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Envelope Function Theory for Direct-gap Semiconductor Superlattices of Arbitrary Grading Profile

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Abstract

A systematic development is given for the construction, at any energy in the conduction or valence bands, of all of the solutions to the coupled second-order equations describing electron, light hole, and spin–orbit split-off envelope functions, for arbitrary superlattice grading profile of direct gap materials, retaining all coupling parameters. While some solutions achieve a clear physical significance, attention is also given to those functions which, on their own, are of questionable significance. The procedures are easy to use, and are applied to the case of a sawtooth superlattice of composition $Ga_{1-x}Al_xAs$.

1. Introduction

Interest in quantum wells and superlattices has now broadened (Jaros *et al.* 1985; Brum *et al.* 1986; Fasolino and Altarelli 1986; Sanders and Bajaj 1987; Cheung and Chen 1988; Chuang *et al.* 1989, 1990) well beyond the study of rectangular potential profiles, and the need is evident for a theory of these systems which is reliable, physically descriptive, and readily adaptable to a wide variety of circumstances. A methodology (Altarelli 1986; Bastard *et al.* 1988) widely regarded as satisfying these criteria is that of the envelope function approximation (EFA). Other methodologies (Giannozzi *et al.* 1990; Smith and Mailhiot 1990), variants of self-consistent field calculations, have the appeal of being closer to first principles than EFA, and have been used for a variety of superlattice (SL) and quantum well (QW) problems. Where comparison has been possible between the results of such calculations and the results of EFA, invariably the first-principles procedures have added confidence to the use of EFA. Thus a preference for EFA may safely be formed on the basis of economy of computational effort together with the above-mentioned criteria. This is the basis of the work reported here, where attention is restricted to superlattices.

The cornerstone of EFA is the Kane matrix, the $\boldsymbol{k}\,.\,\boldsymbol{p}$ interaction matrix derived from the zone-centre conduction, valence, and spin–orbit split-off states. When taken to second order in the components of $\boldsymbol{k}$, the interaction matrix includes to that order indirect interactions via states not specifically included in the basis just mentioned. EFA is achieved by an operator substitution in the matrix and leads, in its full form, to a set of eight coupled second-order differential equations, a daunting prospect. If attention is restricted to those states describing motion wholly in the SL growth direction, and this is the only case treated here, a simpler

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situation arises—two sets of three coupled equations (the two sets are connected by time inversion symmetry) and two uncoupled equations describing the heavy hole states. Even a set of three coupled second-order differential equations can be unattractive, and some authors have sought suitable approximations to reduce the computational complications. Thus, for example, Hass and Kirill (1990), following Johnson *et al.* (1990), recently used an approximation which deleted all but one of the second-order operators, and that one only in the uncoupled heavy-hole equations. Of course the elimination of operators from the equations simultaneously eliminates the associated coupling parameters, and thus there occurs some limitation on the flexibility to tie a non-first-principles theory firmly to the material under consideration. [The further one drifts from first principles the more essential it becomes to insert values for material-dependent properties into the computations. Thus Schuurmans and 't Hooft (1985) pointed out that a class of earlier single-parameter calculations (Bastard 1982) is restricted in its capacity to simultaneously describe both electron and light hole effective masses.] The purpose of the present work is to show that for direct gap materials, physically meaningful uncouplings of the equations can be achieved for arbitrary material gradings retaining the second-order terms, and with a minimum of approximation.

The focus of this work is the construction of algorithms which, for any nominated band energy, reduce the coupled equation problem to the solution of three uncoupled second-order differential equations. The three uncoupled equations can be identified in turn as applying to conduction electron (el), light hole (lh) and spin–orbit (so) states, and each leads to two sets of solutions at any nominated energy. The algorithms may be applied with equal ease to materials of continuously varying composition or to piecewise continuous materials, of any grading profile. In principle, all six sets of solutions are needed to satisfy the usual boundary conditions. However, several authors (White and Sham 1981; Schuurmans and 't Hooft 1985; Smith and Mailhiot 1990) have drawn attention to the fact that EFA, by virtue of its foundation on a limited basis set, inescapably produces a set of spurious solutions which ought not to be included in the description of the physical states of the system under study. In the following section the conditions under which spurious solutions appear are clearly identified, and several strategies for dealing with the consequent difficulties in satisfying boundary conditions are considered. By way of illustration, there follows in Section 3 an application of the theory to the case of a sawtooth SL of composition $Ga_{1-x}Al_xAs$ and, for comparison, some related approximate treatments for that material.

2. Theory

(2a) The Differential Equations

EFA for the description of the electron and hole states in a semiconductor SL or QW has been described by many authors (Altarelli 1986; Bastard *et al.* 1988; Giannozzi *et al.* 1990; Smith and Mailhiot 1990). It involves the operator substitution $\boldsymbol{k} \rightarrow -\mathrm{i}\,\nabla$ in the Kane matrix representing the $\boldsymbol{k}\,.\,\boldsymbol{p}$ interaction among the $\Gamma_6(T_\mathrm{d})$ electron, $\Gamma_8(T_\mathrm{d})$ light and heavy hole, and $\Gamma_7(T_\mathrm{d})$ spin–orbit split-off states. For uniform materials the structure of the Kane matrix may be derived solely from group-theoretical considerations, and when thus derived it contains

symmetry parameters which may be selected to match material properties. It is assumed here that, with arbitrary continuous (or piecewise continuous) grading of composition, locally the appropriate Kane matrix has the same structure as for the uniform materials, subject to the following conditions:

(i) Some procedure is known for specifying continuously the parameter values appropriate to each position in the material (e.g. the parameters describing a uniform material of average composition in the neighbourhood of that position).

(ii) The appropriate form of continuity of the envelope functions from one locality to neighbouring localities of slightly different composition is properly described by adjusting the operator substitution procedure to ensure the hermiticity of the differential operators in the manner usually used to derive matching conditions at boundaries (Eppenga *et al.* 1987; Giannozzi *et al.* 1990). Specifically, following Eppenga *et al.*, we have

$$A(z)\,\frac{\partial^2}{\partial z^2} \to \frac{\partial}{\partial z}\left(A(z)\,\frac{\partial}{\partial z}\right), \tag{1}$$

$$B(z)\,\frac{\partial}{\partial z} \to \tfrac{1}{2}\left(B(z)\,\frac{\partial}{\partial z} + \frac{\partial}{\partial z}\,B(z)\right), \tag{2}$$

where $A(z)$ and $B(z)$ are any composition-dependent functions of position. Clearly, this adjustment has no effect for rectangular composition profiles except at the composition discontinuities.

