RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 7 15 AUGUST 1993-I

Effective-mass Hamiltonian and boundary conditions for the valence bands of semiconductor microstructures

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(Received 1 June 1993)

Using the recently developed exact envelope-function theory, an explicit form for the effective-mass Hamiltonian is derived for the valence bands (including the spin-orbit split-off band) of a semiconductor quantum well or superlattice. It is shown that the correct form of the Hamiltonian gives physically reasonable results, while the commonly used "symmetrized" form can produce nonphysical solutions for the heavy-hole subbands in which the quantum-well effective mass is very sensitive to the difference in Luttinger parameters between the well and the barrier. This problem arises because the correct boundary conditions for the heavy-hole states are determined exclusively through interaction with other p states, while the symmetrized boundary conditions implicitly incorporate the much larger s-state interaction, hence they substantially overestimate the magnitude of the interband coupling.

While the use of the effective-mass theory in homogeneous bulk semiconductors is very well established, its application to heterostructures has until recently been the subject of considerable debate, especially with regard to the boundary conditions connecting the envelope functions across an abrupt heterojunction.[1-3] The controversy has now been conclusively settled, with the development by Burt of an exact envelope-function theory for semiconductor microstructures.[4] The exact theory gives a general solution for the effective-mass Hamiltonian in terms of momentum matrix elements and energy band gaps which applies even at an abrupt interface. This paper is concerned with writing the general multiband effective-mass Hamiltonian given by Burt in an explicit form for use in valence-band problems. This provides an unambiguous prescription for the boundary conditions at an interface; it will be shown that the correct boundary conditions differ substantially from those currently found in the literature.

The specific problem of concern here is the valence-band structure of quantum wells or superlattices composed of semiconductors of the zinc-blende structure (which have a valence-band maximum at the Γ point, neglecting the small linear-k splitting terms). The bulk band structure[5] of these semiconductors is described in terms of the Luttinger mass parameters γ_1, γ_2, and γ_3, which are determined by the $\mathbf{k}\cdot\mathbf{p}$ interaction of the Γ_{15} valence bands with all other states of symmetry Γ_1, Γ_{15}, Γ_{12}, or Γ_{25}. These states are compatible (to lowest order) with the s, p, d, and f orbitals, respectively, of the constituent atoms. Since the contribution of f orbitals to the valence electronic structure of semiconductors is insignificant,[6] the Γ_{25} states will be neglected here.

Each of the remaining (Γ_1, Γ_{15}, and Γ_{12}) interactions will generate terms in the valence-band Hamiltonian with a different form (i.e., a different ordering of the differential operators with respect to the band parameters). It is therefore convenient to write the Luttinger parameters in a manner which explicitly reveals the contribution of each symmetry type:[5]

$$\begin{aligned}&\gamma_1=-1+2\sigma+4\pi+4\delta\ ,\\ &\gamma_2=\sigma-\pi+2\delta,\quad \gamma_3=\sigma+\pi-\delta\ ,\end{aligned}\tag{1}$$

where the dimensionless quantities σ, π, and δ are defined by

$$\begin{aligned}\sigma&=(1/3m_0)\sum_j^{\Gamma_1}|\langle X|p_x|u_j\rangle|^2/(E_j-E_v)\ ,\\ \pi&=(1/3m_0)\sum_j^{\Gamma_{15}}|\langle X|p_y|u_j\rangle|^2/(E_j-E_v)\ ,\\ \delta&=(1/6m_0)\sum_j^{\Gamma_{12}}|\langle X|p_x|u_j\rangle|^2/(E_j-E_v)\ .\end{aligned}\tag{2}$$

Here m_0 is the free-electron mass, $\mathbf{p}$ is the momentum operator, and E_v is the valence-band energy in the absence of spin-orbit splitting; the sum is over the basis states u_j of all remote bands of a given symmetry. These states are functions which have the periodicity of the zinc-blende lattice and the angular dependence shown in Table I. To calculate σ, π, and δ in terms of experimentally determined Luttinger parameters,

$$\begin{aligned}&\overline{\gamma}=\tfrac{1}{2}(\gamma_3+\gamma_2),\quad \mu=\tfrac{1}{2}(\gamma_3-\gamma_2)\ ,\\ &\sigma=\overline{\gamma}-\tfrac{1}{2}\delta,\quad \pi=\mu+\tfrac{3}{2}\delta,\quad \delta=\tfrac{1}{9}(1+\gamma_1+\gamma_2-3\gamma_3)\ .\end{aligned}\tag{3}$$

Taking GaAs as a typical case, $\sigma\approx 4\pi$ and $\pi\approx 4\delta$. (The only qualitatively different semiconductor is Si, in which the conduction-band p states actually lie below the s state,[6] hence $\sigma\approx\pi$.)

