(s)} \approx \{i\hbar p_{rs}/[m(E_s - E_r)\}(\pi/L)\sqrt{2/L}\sin(\pi x/L). \tag{A2}$$

The matrix element $\langle \Psi^{(c)} | x | \Psi^{(v)} \rangle$ is a sum of terms of the type

$$I_{nn'} = \int_{-L/2}^{+L/2} (F_n^{(c)} U_n)^* x (F_{n'}^{(v)} U_{n'})\, dx. \tag{A3}$$

As explained in section 3, one only gets a non-zero contribution to (A3) in the limit of wide wells when $n = n'$. In that case

$$I_{nn} \sim \frac{1}{L^3} \int_{-L/2}^{+L/2} dx\, |U_n|^2 x \sin^2 \frac{\pi x}{L} \sim \frac{1}{L} \tag{A4}$$

when $n \neq$ c or v. So all contributions $I_{nn} \to 0$ as $L \to \infty$, except I_{cc} and I_{vv}. In a similar vein one can show that the effect of the remaining bands on $\langle \Psi^{(c)} | p | \Psi^{(v)} \rangle$ is also negligible in the limit of wide wells.

Appendix B. Evaluation of $\overline{U_c^* x U_v}$

Using the plane-wave expansion

$$U_n(x) = \sum_G U_{nG} e^{iGx} \tag{B1}$$

of the periodic function $U_n(x)$ (period a) one has

$$\overline{U_c^* U_v} = \frac{1}{a} \sum_{GG'} U_{cG}^* U_{vG'} \int_{x_0}^{x_0+a} x e^{-i(G-G')x} \, dx. \tag{B2}$$

For $G = G'$ the integral is independent of G (or G') and the contribution from such terms vanishes because of the orthogonality of U_c and U_v:

$$\sum_G U_{cG}^* U_{vG} = 0. \tag{B3}$$

Restricting the sum to terms for which $G \neq G'$, one obtains

$$\overline{U_c^* x U_v} = i \sum_{G \neq G'} \frac{U_{cG}^* U_{vG'}}{G - G'} e^{-i(G-G')x_0}. \tag{B4}$$

This clearly oscillates about a mean value of zero, as x_0 is varied.

Appendix C. Proof that $\int_{-\infty}^{+\infty} dx \, (F_c^{(c)} U_c)^* x F_v^{(v)} U_v = 0$ for slowly varying envelope functions

Suppose that the quantum well of width L is part of a superlattice of period $\Lambda (\gg L)$ which will eventually be allowed to tend to infinity to get results for the isolated quantum well. The envelope functions, F, will be expanded in plane waves

$$F(x) = \sum_k \tilde{F}(k) e^{ikx} \qquad \tilde{F}(k) = \int_{-\Lambda/2}^{+\Lambda/2} \frac{dx}{\Lambda} F(x) e^{-ikx} \tag{C1}$$

where the wave numbers k obey $k\Lambda = 2n\pi$ with n an integer. The origin has been taken at the centre of the well. Using the plane-wave expansion for the cell periodic functions $U_n(x)$, i.e.

$$U_n(x) = \sum_G U_{nG} e^{iGx} \tag{C2}$$

one has

$$\begin{aligned} I_{cv} &= \int_{-\Lambda/2}^{+\Lambda/2} (F_c^{(c)} U_c)^* x F_v^{(v)} U_v \, dx \\ &= \sum_{kk'} \sum_{GG'} \tilde{F}_c^{(c)}(k)^* \tilde{F}_v^{(v)}(k') U_{cG}^* U_{vG'} \int_{-\Lambda/2}^{+\Lambda/2} dx \, x e^{-i(k-k'+G-G')x}. \end{aligned} \tag{C3}$$