For notational simplicity in the following theory, the envelope functions for the conduction, light hole, spin–orbit split-off, and heavy hole states will be designated by ψ, θ, ϕ, η respectively. For the present purpose a useful enunciation of the Kane matrix is that of Schuurmans and 't Hooft (1985). On making the operator substitution and adjustments (as described above) in their Kane matrix (but incorporating a slight change of notation), the equations satisfied by ψ, θ, ϕ, η are

$$-\frac{\partial}{\partial z}\left(S\,\frac{\partial\psi}{\partial z}\right) - \left(P\,\frac{\partial\theta}{\partial z} + \frac{\theta}{2}\,\frac{\partial P}{\partial z}\right) + \sqrt{\tfrac{1}{2}}\left(P\,\frac{\partial\phi}{\partial z} + \frac{\phi}{2}\,\frac{\partial P}{\partial z}\right) = (E - E_{\mathrm{el}})\psi\,, \tag{3}$$

$$P\,\frac{\partial\psi}{\partial z} + \frac{\psi}{2}\,\frac{\partial P}{\partial z} + \frac{\partial}{\partial z}\left((\gamma_1 + 2\gamma_2)\,\frac{\partial\theta}{\partial z}\right) - 2\sqrt{2}\,\frac{\partial}{\partial z}\left(\gamma_2\,\frac{\partial\phi}{\partial z}\right) = (E - E_{\mathrm{v}})\theta\,, \tag{4}$$

$$-\sqrt{\tfrac{1}{2}}\left(P\,\frac{\partial\psi}{\partial z} + \frac{\psi}{2}\,\frac{\partial P}{\partial z}\right) - 2\sqrt{2}\,\frac{\partial}{\partial z}\left(\gamma_2\,\frac{\partial\theta}{\partial z}\right) + \frac{\partial}{\partial z}\left(\gamma_1\,\frac{\partial\phi}{\partial z}\right) = (E - E_{\mathrm{so}})\phi\,, \tag{5}$$

$$-\frac{\partial}{\partial z}\left((2\gamma_2 - \gamma_1)\,\frac{\partial\eta}{\partial z}\right) = (E - E_{\mathrm{v}})\eta\,. \tag{6}$$

In these equations the fundamental constants have been eliminated by choosing the energy unit to be the Rydberg, and the unit of distance to be the Bohr radius; E is the (position-independent) energy eigenvalue for the SL state under consideration; and E_{el}, E_{v}, E_{so} are position-dependent parameters locally specifying respectively the conduction, valence and spin–orbit split-off band edges for the Γ-point basis

states from which the $\boldsymbol{k}\,.\,\boldsymbol{p}$ interaction is constructed. (If the interband matrix element P employed here were replaced by $\sqrt{\frac{2}{3}}\,P$ it would then have the same form as has been used by other authors.) It is convenient to introduce the standard symnbols for the energy gap E_{g} and the spin–orbit splitting Δ:

$$E_{\mathrm{g}} = E_{\mathrm{el}} - E_{\mathrm{v}}\,, \tag{7}$$

$$\Delta = E_{\mathrm{v}} - E_{\mathrm{so}}\,. \tag{8}$$

Schuurmans and 't Hooft (1985) have established the following relationships which here have the effect of defining the other parameters used in equations (3)–(6):

$$m/m_{\mathrm{el}} = S + \lambda(1 + \tfrac{1}{2}r)\,, \tag{9}$$

$$m/m_{\mathrm{lh}} = \gamma_1 + 2\gamma_2 + \lambda\,, \tag{10}$$

$$m/m_{\mathrm{so}} = \gamma_1 + \tfrac{1}{2}\lambda r\,, \tag{11}$$

$$m/m_{\mathrm{hh}} = \gamma_1 - 2\gamma_2\,, \tag{12}$$

where

$$r = \frac{E_{\mathrm{g}}}{E_{\mathrm{g}} + \Delta}\,, \tag{13}$$

$$\lambda = P^2/E_{\mathrm{g}}\,. \tag{14}$$

Here m_{el}, m_{lh}, m_{so} and m_{hh} are the effective masses for conduction, light holes, spin–orbit split-off and heavy hole states respectively.

Equation (14) does not determine the sign of P, but this is of no consequence as a simultaneous reversal of the signs of P, θ and ϕ leaves equations (3)–(5) invariant. Equation (6) describing the heavy hole envelope function contains no coupling to the other functions. The use of equation (12) in (6) renders it physically transparent with no particular difficulty of solution, and so will be subject to no further comment here:

$$-\frac{\partial}{\partial z}\left(\frac{m}{m_{\mathrm{hh}}}\,\frac{\partial \eta}{\partial z}\right) = (E_{\mathrm{v}} - E)\eta\,. \tag{15}$$

In uncoupling equations (3)–(5) it is always assumed that derivatives of the parameters γ_1, γ_2, P, S, E_{el}, E_{v}, E_{so} are all small quantities and that products and derivatives of such small quantities may be neglected. For the uncoupling procedures of the following subsections, it is convenient to introduce the notations

$$\epsilon_1 = E - E_{\mathrm{el}} - SK^2\,, \qquad \epsilon_2 = E - E_{\mathrm{v}} + (\gamma_1 + 2\gamma_2)K^2\,, \tag{16a, b}$$

$$\epsilon_3 = E - E_{\mathrm{so}} + \gamma_1 K^2\,, \qquad \epsilon_4 = E - E_{\mathrm{v}} + (\gamma_1 - 2\gamma_2)K^2\,, \tag{16c, d}$$

where the parameter K^2 will be defined below.

(2b) Conduction States

Intuitively one expects that for energy E in the conduction band, the function ψ will be oscillatory with a wavelength locally determined from $E - E_{\mathrm{el}}$ and an appropriate effective mass. This wavelength would be echoed in the coupled functions θ and ϕ, but these two functions need not be in phase with ψ; inspection of equations (3)–(5) shows that θ and ϕ are predominantly out of phase with ψ, and so prototype solutions for these functions are

$$\theta = A\,\frac{\partial\psi}{\partial z} + a\psi\,, \tag{17}$$

$$\phi = B\,\frac{\partial\psi}{\partial z} + b\psi\,. \tag{18}$$

In these, and in all subsequent equations, all coefficients written as small Latin letters are assumed to be small quantities. That is, here it is anticipated that all terms in an expansion of a and b contain factors which are derivatives of the parameters entering (3)–(5). All coefficients are expected to be position-dependent. On substitution of (17) and (18) into (3), the result is

$$-\frac{\partial}{\partial z}\left((S + PA - \sqrt{\tfrac{1}{2}}\,PB)\,\frac{\partial\psi}{\partial z}\right)$$
$$-\left(P(a - \sqrt{\tfrac{1}{2}}\,b) - \tfrac{1}{2}(A - \sqrt{\tfrac{1}{2}}\,B)\,\frac{\partial P}{\partial z}\right)\frac{\partial\psi}{\partial z} = (E - E_{\mathrm{el}})\psi\,. \tag{19}$$

If the small quantity $P(a - \sqrt{\frac{1}{2}}b) - \frac{1}{2}(A - \sqrt{\frac{1}{2}}\,B)\partial P/\partial z$ is set equal to zero, then equation (19) has the same form and physical transparency as equation (15); however, it is not necessary to make this approximation as the coefficients can be determined by substitution of (17) and (18) into (4) and (5), then separating the two quadratures in each equation.