Using these parameters and the basis functions in Table I, it is straightforward to evaluate the effective-mass Hamiltonian given by the exact envelope-function theory.[4] However, the spin-orbit interaction splits the Γ_{15} states, so it is most convenient to work with eigenfunctions of the total angular momentum $|J,m_J\rangle$ which diagonalize this interaction:[7]

$$\begin{aligned}&|\tfrac{3}{2},\tfrac{3}{2}\rangle=(1/\sqrt{2})|(X+iY)\uparrow\rangle\ ,\\ &|\tfrac{3}{2},-\tfrac{3}{2}\rangle=(1/\sqrt{2})|(X-iY)\downarrow\rangle\ ,\\ &|\tfrac{3}{2},\tfrac{1}{2}\rangle=(1/\sqrt{6})|(X+iY)\downarrow\rangle-\sqrt{\tfrac{2}{3}}|Z\uparrow\rangle\ ,\\ &|\tfrac{3}{2},-\tfrac{1}{2}\rangle=-(1/\sqrt{6})|(X-iY)\uparrow\rangle-\sqrt{\tfrac{2}{3}}|Z\downarrow\rangle\ ,\\ &|\tfrac{1}{2},\tfrac{1}{2}\rangle=(1/\sqrt{3})|(X+iY)\downarrow\rangle+(1/\sqrt{3})|Z\uparrow\rangle\ ,\\ &|\tfrac{1}{2},-\tfrac{1}{2}\rangle=-(1/\sqrt{3})|(X-iY)\uparrow\rangle+(1/\sqrt{3})|Z\downarrow\rangle\ .\end{aligned}\tag{4}$$

0163-1829/93/48(7)/4964(4)/$06.00

In the exact envelope-function theory, these functions are required to be the same throughout the structure, independent of material composition. In this basis, the effective-mass Hamiltonian takes the form

$$H=\begin{bmatrix} P+Q & 0 & -S_- & R & (1/\sqrt{2})S_- & \sqrt{2}R \\ 0 & P+Q & -R^\dagger & -S_+ & -\sqrt{2}R^\dagger & (1/\sqrt{2})S_+ \\ -S_-^\dagger & -R & P-Q & C & \sqrt{2}Q & \sqrt{\tfrac{3}{2}}\Sigma_- \\ R^\dagger & -S_+^\dagger & C^\dagger & P-Q & -\sqrt{\tfrac{3}{2}}\Sigma_+ & \sqrt{2}Q \\ (1/\sqrt{2})S_-^\dagger & -\sqrt{2}R & \sqrt{2}Q & -\sqrt{\tfrac{3}{2}}\Sigma_+^\dagger & P+\Delta & -C \\ \sqrt{2}R^\dagger & (1/\sqrt{2})S_+^\dagger & \sqrt{\tfrac{3}{2}}\Sigma_-^\dagger & \sqrt{2}Q & -C^\dagger & P+\Delta \end{bmatrix}, \tag{5a}$$

where, in atomic units ($\hbar=m_0=1$), and with the hole energy positive,

$$\begin{aligned} P&=E_v(z)+\tfrac{1}{2}(\gamma_1 k_\parallel^2+k_z\gamma_1 k_z)\ , \\ Q&=\zeta(z)+\tfrac{1}{2}(\gamma_2 k_\parallel^2-2k_z\gamma_2 k_z)\ , \\ R&=-(\sqrt{3}/2)\bar{\gamma}k_-^2+(\sqrt{3}/2)\mu k_+^2\ , \\ S_\pm&=\sqrt{3}k_\pm[(\sigma-\delta)k_z+k_z\pi]\ , \\ \Sigma_\pm&=\sqrt{3}k_\pm\{[\tfrac{1}{3}(\sigma-\delta)+\tfrac{2}{3}\pi]k_z+k_z[\tfrac{2}{3}(\sigma-\delta)+\tfrac{1}{3}\pi]\}\ , \\ C&=k_-[k_z(\sigma-\delta-\pi)-(\sigma-\delta-\pi)k_z]\ , \\ k_\parallel^2&=k_x^2+k_y^2,\quad k_\pm=k_x\pm ik_y,\quad k_z=-i\partial/\partial z\ . \end{aligned} \tag{5b}$$

