Generalization of the effective mass method for semiconductor structures with atomically sharp heterojunctions

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Abstract

The Kohn-Luttinger envelope-function method is generalized to the case of heterostructures with atomically sharp heterojunctions based on lattice-matched layers of related semiconductors with zinc-blende symmetry. For electron states near the Γ point in (001) heterostructures the single-band effective-mass equation is derived, taking into account both the spatial dependence of the effective mass and effects associated with the atomically sharp heterojunctions. A small parameter is identified, in powers of which it is possible to classify the various contributions to this equation. For hole states only the main contributions to the effective Hamiltonian, due to the sharpness of the heterojunctions, are taken into account. An expression is derived for the parameter governing mixing of states of heavy and light holes at the center of the 2D Brillouin zone.

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1 Introduction

The Kohn-Luttinger effective-mass method [1, 2] is widely used to describe electron states in semiconductors when applied are external fields varying smoothly over scales of the lattice constant a. Although the original method, based on the formalism of envelope functions, is applicable only to homogeneous semiconductors, various modifications of it have been used to describe the electron states in semiconductor heterostructures. In recent years there has been a revival of discussion on the applicability of the effective-mass method to describe electron and hole states in real nanostructures [3-22]. Many different modifications of the effective-mass method have been proposed, which apply
to the case of a spatially varying effective mass $m(r)$. There are two ways of constructing the effective-mass approximation for heterostructures. 1) Derivation of the effective Hamiltonian for the envelope functions, defined over all space. By integrating the effective-mass equation, which contains this Hamiltonian, near the heteroboundary it is possible to obtain boundary conditions on the envelope functions if needed. 2) Derivation or, as is done much more often, postulation of phenomenological boundary conditions on the envelope functions at the heteroboundary. This approach makes use of symmetry arguments, continuity of the probability flux density, etc. But these arguments, as a rule, are insufficient to uniquely determine the boundary conditions. The second approach is applicable in the case of sharp heterojunctions; all the models in which such boundary conditions were obtained dealt with mathematically sharp heterojunctions between the left-hand and right-hand materials. It is implicitly assumed that the envelope function on the left side (on the right side) of the heteroboundary satisfies the same equation as in the bulk case for the left-hand (right-hand) material. In this case the very delicate problem of the accuracy excess arises, which, by the way, has not been discussed to this date: the boundary conditions should hold with the same accuracy as the equations for the envelope functions hold.

Below we will follow the first approach, in which it is possible to rigorously treat the problem of accuracy, see Sec. 3.

It is well known that two main problems arise along the path of constructing a common equation for the envelope functions. The first is the problem of ordering the momentum operators in the kinetic-energy operator (due to the non-commutativity of the momentum operator and the function $m(r)$), on the form of which the solutions of the effective-mass equations can depend substantially [18]. The second problem is that the effective potential near a heteroboundary, as a rule, is not a smooth function on scales of the order of $a$. This calls into question even the validity of using differential equations in the method of envelope functions. Let us discuss these problems in the indicated order.

1.1 Account of the spatial dependence of the effective mass

A necessary condition for the applicability of the one-band equations for the envelope functions [one equation is understood here, valid near the bottom of the non-degenerate conduction band, or a system of equations for the degenerate valence band] used in the effective-mass method is “shallowness” of these states: their energy, measured from the band edge, should be small in comparison with the inter-band energy. Therefore, bearing in mind the one-band version of the effective-mass method, we restrict the discussion to heterostructures consisting of related materials, where the band offsets are small in comparison with the characteristic band gaps; this means, as a rule, that other band parameters of the semiconductors differ only slightly. Let us consider the first problem, which arises even for heterostructures whose chemical composition varies smoothly on scales of the order of $a$. As the zeroth-order potential we choose the potential of the crystalline lattice, continued to all space, of one of the materials of the structure [this
is not a unique choice, see Ref. [7], and we treat the difference between the potentials of the lattices of the remaining semiconductors as a small perturbation. Following the approach of Luttinger and Kohn and deriving the many-band $k \cdot p$ system of equations (see, e.g., Ref. [8]), we can next attempt to solve the problem of the correct order of the non-commuting operators in the kinetic-energy operator for the one-band equations. But here yet another problem arises.