Using similar arguments to those used in appendix B, one sees that the $G = G'$ terms give no overall contribution and one obtains

$$I_{cv} = i \sum_{kk'} \sum_{G \neq G'} \tilde{F}_c^{(c)}(k)^* \tilde{F}_v^{(v)}(k') U_{cG}^* U_{vG'} \left[\frac{x e^{-i(k-k'+G-G')x}}{(k-k'+G-G')} \right]_{x=-\Lambda/2}^{x=+\Lambda/2}. \quad \text{(C4)}$$

At this stage one remembers that only wide wells and slowly varying envelope functions are being considered. It is then permissible to make a binomial expansion of $(k - k' + G - G')^{-1}$ and retain only the first term since all other terms will be smaller by the factor $(k - k')/(G - G')$ or its powers. Asymptotically one then obtains

$$I_{cv} \simeq [x F_c^{(c)}(x)^* F_v^{(v)}(x)\, d_{cv}(x)]_{x=-\Lambda/2}^{x=+\Lambda/2} \quad \text{(C5)}$$

where

$$d_{cv}(x) = i \sum_{G \neq G'} U_{cG}^* \frac{e^{-i(G-G')x}}{G - G'} U_{vG'}. \quad \text{(C6)}$$

For bound states $\Psi^{(c)}$ and $\Psi^{(v)}$, the envelope functions will be exponentially small at the centre of the barriers. One expects them to vary as $e^{-q\Lambda/2}$ where q is positive. As Λ tends to infinity, the exponential terms overwhelm the linear Λ factor and I_{cv} tends to zero. One may repeat the above procedure with the other terms in the binomial expansion. The nth-order term leads to a term similar to (C5) but with $F_c^{(c)}(x)^* F_v^{(v)}(x)$ replaced by its nth derivative, which will also be exponentially small at $x = \pm\Lambda/2$, and with d_{cv} replaced by a 2^n-pole moment ($G - G'$ replaced by $(G - G')^n$ in (C6)). So the conclusion that $I_{cv} \to 0$ still holds provided the envelope functions are sufficiently slowly varying to keep the expansion convergent.

References

[1] West L C and Egalsh S J 1985 *Appl. Phys. Lett.* **46** 1156
[2] Asai H and Kawamura Y 1991 *Phys. Rev.* B **43** 4748
[3] Levine B F, Hasnain G, Bethea C G and Chand N 1989 *Appl. Phys. Lett.* **54** 2704
[4] Rosencher E, Bois P, Nagle J, Costard E and Delaitre S 1989 *Appl. Phys. Lett.* **55** 1597
[5] Sirtori C, Capasso F, Sivco D L, Chu S N G and Cho A Y 1991 *Appl. Phys. Lett.* **59** 2302
[6] Cotter D, Ainslie B J, Burt M G, Davey S T and Manning R J 1991 *Proc. Conf. on Lasers and Electrooptics* (Washington, DC: Optical Society of America, 1991) paper CTuE7
[7] Morrison I and Jaros M 1990 *Phys. Rev.* B **24** 3749
[8] Walrod D, Auyang S Y, Wolff P A and Sugimoto M 1991 *Appl. Phys. Lett.* **59** 2932
[9] Kane E O 1966 *Semiconductors and Semimetals* ed R K Willardson and A C Beer (New York: Academic) p 75
[10] Bastard G 1981 *Phys. Rev.* B **24** 5693
[11] Altarelli M 1983 *Phys. Rev.* B **28** 842
[12] Burt M G 1992 *J. Phys.: Condens. Matter* **4** 6651
[13] See, e.g.,
Merzbacher E 1961 *Quantum Mechanics* (New York: Wiley) p 453
[14] Lawaetz P 1971 *Phys. Rev.* B **4** 3460
[15] Vahala K J and Sercel P C 1990 *Phys. Rev. Lett.* **65** 239; 1990 *Phys. Rev.* B **42** 3690
[16] Sheik-Bahae M, Hagan D J and van Stryland F W 1990 *Phys. Rev. Lett.* **65** 96
[17] Cotter D, Burt M G and Manning R J 1992 *Phys. Rev. Lett.* **68** 1200
[18] Ridley B K 1992 private communication