Here the quantum well or superlattice is assumed to be grown on a (001) substrate, and the possibility of lattice mismatch has been taken into account in the matrix elements P and Q.[8] In these equations, $E_v(z)$ is the bulk Γ_8 valence-band profile (including hydrostatic but not shear strain), Δ is the spin-orbit splitting, and ζ is the shear-strain splitting energy. Note the asymmetry with respect to k_z of $S_\pm$, which will be of fundamental importance in the boundary conditions. Also, the matrix element C, which is zero in bulk material, introduces a coupling of the states $|J,\pm m_J\rangle$ in the light-hole (LH) and split-off (SO) bands. It arises because any change in material composition breaks the local inversion symmetry of the lattice (since the inversion asymmetry of the zinc-blende lattice has already been neglected). A similar term[9] will couple the heavy-hole (HH) states if the spin-orbit interaction is included in the Luttinger parameters. Finally, note that $S_\pm=\Sigma_\pm=\sqrt{3}\gamma_3 k_\pm k_z$ in bulk material.

For theoretical work on a quantum well or superlattice, the Hamiltonian (5) is not the most convenient, since a change of basis will reduce it to block diagonal form.[10,11] One possible choice for the transformation is

TABLE I. Basis functions.

Representation	Basis functions
Γ_1	$x^2+y^2+z^2$ or xyz
Γ_{15}	x,y,z
Γ_{12}	$2z^2-x^2-y^2,\sqrt{3}(x^2-y^2)$

$$\begin{aligned} |u_1\rangle&=\alpha|\tfrac{3}{2},-\tfrac{3}{2}\rangle-\alpha^*|\tfrac{3}{2},\tfrac{3}{2}\rangle\ , \\ |u_2\rangle&=\beta|\tfrac{3}{2},\tfrac{1}{2}\rangle+\beta^*|\tfrac{3}{2},-\tfrac{1}{2}\rangle\ , \\ |u_3\rangle&=\beta|\tfrac{1}{2},\tfrac{1}{2}\rangle+\beta^*|\tfrac{1}{2},-\tfrac{1}{2}\rangle\ , \\ |u_4\rangle&=\alpha|\tfrac{3}{2},-\tfrac{3}{2}\rangle+\alpha^*|\tfrac{3}{2},\tfrac{3}{2}\rangle\ , \\ |u_5\rangle&=\beta|\tfrac{3}{2},\tfrac{1}{2}\rangle-\beta^*|\tfrac{3}{2},-\tfrac{1}{2}\rangle\ , \\ |u_6\rangle&=\beta|\tfrac{1}{2},\tfrac{1}{2}\rangle-\beta^*|\tfrac{1}{2},-\tfrac{1}{2}\rangle\ , \end{aligned} \tag{6a}$$

where

$$\begin{aligned} \alpha&=(1/\sqrt{2})e^{i\pi/4}e^{i(\phi/2+\eta)}\ , \\ \beta&=(1/\sqrt{2})e^{-i3\pi/4}e^{i(\phi/2-\eta)}\ , \\ \phi&=\arctan(k_y/k_x)\ , \\ \eta&=\tfrac{1}{2}\arctan[(\gamma_3/\gamma_2)\tan(2\phi)]\ . \end{aligned} \tag{6b}$$