The substitution of (17) and (18) into (4) and (5) introduces a third-order derivative of ψ, and this will be reduced to first order by the assumption that *locally*

$$\frac{\partial^2\psi}{\partial z^2} = -K^2\psi + k\,\frac{\partial\psi}{\partial z}\,, \tag{20}$$

an immediate analogue of equation (19). The second term on the right in (20) indicates that the wavelength and/or amplitude of ψ may be slowly varying. Two of the relationships provided by the separation of quadratures (SOQ) process for equations (4) and (5) are

$$[E - E_{\mathrm{v}} + (\gamma_1 + 2\gamma_2)K^2]A - (2\sqrt{2}\,\gamma_2\,K^2)B = P\,, \tag{21}$$

$$(2\sqrt{2}\,\gamma_2\,K^2)A - (E - E_{\mathrm{so}} + \gamma_1\,K^2)B = \sqrt{\tfrac{1}{2}}\,P\,. \tag{22}$$

The remaining two relationships are stated below. A comparison of equations (19) and (20) yields

$$K^2 = \frac{E - E_{\mathrm{el}}}{S + PA - \sqrt{\frac{1}{2}}\,PB}\,. \tag{23}$$

The set of simultaneous equations (21)–(23) determine A, B and K^2, but they are a nonlinear set; they are locally equivalent to equation (8) of Schuurmans and 't Hooft (1985). If E is low in the conduction band the envelope function will be of long wavelength, so K will be small. Neglecting K^2 in (20) and (21) yields zero-order estimates of A and B:

$$A \approx \frac{P}{E - E_{\mathrm{v}}}\,, \tag{24}$$

$$B \approx -\frac{P}{\sqrt{2}\,(E - E_{\mathrm{so}})}\,. \tag{25}$$

These estimates, when used in (23), give a zero-order estimate of K^2:

$$\left(S + \frac{P^2}{E - E_{\mathrm{v}}} + \frac{P^2}{2(E - E_{\mathrm{so}})}\right)K^2 \approx E - E_{\mathrm{el}}\,. \tag{26}$$

Comparison of (26) and (9) using (14) shows that the value of K^2 as estimated in (26) is indeed a physically sound approximation in that the coefficient of K^2 closely resembles the local zone-centre inverse effective mass. The estimate of K^2 may then be used to initiate a rapidly converging iterative procedure determining A, B and K^2 by the use of equations (21)–(23), exploiting the fact that for known K^2 equations (21) and (22) are linear. The meaningful starting value of K^2 ensures that, within the conduction band, the converged values will not belong to the spurious solutions identified by a number of authors (White and Sham 1981; Schuurmans and 't Hooft 1985; Smith and Mailhiot 1990). Once a self-consistent set of A, B and K^2 is found at any one site in the sample, it becomes the initial estimate for use at neighbouring locations of slightly different composition. So with minimal further iteration A, B and K^2 may be quickly calculated as functions of position throughout the sample.

Returning to equations (4) and (5) as substituted by (17), (18) and (20), the second pair of equations deduced by SOQ is

$$\begin{aligned}[E - E_{\mathrm{v}} + (\gamma_1 + 2\gamma_2)K^2]a - 2\sqrt{2}\,\gamma_2 K^2 b + [(\gamma_1 + 2\gamma_2)A - 2\sqrt{2}\,\gamma_2\,B]K^2 k \\ = -\frac{\partial}{\partial z}\{[(\gamma_1 + 2\gamma_2)A - 2\sqrt{2}\,\gamma_2\,B]K^2\} \\ - \left((\gamma_1 + 2\gamma_2)\frac{\partial A}{\partial z} - 2\sqrt{2}\,\gamma_2\,\frac{\partial B}{\partial z}\right)K^2 + \tfrac{1}{2}\,\frac{\partial P}{\partial z}\,,\end{aligned} \tag{27}$$

$$\begin{aligned}-2\sqrt{2}\,\gamma_2\,K^2 a + (E - E_{\mathrm{so}} + \gamma_1\,K^2)b + (\gamma_1\,B - 2\sqrt{2}\,\gamma_2\,A)K^2 k \\ = -\frac{\partial}{\partial z}[(\gamma_1\,B - 2\sqrt{2}\,\gamma_2\,A)K^2] - \left(\gamma_1\,\frac{\partial B}{\partial z} - 2\sqrt{2}\,\gamma_2\,\frac{\partial A}{\partial z}\right)K^2 - \frac{1}{2\sqrt{2}}\,\frac{\partial P}{\partial z}\,.\end{aligned} \tag{28}$$

In like manner, (20) substituted into (19) proves a third relation

$$-Pa + \sqrt{\tfrac{1}{2}}\,Pb - (S + PA - \sqrt{\tfrac{1}{2}}\,PB)k$$
$$= \frac{\partial}{\partial z}(S + PA - \sqrt{\tfrac{1}{2}}\,PB) - \tfrac{1}{2}(A - \sqrt{\tfrac{1}{2}}\,B)\frac{\partial P}{\partial z}\,. \quad (29)$$

With all parameters tabulated, including A, B and K^2, equations (27)–(29) form a set of linear equations determining a, b and k, and as expected these are all seen to be small quantities, as is shown by the explicit forms of the equations. If K^2 is small, these relations simplify to

$$a = \tfrac{1}{2}(E - E_{\mathrm{v}})^{-1}\,\frac{\partial P}{\partial z}\,, \quad (30)$$

$$b = \frac{1}{2\sqrt{2}}(E - E_{\mathrm{so}})^{-1}\,\frac{\partial P}{\partial z}\,, \quad (31)$$

$$k = \frac{\partial}{\partial z}\,\ln[K^2/(E - E_{\mathrm{el}})]\,. \quad (32)$$

Thus the procedure for deducing the coupled functions ψ, θ, ϕ for some nominated energy E is as follows:

(i) Tabulate the band parameters $\gamma_1, \gamma_2, S, P, E_{\mathrm{el}}, E_{\mathrm{v}}, E_{\mathrm{so}}$ at each of the grid positions using equations (7)–(14); (ii) initiate an iterative process using (26) and thus tabulate at all grid positions A, B and K^2 from equations (21)–(23); (iii) use equations (27)–(29) to deduce a, b and k at each grid position; (iv) solve equations (20) for ψ using any standard numerical procedure; and (v) construct θ and ϕ from equations (17) and (18) respectively.

Since equation (20) is second order, steps (iv) and (v) yield two linearly independent sets of solutions.