Note that $\eta=\phi$ for $\mathbf{k}_\parallel$ along the $\langle 100\rangle$ and $\langle 110\rangle$ directions. In other directions, because the basis functions must remain independent of material composition, an average value for η is used. (This choice is consistent with the approximations made in deriving the effective-mass Hamiltonian from the exact envelope-function equations.[4]) In the new basis, the Hamiltonian is transformed to a pair of 3×3 blocks,

$$H_\pm=\begin{bmatrix} P+Q & R\mp iS & \sqrt{2}R\pm\dfrac{i}{\sqrt{2}}S \\ R\pm iS^\dagger & P-Q\mp iC & \sqrt{2}Q\mp i\sqrt{\tfrac{3}{2}}\Sigma \\ \sqrt{2}R\mp\dfrac{i}{\sqrt{2}}S^\dagger & \sqrt{2}Q\pm i\sqrt{\tfrac{3}{2}}\Sigma^\dagger & P+\Delta\pm iC \end{bmatrix}, \tag{7a}$$

where the upper and lower blocks correspond to the upper and lower signs. Here P and Q are the same as before, but R, S, Σ, and C are altered:

$$\begin{aligned} R&=-(\sqrt{3}/2)\gamma_\phi k_\parallel^2\ , \\ \gamma_\phi&=\sqrt{\bar{\gamma}^2+\mu^2-2\bar{\gamma}\mu\cos 4\phi}\ , \\ S&=\sqrt{3}k_\parallel[(\sigma-\delta)k_z+k_z\pi]\ , \\ \Sigma&=\sqrt{3}k_\parallel\{[\tfrac{1}{3}(\sigma-\delta)+\tfrac{2}{3}\pi]k_z+k_z[\tfrac{2}{3}(\sigma-\delta)+\tfrac{1}{3}\pi]\}\ , \\ C&=k_\parallel[k_z(\sigma-\delta-\pi)-(\sigma-\delta-\pi)k_z]\ . \end{aligned} \tag{7b}$$

In order to eliminate off-block-diagonal terms involving the matrix elements Σ and C, it was necessary to assume that $\eta=\phi$. Therefore, the Hamiltonian (7) is strictly applicable only along the $\langle 100\rangle$ and $\langle 110\rangle$ directions; nonetheless, it provides an excellent approximation to the in-plane angular dependence of (5), which is entirely neglected in the conventional axial approximation.[10] Also, the transformation (6) was chosen so that the upper and lower block basis functions transform into one another upon reflection in the $z=0$ plane. Therefore, if the structure under consideration has reflection symmetry, the eigenfunctions of the upper and lower block Hamiltonians will be reflections of one another, and their corresponding eigenenergies will be degenerate.

To determine the boundary conditions[4] on the envelope functions, one integrates the effective-mass equation,

$$H\mathbf{F}=E\mathbf{F}\ , \tag{8}$$

across an interface, where $\mathbf{F}(\mathbf{r})$ is a three-component envelope-function vector and H is either of the blocks in (7a). The boundary conditions require the continuity of $\mathbf{F}$ and $B\mathbf{F}$, where

$$B_{\pm}=\begin{bmatrix} (\gamma_1-2\gamma_2)\partial/\partial z & \pm 2\sqrt{3}\pi k_{\parallel} & \mp\sqrt{6}\pi k_{\parallel} \\ \mp 2\sqrt{3}(\sigma-\delta)k_{\parallel} & (\gamma_1+2\gamma_2)\partial/\partial z\pm 2(\sigma-\delta-\pi)k_{\parallel} & -2\sqrt{2}\gamma_2\partial/\partial z\pm\sqrt{2}(2\sigma-2\delta+\pi)k_{\parallel} \\ \pm\sqrt{6}(\sigma-\delta)k_{\parallel} & -2\sqrt{2}\gamma_2\partial/\partial z\mp\sqrt{2}(\sigma-\delta+2\pi)k_{\parallel} & \gamma_1\partial/\partial z\mp 2(\sigma-\delta-\pi)k_{\parallel} \end{bmatrix} . \tag{9}$$

Note that since $\gamma_1-2\gamma_2=-1+6\pi$, only the small π terms appear in the HH equation, while in the LH and SO equations, the coefficients are dominated by the large value of σ. Thus in all three cases the interband coupling due to the derivative boundary condition is roughly of order $k_{\parallel}/k_z$.