If the energy E is in the valence range, it is clear that equations (24)–(26) are unsuitable for starting the iterative process. More suitable expressions may be constructed by rewriting (23) as

$$K^2 = [E - E_{\mathrm{el}} - PK^2(A - \sqrt{\tfrac{1}{2}}\,B)]/S\,, \quad (33)$$

and then in equations (21) and (22) neglecting the energy differences that cause the difficulties in (24)–(26). The alternative initial estimate of A and B is then

$$A = (P/K^2)/(\gamma_1 + 4\gamma_2)\,, \quad (34)$$

$$\sqrt{\tfrac{1}{2}}B = -\,\tfrac{1}{2}A\,, \quad (35)$$

and this leads to the alternative initial estimate of K^2 of

$$K^2 = [E - E_{\mathrm{el}} - 1{\cdot}5P^2/(\gamma_1 + 4\gamma_2)]/S\,, \quad (36)$$

Again iterative refinement is rapid and is then followed by steps (iii)–(v) above. The solutions corresponding to these values of K^2 are of short-scale distance and thus have large magnitudes for K^2, thereby *post facto* adding legitimacy to the neglect of $(E - E_{\mathrm{v}})/K^2$ and $(E - E_{\mathrm{so}})/K^2$ in constructing the initial estimate. These solutions are the 'spurious solutions' mentioned above.

(2c) Light Holes

The procedure for light holes parallels that for the conduction states. For the purposes of derivation, the notion is that an energy appropriate to light hole states allows oscillatory solutions, this time with θ leading the establishment of wavelength, and with ψ and ϕ locally following. Thus, again recognising θ and ϕ to be more or less in phase, and ψ to be more or less out of phase with these two, the parametrised equations which start the derivation are

$$\psi = A\frac{\partial\theta}{\partial z} + a\theta\,, \tag{37}$$

$$\phi = B\theta + b\frac{\partial\theta}{\partial z}\,, \tag{38}$$

$$\frac{\partial^2\theta}{\partial z^2} = -K^2\theta + k\frac{\partial\theta}{\partial z}\,. \tag{39}$$

The SOQ procedure is used again following substitution of (37)–(39) into (3)–(5), and this leads directly to

$$A = \frac{P(-\epsilon_3 + 2\gamma_2 K^2)}{\epsilon_1\,\epsilon_3 - \frac{1}{2}P^2K^2}\,, \tag{40}$$

$$B = \frac{(2\sqrt{2}\,\gamma_2\,\epsilon_1 - \sqrt{\tfrac{1}{2}}\,P^2)K^2}{\epsilon_1\,\epsilon_3 - \frac{1}{2}P^2K^2} \tag{41a}$$

$$= \sqrt{2}(1 + \epsilon_1\,A/P)\,, \tag{41b}$$

$$-(\gamma_1 + 2\gamma_2 + PA - 2\sqrt{2}\,\gamma_2\,B)K^2 = E - E_{\mathrm{v}}\,. \tag{42}$$

The coefficient of K^2 in (42) resembles the inverse effective mass for light holes as is seen by comparison of (42) with (10), a comparison made more vivid when the small K approximation is made. Thus, for energies near the top of the light hole band,

$$A \approx \frac{P}{E_{\mathrm{el}} - E}\,, \tag{43}$$

$$B \approx 0\,, \tag{44}$$

and the initial estimate of K^2 is

$$K^2 \approx \frac{E_\mathrm{v} - E}{\gamma_1 + 2\gamma_2 + P^2/(E_\mathrm{el} - E)} \,. \tag{45}$$

The initial estimate of K^2 from (45) launches the iterative determination of A, B and K^2 through the use of equations (40)–(42), a rapidly converging procedure. Once more the appearance of a coefficient for K^2 resembling the effective mass expression ensures that, for energies in the valence band, K^2 will not correspond to a spurious solution.

If the energy E is in the conduction band, the initial estimates (43)–(45) are not appropriate because of the potentially vanishing energy denominator $E - E_\mathrm{el}$. More convenient forms can be found by a minor extension of the derivation. Using equations (37), (38) and (41b) in (4) provides A in terms of K^2:

$$A = P\epsilon_4/(4\gamma_2\,\epsilon_1 - P^2)K^2 \,. \tag{46}$$

Next we eliminate ψ between equations (4) and (5):

$$K^2 = -[E - E_\mathrm{v} + \sqrt{2}\Delta\, B/(1 + \sqrt{2}\, B)]/(\gamma_1 - 2\gamma_2) \,. \tag{47}$$

For K^2 given by this relationship it immediately follows that

$$\epsilon_4 = -\sqrt{2}\Delta\, B/(1 + \sqrt{2}\, B) \,. \tag{48}$$

Since this is small when Δ is small, it is reasonable to expect that A, which contains a factor of ϵ_4, will also be small. Thus the estimates for this case, replacing (43)–(45), are

$$A \approx 0 \,, \tag{49}$$

$$B \approx \sqrt{2} \,, \tag{50}$$

$$K^2 = (E_\mathrm{v} - E - 2\Delta/3)/(\gamma_1 - 2\gamma_2) \,. \tag{51}$$

Self-consistency is rapidly achieved by the use of these initial estimates in equation (46) which then leads to (41b) and (47), yielding A, B and K^2 respectively.

The set of equations complementary to those used to determine A, B and K^2, as provided by SOQ, determines a, b and k. They are

$$\epsilon_1\, a + \frac{PK^2}{\sqrt{2}}\, b - SAK^2 k$$

$$= \frac{\partial}{\partial z}\left(SAK^2 + \frac{PB}{2\sqrt{2})}\right) + SK^2\,\frac{\partial A}{\partial z} + \frac{P}{2\sqrt{2}}\,\frac{\partial B}{\partial z} - \tfrac{1}{2}\,\frac{\partial P}{\partial z} \,, \tag{52}$$

$$Pa + 2\sqrt{2}\,\gamma_2 K^2 b + (PA + \gamma_1 + 2\gamma_2 - 2\sqrt{2}\,\gamma_2 B)k = -P\frac{\partial A}{\partial z} - \frac{A}{2}\frac{\partial P}{\partial z}$$

$$- \frac{\partial}{\partial z}(\gamma_1 + 2\gamma_2) + 2\sqrt{2}\left(B\frac{\partial \gamma_2}{\partial z} + 2\gamma_2\frac{\partial B}{\partial z}\right), \qquad (53)$$

$$Pa + \sqrt{2}\,\epsilon_3 b + (PA + 4\gamma_2 - \sqrt{2}\,\gamma_1 B)k = -P\frac{\partial A}{\partial z} - \frac{A}{2}\frac{\partial P}{\partial z} - 4\frac{\partial \gamma_2}{\partial z}$$

$$+ \sqrt{2}\left(\frac{\partial \gamma_1}{\partial z}B + 2\gamma_1\frac{\partial B}{\partial z}\right). \qquad (54)$$

Once (40)–(42) have been solved, all coefficients in (52)–(54) are known and so elementary procedures yield the desired values of a, b and k.

It follows that a second set of ψ, θ, ϕ which satisfy the coupled equations (3)–(5) may be obtained as follows:

(i) Tabulate the band parameters $\gamma_1, \gamma_2, S, P, E_{\mathrm{el}}, E_{\mathrm{v}}, E_{\mathrm{so}}$ at each grid position as before: (ii) commence the self-consistent determination of A, B and K^2 at each grid position with the estimate of K^2 given by equations (43)–(45), or for conduction band energies the alternate set (49)–(51), then proceed via the iterative use of (40), (41) and (42); (iii) use equations (52)–(54) to solve for a, b and k; (iv) use standard methods to solve equation (39)—two linearly independent solutions may be obtained; and (v) construct ψ and ϕ from (37) and (38)—for each of the two solutions θ obtained in the previous step, separate pairs of functions ψ and ϕ may be constructed.