The boundary conditions found in the current literature are significantly different. Prior to the development of the exact envelope-function theory, the only guidelines available for the construction of the effective-mass Hamiltonian were that it must be Hermitian and that it must reduce to the correct bulk form away from an interface. This ambiguity allows for an infinite set of possible boundary conditions, but the most common choice in the literature is obtained from a "symmetrized" Hamiltonian[7,8] in which all operators linear in k_z are written in the form $\frac{1}{2}[k_z f(z)+f(z)k_z]$. Applying the symmetrization procedure to the Hamiltonian (7) is equivalent to substituting $\frac{1}{2}\gamma_3$ for both $\sigma-\delta$ and π in the matrix elements S, Σ, and C, thus changing the matrix B to

$$B_{\pm}=\begin{bmatrix} (\gamma_1-2\gamma_2)\partial/\partial z & \pm\sqrt{3}\gamma_3 k_{\parallel} & \mp\sqrt{\tfrac{3}{2}}\gamma_3 k_{\parallel} \\ \mp\sqrt{3}\gamma_3 k_{\parallel} & (\gamma_1+2\gamma_2)\partial/\partial z & -2\sqrt{2}\gamma_2\partial/\partial z\pm(3/\sqrt{2})\gamma_3 k_{\parallel} \\ \pm\sqrt{\tfrac{3}{2}}\gamma_3 k_{\parallel} & -2\sqrt{2}\gamma_2\partial/\partial z\mp(3/\sqrt{2})\gamma_3 k_{\parallel} & \gamma_1\partial/\partial z \end{bmatrix} . \tag{10}$$

The most important change caused by symmetrization occurs in the boundary condition for the HH band, where the large quantity σ is incorporated into the coupling terms. The use of symmetrized boundary conditions will therefore overestimate the magnitude of this interband coupling, which can lead to qualitative errors in the band structure, as shown below. The changes in the LH and SO boundary conditions are not as significant since the resulting underestimate of the coupling causes only small numerical modifications.

An example of the consequences of the symmetrized boundary conditions is presented in Fig. 1, where the zone-center effective masses of the heavy-hole subbands for an $In_{0.2}Ga_{0.8}As/GaAs$ quantum well are plotted versus quantum-well width. (The details of these calculations will be presented in a forthcoming paper.[12]) Results are given for three sets of boundary conditions: correct, symmetrized, and uncoupled. (In the approximation that the Luttinger parameters are independent of position, the boundary conditions are not coupled.) On a physical basis, one would expect the coupled solution for the effective mass to differ from the uncoupled solution by only a small amount (i.e., something on the order of the relative change in Luttinger parameters at the interface), and indeed this is true for the correct boundary conditions. However, the exaggeration of the interband coupling due to the symmetrized boundary conditions causes the mass of the HH2 subband to become a very volatile function of both the physical dimensions of the quantum well and the precise numerical values chosen for the Lut-

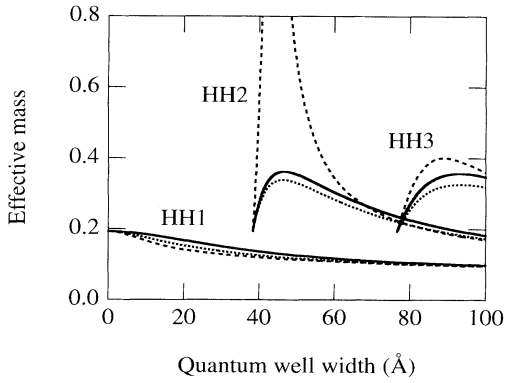

FIG. 1. Zone-center heavy-hole subband effective masses vs quantum-well width for an $In_{0.2}Ga_{0.8}As/GaAs$ quantum well. Three different boundary conditions are shown: correct (solid line), symmetrized (dashed line), and uncoupled (dotted line). The symmetrized HH2 mass reaches a peak value of 1.42, more than triple the mass obtained from the correct boundary conditions.

tinger parameters. This nonphysical behavior clearly demonstrates that the choice of Hamiltonian is not arbitrary, and that the correct boundary conditions are required for physically reasonable solutions.

In conclusion, the effective-mass Hamiltonian given by the exact envelope-function theory has been evaluated for the valence band. In the boundary conditions obtained from this Hamiltonian, the heavy-hole states are coupled to the light-hole and split-off states only through the interaction with remote bands of p symmetry. The symmetrized boundary conditions implicitly include the much larger interaction with s states. This exaggerates the interband coupling; consequently, nonphysical solutions are obtained for the heavy-hole subbands in which the quantum-well effective mass is very sensitive to the change in Luttinger parameters at the well-barrier interface.

I would like to thank Brian Ridley for introducing me to this topic. This work was supported by AT&T Bell Laboratories.

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