(2d) Spin–Orbit Split-off States

The theme used in the previous two subsections is replayed here with the appropriate variations. The previously recognised phase relations commence the derivation with

$$\psi = A\frac{\partial \phi}{\partial z} + a\phi, \qquad (55)$$

$$\theta = B\phi + b\frac{\partial \phi}{\partial z}, \qquad (56)$$

and the local variation of ϕ is given by

$$\frac{\partial^2 \phi}{\partial z^2} = -K^2\phi + k\frac{\partial \phi}{\partial z}. \qquad (57)$$

Substitution of (55)–(57) into (3)–(5) followed by SOQ yields

$$A = \frac{P}{\sqrt{2}}\left(\frac{\epsilon_2 - 4\gamma_2 K^2}{\epsilon_1 \epsilon_2 - P^2 K^2}\right), \tag{58}$$

$$B = \frac{K^2}{\sqrt{2}}\left(\frac{4\gamma_2 \epsilon_1 - P^2}{\epsilon_1 \epsilon_2 - P^2 K^2}\right) \tag{59a}$$

$$= \sqrt{\tfrac{1}{2}} - \epsilon_1 A/P, \tag{59b}$$

$$(\gamma_1 - \sqrt{\tfrac{1}{2}}\, PA - 2\sqrt{2}\,\gamma_2 B)K^2 = E_{\mathrm{so}} - E. \tag{60}$$

The small-K approximation is appropriate to energies high in the spin–orbit split-off band, and leads to initial estimates of

$$A \approx \frac{P}{\sqrt{2}}\left(\frac{1}{E - E_{\mathrm{el}}}\right), \tag{61}$$

$$B \approx 0, \tag{62}$$

$$\left(\gamma_1 + \tfrac{1}{2}\frac{P^2}{E_{\mathrm{el}} - E}\right)K^2 \approx E_{\mathrm{so}} - E. \tag{63}$$

Comparison of (63) with (11) [using (13) and (14)] clearly shows that (60) is structured to present a similarity to the effective mass equation for such states. Iteration is commenced with the estimate from (63), or from the alternative result below, and leads to the self-consistent solutions at each grid position for A, B and K^2 from (58)–(60), and for energies E in the range appropriate to spin–orbit states they would not be on a spurious solutions branch.

The starting values (61)–(63) are inappropriate for energies in the conduction band because of the potentially vanishing energy denominator. Alternative starting values may be derived by similar procedures to those used already. Elimination of ψ between equations (4) and (5) yields

$$B = -\sqrt{2}[1 + \Delta/(\epsilon_2 - 4\gamma_2 K^2)], \tag{64}$$

so that, on regarding Δ as a small quantity, the initial value of B is

$$B \approx -\sqrt{2}. \tag{65}$$

Use of this together with $\epsilon_1 \to -SK^2$ in (59b) provides the alternative estimate of A:

$$A \approx -3P/\sqrt{2}\,SK^2. \tag{66}$$

These estimates of A and B when used in (60) provides the alternative starting estimate

$$K^2 \approx -(E - E_{\mathrm{so}} + 1{\cdot}5P^2/S)/(\gamma_1 + 4\gamma_2). \tag{67}$$

The parallel with the estimate (36) is evident, so these are the short-scale distance solutions for conduction states.

The relations complementary to (58)–(60) as derived by SOQ are

$$\epsilon_1 a - PK^2 b - SAK^2 k = \frac{\partial}{\partial z}(SAK^2 - PB) + SK^2 \frac{\partial A}{\partial z} + \tfrac{1}{2}(B + \sqrt{\tfrac{1}{2}})\frac{\partial P}{\partial z}, \tag{68}$$

$$-Pa + \epsilon_2 b - [PA + (\gamma_1 + 2\gamma_2)B - 2\sqrt{2}\,\gamma_2]k = P\frac{\partial A}{\partial z} + \frac{A}{2}\frac{\partial P}{\partial z} + B\frac{\partial}{\partial z}(\gamma_1 + 2\gamma_2) + 2(\gamma_1 + 2\gamma_2)\frac{\partial B}{\partial z} - 2\sqrt{2}\frac{\partial \gamma_2}{\partial z}, \tag{69}$$

$$Pa - 4\gamma_2 K^2 b + (PA - \sqrt{2}\gamma_1 + 4\gamma_2 B)k = -P\frac{\partial A}{\partial z} - \frac{A}{2}\frac{\partial P}{\partial z} - 4\frac{\partial \gamma_2}{\partial z}B - 8\gamma_2\frac{\partial B}{\partial z} + \sqrt{2}\frac{\partial \gamma_1}{\partial z}. \tag{70}$$

Thus the steps required for the determination of this third set of functions which solve the coupled equations (3)–(5) are similar to the other procedures:

(i) Tabulate the band parameters $\gamma_1, \gamma_2, S, P, E_{\mathrm{el}}, E_{\mathrm{v}}, E_{\mathrm{so}}$ at each grid position as the most elementary requirement; (ii) initiate the self-consistent determination of A, B and K^2 with the use of (63) or (67), then iterate to desired tolerance the relations (58)–(60); (iii) calculate the remaining parameters a, b, k provided by the linear equations (68)–(70); (iv) solve the second-order differential equation (57) which can provide two linearly independent solutions; and (v) construct the dependent functions ψ and ϕ from (55) and (56), one set of ψ and θ for each of the two linearly independent solutions from the previous step.

(2e) The Physical Solutions

The boundary conditions usually specified for solutions of the coupled set of equations (3)–(5) are continuity across the boundary of the functions ψ, θ, ϕ and of the first integrals of equations (3)–(5). Thus six conditions are to be met, and the procedures of the previous three subsections can each supply two linearly independent sets of solutions, apparently meeting the requirement. That is, routine application of standard procedures suggests the construction of physical solutions as linear combinations of the six sets

$$\begin{bmatrix} \Psi \\ \Theta \\ \Phi \end{bmatrix} = \sum_{i=1}^{6} \alpha_i \begin{bmatrix} \psi_i \\ \theta_i \\ \phi_i \end{bmatrix}. \tag{71}$$

However, serious difficulties arise in following this apparently innocuous process, and inevitably some physical compromise is required. In order to establish a foundation for making some possible choice of compromises, such considerations will be set aside temporarily, and the discussion will proceed as if the difficulties were not present. The topic will be resumed.

If in the SL repetition length d there is more than one section of piecewise continuous material, matching at all but one of the boundaries (as described above) within length d is otherwise unconstrained. Once such matching has taken place the SL may be treated as though all repetition intervals consist of just one continuous material, so without loss of generality the assumption can be made that the material is of this latter kind. The matching across the boundary at the end of the repetition length must additionally satisfy the Bloch theorem, and thus the secular equation determining the wavevector q is generated:

$$\sum_{i=1}^{6} C_{ji}(d)\alpha_i = \mathrm{e}^{\mathrm{i}qd} \sum_{i=1}^{6} C_{ji}(0)\alpha_i \,, \tag{72}$$

where

$$C_{1i}(z) = \psi_i(z) \,, \tag{73}$$

$$C_{2i}(z) = -S\,\frac{\partial\psi_i}{\partial z} - \frac{P}{2}(\theta_i - \sqrt{\tfrac{1}{2}}\,\phi_i) \,, \tag{74}$$

$$C_{3i}(z) = \theta_i \,, \tag{75}$$

$$C_{4i}(z) = (\gamma_1 + 2\gamma_2)\frac{\partial\theta_i}{\partial z} + \frac{P}{2}\,\psi_i - 2\sqrt{2}\,\gamma_2\,\frac{\partial\phi_1}{\partial z} \,, \tag{76}$$

$$C_{5i}(z) = \phi_i(z) \,, \tag{77}$$

$$C_{6i}(z) = \gamma_1\,\frac{\partial\phi_i}{\partial z} - 2\sqrt{2}\gamma_2\,\frac{\partial\theta_i}{\partial z} - \frac{P}{2\sqrt{2}}\,\psi_i \,. \tag{78}$$

As described in Sections $2b$–$2d$ the procedure in each centred on what may be called a prime function, with the other functions being derivative from the prime function. For each subsection the prime function achieves a physical significance for energy ranges appropriate to that function, in that a meaningful effective mass is associated with that function. Thus, in each range physical solutions should exist where these prime functions dominate the expansion (71). A check is now made to confirm that the structure of the matrix $C(z)$ as specified in (73)–(78) permits the fulfilment of this expectation.

First consider the conduction states. Let $i = 1$ and 2 in equations (72)–(78) indicate the two sets of solutions from Section $2b$. Consider the possibility of $\alpha_3 = \alpha_4 = \alpha_5 = \alpha_6 = 0$ in equation (71). In this case the eigenvalue problem posed by (72) would reduce to three 2×2 matrix equations which must be satisfied simultaneously:

$$\begin{pmatrix} C_{j,1}(d) & C_{j,2}(d) \\ C_{j+1,1}(d) & C_{j+1,2}(d) \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \mathrm{e}^{\mathrm{i}qd} \begin{pmatrix} C_{j,1}(0) & C_{j,2}(0) \\ C_{j+1,1}(0) & C_{j+1,2}(0) \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} . \tag{79}$$

Equations (17) and (18) show that at either $z = 0$ or $z = d$ both θ and ϕ are almost proportional to $\partial\psi/\partial z$ (in as much as a and b have been demonstrated to be small), so that $C_{3,i}$ and $C_{5,i}$ are multiples of $C_{2,i}$, also C_{4i} and C_{6i} are

multiples of C_{1i}, and the multiples are independent of the two values of i. If the multiples were also independent of z, then they could be cancelled throughout equation (79), leaving the three 2×2 matrix equations identical, justifying the solutions α_1, $\alpha_2 \neq 0$, $\alpha_3 = ... = \alpha_6 = 0$. This is the case of a uniform material. Thus the appearance of nonzero coefficients $\alpha_3, ..., \alpha_6$ for the conduction states is dependent on the extent to which the multiples (composed of the spatially dependent band parameters) change in the repetition length d. These coefficients would be small in the sense that, if it were possible to start with a uniform material and then continuously vary the concentrations to reach the final composition, the coefficients $\alpha_3, ..., \alpha_6$ would start at zero and grow as the composition varied. Similar considerations may be used to show that, in the appropriate energy ranges, expansions (71) may be found in which solutions from Section $2c$ and then from Section $2d$ respectively dominate the physical solutions.

The problem with this comfortable procedure has been well enunciated by Schuurmans and 't Hooft (1985), and in the above it has been pointed out that crucial relationships are equivalent to features of their work. At any nominated energy E, the set of coupled equations (3)–(5) permits three values of K^2. One of these values represents solutions of such short wavelength or scale distance as to compromise the very meaning of an envelope function and it is undesirable to rely on such functions for an expansion such as (71). It is therefore not possible to find three sets of linearly independent, physically significant functions with which to carry out the matching procedure described above, and compromise is essential. The choices would seem to be as follows.

(a) Accept the short-scale distance solutions on the basis that the admixture of such functions will be small, and thereby unimportant, and it is of the nature of discontinuities to produce ripples or small-scale distance effects. This allows six sets of functions and the carrying through of the matching procedures described above. The compromise is in the level of physical significance to be given to details of such functions. The inclusion of short-scale distance functions is not without precedent (White and Sham 1981).

(b) Accept only the four sets of functions which conform to the usual concepts about envelope functions, and in this case two of the matching conditions must be abandoned. For the conduction states it would seem reasonable, if this course is adopted, that the conditions to retain would be those relating to the magnitudes of the three functions Ψ, Θ and Φ, and to the first integral of equation (3). That is, in (72) delete from consideration $C_{4,i}$ and $C_{6,i}$. For light holes and spin–orbit split-off states, the energetic proximity of the functions would make conditions on the magnitudes of Θ and Φ and on the first integrals of equations (4) and (5) the desirable conditions to meet. That is, in (72) $C_{1,i}$ and $C_{2,i}$ would be ignored, the latter in parallel with the Schuurman and 't Hooft choice of $s = 0$ for valence states.

(c) Abandon all but the two solutions produced by the equation for the prime function in its appropriate energy range. In this case only the prime function and its derivative can be matched, or else the prime function and the first integral of the differential equation which was solved to produce the prime function. In this case the support functions which led to the establishment of that differential equation are not subject to any form of explicit matching.

(d) Approximate the prime function differential equations by replacing the effective-mass-like coefficients with the spatially varying effective masses. That is, in analogy to equation (15), solve in the appropriate energy ranges the equations

$$-\frac{\partial}{\partial z}\left(\frac{m}{m_{\mathrm{el}}}\frac{\partial\psi}{\partial z}\right) = (E - E_{\mathrm{so}})\psi\,, \tag{80}$$

$$-\frac{\partial}{\partial z}\left(\frac{m}{m_{\mathrm{lh}}}\frac{\partial\theta}{\partial z}\right) = (E_{\mathrm{v}} - E)\theta\,, \tag{81}$$

$$-\frac{\partial}{\partial z}\left(\frac{m}{m_{\mathrm{so}}}\frac{\partial\phi}{\partial z}\right) = (E_{\mathrm{so}} - E)\phi\,. \tag{82}$$

Again only two conditions are to be met and two functions are available.

3. Application

The principles emerging from the above theory are as follows:

(i) At the principal extrema, the decoupled equations exhibit a strong similarity to the very much simplified equations (80)–(82). Thus one would expect that both approaches would yield similar values for the principal energy gaps and effective masses. Of course, with spatially varying E_{v} and E_{so} the energy denominators in equations (26), (45) and (63) are not strictly equal to the energy gaps required by equations (9)–(11), (13) and (14), so the agreement is not exact.

(ii) The decoupled equations incorporate the non-parabolicity expected of the coupled set of equations (3)–(5), and this can make the sub-band widths and gaps deduced from them differ strongly from those deduced from the simplified set (80)–(82) which do not incorporate non-parabolicity.

(iii) There is an inevitable approximation which is built into the coupled equations themselves by virtue of their origin in a limited basis set, and this is reflected in the character of the solutions available. Several practical methods of meeting the difficulties have been suggested, but the degree to which their predictions would differ is not easily assessed *a priori*, and thus a numerical test is worth while. However, it is expected that the physically reasonable criterion that differences will mostly be dependent on the changes in the band parameters in one repetition length will be met.

(iv) An important parameter, the band offset ratio, has made no explicit appearance in the above theory, but will have an important impact on the spatial variation at all energy differences, and thereby on the detailed solutions, bandwidths and bandgaps. This consideration is not unique to the present methodologies.

Table 1. Input parameters for the calculations

	m_{el}/m_0	m_{hh}/m_0	m_{lh}/m_0	m_{so}/m_0	E_{g} (eV)	Δ (eV)
GaAs	0·067	0·454	0·070	0·143	1·43	0·343
$Ga_{0\cdot25}Al_{0\cdot75}As$	0·094	0·510	0·090	0·172	1·82	0·327

In order to make a numerical assessment of principles (i)–(iii), model calculations have been carried out for a sawtooth SL of composition $Ga_{1-x}Al_xAs$; that is, x varies linearly with distance from zero at one side of a layer to some maximum value at the other side, then abruptly drops back to zero at the start of the next layer. The sawtooth grading profile was selected for computational advantage in that it permits a single solution to yield results for a range of superlattice repetition lengths (SRL), representing a range of effective confinement potentials. Three gradings of aluminum concentration were used. The first, indicated by the numeral 1 in the accompanying tables, assumed $x = 0\cdot25$ at 16 nm from the pure GaAs side of the layer; in like manner the second and third gradings, indicated in the tables by the numerals 2 and 3 respectively, had $x = 0\cdot25$ at 14 and 12 nm respectively. thus, for a SL of given length, increasing confinement potential corresponds to grade 1, grade 2 and grade 3 in that order. For a SL

Table 2. Conduction band energy (meV) and effective mass ($m/m_0\times10^3$) at the principal conduction band minimum as calculated by the four methods of Section 2*e* for a $Ga_{1-x}Al_xAs$ sawtooth superlattice for three superlattice repetition lengths

The grades of aluminium concentration and the definition of the energy origin are described in Section 2

Grade	SRL (nm)	External energy (a)	(b)	(c)	(d)	Effective mass (a)	(b)	(c)	(d)
1	2	872·4	872·5	872·8	872·7	69·6	69·5	69·1	68·2
	8	914·3	914·6	915·2	914·6	74·5	74·5	74·2	74·8
	14	940·8	941·1	942·7	940·6	160·3	156·3	155·8	166·1
2	2	874·4	874·6	874·9	874·8	69·8	69·8	69·2	68·4
	8	921·9	922·3	923·1	922·3	76·2	76·1	76·0	76·6
	14	949·9	950·1	952·3	949·5	200·1	194·7	183·9	214·7
3	2	877·0	877·3	877·7	877·6	69·5	69·5	69·5	68·7
	8	931·9	932·3	933·5	932·3	78·4	78·4	78·3	79·3
	14	961·3	961·2	964·4	960·4	272·5	273·1	268·5	330·9

Table 3. Conduction bandwidths (bold type) and bandgaps (meV) and zone-centre (bold) and zone-boundary effective masses ($m/m_0\times10^3$) calculated by the four methods of Section 2*e*

The data are for the first five bands of the sample with the largest confinement potential considered, i.e. the one with the steepest composition grading (grade 3) and the largest repetition length, 14 nm

Band number	Bandwidth/bandgap (a)	(b)	(c)	(d)	Zone centre/zone boundary eff. mass (a)	(b)	(c)	(d)
1	**3·20**	**3·14**	**3·34**	**2·74**	**272·5**	**273·1**	**268·5**	**330·9**
	82·2	82·2	80·3	87·2	−223·1	−228·6	−202·2	−256·0
2	**22·1**	**22·0**	**23·4**	**24·1**	47·8	48·1	46·3	45·1
	46·7	47·2	43·9	52·9	**−22·7**	**−23·0**	**−20·7**	**−20·3**
3	**58·0**	**57·3**	**60·9**	**71·4**	**13·5**	**15·1**	**14·2**	**12·4**
	28·4	29·3	24·2	38·4	−6·2	−6·3	−5·3	−5·0
4	**90·5**	**89·3**	**94·8**	**126·5**	5·7	5·8	5·0	4·4
	19·4	21·1	14·8	33·9	**−3·5**	**−3·6**	**−2·9**	**−2·5**
5	**110·4**	**108·3**	**114·9**	**177·4**	**3·3**	**3·6**	**2·9**	**2·3**

Table 4. Light hole band energy (me V) and effective mass ($m/m_0 \times 10^3$) at the principal extremum calculated by the four methods of Section 2*e* for the same samples in Table 2

Grade	SRL (nm)	Extremal energy (a)	(b)	(c)	(d)	Effective mass (a)	(b)	(c)	(d)
1	2	579·8	579·8	581·5	581·8	72·6	72·6	72·0	71·0
	8	609·1	607·8	609·8	610·2	75·5	76·3	75·5	75·5
	14	626·9	628·2	630·8	630·9	89·8	115·6	111·1	115·4
2	2	582·8	580·8	582·8	583·2	72·3	73·0	72·3	71·1
	8	615·0	612·6	615·0	615·5	76·5	77·5	76·5	76·5
	14	637·8	634·8	637·8	637·8	125·8	131·7	125·8	107·5
3	2	582·2	582·1	584·5	585·1	73·6	73·5	72·7	71·3
	8	618·7	618·9	621·9	622·5	81·2	79·4	78·0	78·0
	14	641·7	643·1	646·8	646·4	95·5	156·3	148·0	162·4

Table 5. Light hole bandwidths (bold) and bandgaps (meV) and zone-centre (bold) and zone-boundary secondary effective masses ($m/m_0 \times 10^3$) for the first five bands, using the same 'maximum confinement potential' as in Table 3

Band number	Bandwidth/bandgap (a)	(b)	(c)	(d)	Zone-centre/zone-boundary eff. mass (a)	(b)	(c)	(d)
1	**8·52**	**5·89**	**6·21**	**5·74**	**95·5**	**156·3**	**148·0**	**162·4**
	50·2	54·4	53·8	59·6	−109·5	−110·4	−103·7	−112·2
2	**30·0**	**27·0**	**28·8**	**35·4**	44·5	39·3	37·4	32·6
	27·5	27·4	25·6	34·7	**−15·6**	**−15·8**	**−14·0**	**−10·6**
3	**47·1**	**49·7**	**51·8**	**86·9**	**13·3**	**13·4**	**12·1**	**8·1**
	13·4	12·1	11·9	26·2	−5·6	−6·4	−6·2	−3·4
4	**54·9**	**58·4**	**56·9**	**140·0**	6·7	6·4	6·3	3·1
	2·4	3·8	6·4	23·5	**−15·5**	**−4·1**	**−5·1**	**−1·8**
5	**56·3**	**55·5**	**54·6**	**189·5**	**8·3**	**4·1**	**5·1**	**1·7**

Table 6. Spin–orbit hole energy (meV) and effective mass ($m/m_0 \times 10^3$) at the principal extrema calculated by the four methods of Section 2*e*, for the same samples as in Tables 2 and 4

Grade	SRL (nm)	Extremal energy (a)	(b)	(c)	(d)	Effective mass (a)	(b)	(c)	(d)
1	2	923·9	923·9	924·0	923·8	144·5	144·5	144·0	144·9
	8	949·3	949·4	949·1	948·6	162·6	161·4	159·9	156·7
	14	963·7	963·9	963·5	962·6	137·1	154·2	478·7	419·7
2	2	925·3	925·2	925·3	925·1	143·5	144·3	143·5	145·2
	8	953·7	954·1	953·7	953·1	162·3	166·3	162·7	160·1
	14	967·4	969·7	968·8	967·7	163·9	164·5	673·2	510·9
3	2	927·0	927·0	927·1	926·8	145·5	145·9	144·2	145·4
	8	960·7	960·4	959·9	959·0	165·0	175·6	169·1	165·3
	14	977·5	977·2	975·6	974·0	152·6	191·2	1111·8	750·3

Table 7. Spin–orbit hole bandwidths (bold) and bandgaps (meV) and zone-centre (bold) and zone-boundary effective masses ($m/m_0 \times 10^3$) for the first five bands, using the same 'maximum confinement potential' as in Tables 3 and 5

Band number	Bandwidth/bandgap (a)	(b)	(c)	(d)	Zone-centre/zone-boundary eff. mass (a)	(b)	(c)	(d)
1	**3·68**	**4·3**	**0·80**	**1·06**	**152·6**	**191·2**	**111·8**	**750·3**
	48·9	47·6	53·0	50·1	−367·6	−485·6	−1271·5	−668·9
2	**15·4**	**17·0**	**13·3**	**10·7**	64·5	105·8	86·1	99·0
	29·7	28·3	32·9	30·7	**−30·4**	**−30·1**	**−35·0**	**−49·2**
3	**47·0**	**57·6**	**53·4**	**34·5**	**20·8**	**13·8**	**18·7**	**27·6**
	5·0	17·0	23·0	20·6	−6·0	−4·1	−5·3	−10·3
4	**136·4**	**113·7**	**112·4**	**64·2**	3·8	3·8	4·5	8·9
	43·3	15·6	16·6	16·5	**−2·8**	**−2·9**	**−2·1**	**−4·7**
5	**139·2**	**167·4**	**164·0**	**91·9**	**5·0**	**2·8**	**2·0**	**4·4**

of a given grade, increasing confinement potential increases with increasing SRL. In each case the parameters S, P, γ_1 and γ_2 needed for the application of the procedures described above were determined by first linearly interpolating (and, as needed, extrapolating) to all grid positions the principal energy gaps, the spin–orbit splittings, and the inverse effective masses, then at each grid position applying equations (7)–(14). The basis for the interpolation/extrapolation is the values given in Table 1 for GaAs and $Ga_{0\cdot75}Al_{0\cdot25}As$ which have been drawn from Schuurmans and 't Hooft (1985). For the purpose of interpolation/extrapolation of the quantities E_{el}, E_v and E_{so} appearing in equations (3)–(5), at every grid position the energy origin was taken in the gap with E_{el} equal to 60% of the gap at that position, in accordance with recent determinations (Miller *et al.* 1985; Menendez *et al.* 1986) of the band offsets in these materials. Four methodologies were used as described in the paragraphs (a), (b), (c) and (d) in Section 2*e* and in the tables these procedures are identified by these letters. Some preliminary results have already been reported (Duff and Hass 1990).

Some results of the model calculations for three SRL are given for conduction states in Tables 2 and 3, for valence states in Tables 4 and 5, and for spin–orbit states in Tables 6 and 7. The first of each pair of tables lists the principal band edges and effective masses. The second of each pair deals with the sample with the largest confinement potential of any treated in this study, i.e. the one with the steepest grading of aluminum (grade 3) and largest repetition length (14 nm), and for that sample lists the bandwidth, bandgap, zone-centre and zone-boundary effective masses for each of the first five bands.

In general the results are well described in terms of the principles enunciated above. In particular, at the principal band edges (Tables 2, 4 and 6) the band energies and effective masses calculated by the various methodologies are in substantial agreement, and any differences vary in a meaningful way with concentration gradient and repetition length. However, as expected, significant differences between the methodologies emerge for the properties at energies other than the principal extrema. Thus, in Tables 3, 5 and 7 the calculated bandwidths, bandgaps and secondary effective masses show greater sensitivity to the method used than the other data. Mostly, the inclusion of the short-scale distance functions appears to have little effect, as evidenced by the parallelism between

the results for methods (a) and (b), in agreement with the notion that the admixture of these functions would be small; this is encouraging as it is desirable to avoid the computational complexity of such functions if possible. There is also a measure of parallelism between the results of methods (c) and (d), and this is understandable as both approaches use a single differential equation with effective mass or effective-mass-like coefficients.

Which method should be used for grading profiles more general than the sawtooth grading considered here? If the properties of interest are confined to the neighbourhoods of the principal extrema, both the theoretical considerations and the detailed calculations show that the simplest procedures, methods (c) or (d) should be adequate. An exception occurs for the spin–orbit effective mass, where the energetic proximity of the valence levels have had a significant impact for the more highly confined states. For properties other than those mentioned, method (b) recommends itself as reflecting the best features of the full solution to the coupled equations without the complexity of the short-scale distance functions. There is a caution: the only properties considered here were those directly related to energy band structure—no wavefunction properties such as transition rates were considered. It is entirely possible that small admixtures of the undesirable functions may have a significant impact on transition rates and other properties, and provided the admixture is small, their presence may be tolerated. In this case the full complexity of method (a) would be needed, and it would be up to experiment to adjudicate on the level of credibility small admixtures of such functions may have.

4. Conclusion

The full content of the coupled equations derived from the Kane matrix, equations (3)—(5), is available for superlattices of arbitrary layer composition profile, using only relatively elementary procedures based on uncoupled equations. The key to the development of the methodology is the recognition of the phase relationships between the various envelope functions. At any energy the required mutual consistency between the conduction, valence and spin–orbit envelope functions is provided by the *local* self-consistency of the parameters A, B and K^2 as defined in the foregoing procedures. However, part of the 'full content' involves envelope functions of questionable validity, but the admixture of such functions should be small. For the applications of the procedures made in this work, the undesirable functions did not play an important role in the properties calculated, as anticipated.

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