Reduction of the many-band system of equations to a one-band effective-mass equation is achieved by eliminating the small envelope functions from the many-band $k \cdot p$ system in favor of the large ones by means of some procedure. We make a small departure here and make use of a formal analogy between the relativistic Dirac equation and the many-band $k \cdot p$ system of equations for the envelope functions [23], which is most simply seen in the two-band approximation (the conduction band and the non-degenerate valence band). In the relativistic theory there are two approaches to deriving an equation for shallow electron states. One of them consists in eliminating the small positron component of the wave function by the method of substitution. In this case, we obtain either an exact equation for the electron component, which is not an eigenvalue equation, Ref. [24], Ch. 20, Sec. 28, or an approximate equation whose Hermitian nature must be checked separately [25]. The second approach is a Foldy-Wouthuysen transformation, an approximate unitary transformation of the Dirac equation, Ref. [24], Ch. 20, Sec. 33.

In our case the first approach is comparatively simple to realize only in the two-band approximation, see, e.g., Ref. [26]. In a treatment of the contribution of distant bands, and this is necessary, in particular, for a valid description of the heavy holes, a number of problems arises. Thus, the authors of Refs. [14] and [20] were able to take into account only a few of the first-order corrections to the “standard” Kohn-Luttinger equation with position-independent effective mass [the small parameter here is the ratio of the characteristic band offset to the characteristic inter-band energy]. However, treating the expression obtained, for example, in Ref. [14] for the position-dependent effective mass, it can be shown that the effective mass of the edge of the conduction band of one of the non-basis semiconductors does not contain inter-band matrix elements of the perturbation potential, obtained using Bloch functions of the band edge of the basis crystal (see Sec. 4.1 below). It can be easily seen that this is equivalent to the poorly justified approach of neglecting the difference between the inter-band matrix elements of the momentum operator or, what is equivalent, the difference between the Bloch functions for the materials making up the structure.

Hence it follows that we should give special attention to the problem of taking distant bands into account. Efforts at solving it by direct elimination of the small envelope functions by the method of substitution, in addition to its laboriousness, lead finally to a non-Hermitian equation, whose solution is still in need of a valid interpretation.

Below we will follow the second approach, i.e., we will apply the unitary transformation eliminating the small envelope functions [1, 27]. Since we are considering heterostructures consisting of related materials, the standard effective-mass method will play the role of a first approximation. An account of the spatial dependence of the effec-
tive mass necessitates treating corrections to the standard theory, where it is necessary to take into account all corrections of the same order without the accuracy excess.

In order to understand what corrections should be taken into account, let us turn to the relativistic analogy with the hypothetical Dirac equation containing the inhomogeneous gap $2m(r)c^2$, where $c$ is the speed of light in vacuum (see Appendix A). The ordinary one-band effective-mass equation is an analog of the non-relativistic Schrödinger equation. It is important, however, that the effective mass in the two-band approximation is proportional to the local band gap $E_g(r)$ [this is valid if the effective mass is formed mainly by $k \cdot p$ interaction], and its relative variation $\delta m/m \approx \delta E_g/E_g$. Since the correction to the kinetic energy describing the spatial dependence of the effective mass will have a “relativistic” character, the desired equations for the heterostructures will be analogous to the Schrödinger equation with all relativistic corrections—both the usual ones (the contribution of nonparabolicity of the dispersion law, proportional to $p^4$, where $p$ is the momentum operator; the contribution of the spin-orbit interaction; and the so-called Darwin term, proportional to the second derivative of the potential energy) and a new pseudo-relativistic correction describing $\delta m(r)$. Of course, the present arguments are valid for describing states whose energies, reckoned from the band edge of any of the materials making up the structure, are of the order of the band offset. The case of a very small band offset, where the offset is small in comparison with the energies of the states is quite trivial: depending on the energies of the states under consideration an account of the spatial dependence of the effective mass can require treating terms with higher and higher powers of the momentum operator. We will not consider such a situation. In this sense, introducing a term proportional to the fourth power of the momentum operator into the effective-mass equation is a necessary condition for a consideration of the effective mass spatial dependence. Note that for homogeneous semiconductors an effective-mass equation analogous to the Schrödinger equation with first relativistic corrections was discussed already in Ref. \[27\] (Sec. 27).

A typical shortcoming of previous works dedicated to a generalization of the effective-mass method to electron states in heterostructures is that they take account within the framework of perturbation theory of only some of the terms of a given order. Thus, Refs. \[3\]-\[22\] take account of the spatial dependence of the effective mass parameters, but neglect corrections $\propto p^4$. In Refs. \[3\], \[10\], \[14\], \[21\], dedicated to deriving the one-band equations for the envelope functions directly from a many-band $k \cdot p$ system, the main error, leading to an invalid result, is an incorrect estimate, according to which the contribution of the $k \cdot p$ interaction terms [i.e., the terms $\hbar k p_{nn'}/m_0$, where $m_0$ is the free electron mass and $p_{nn'}$ is the inter-band matrix element of the momentum] is of order the contribution of the potential energy terms [by potential energy here we mean the difference in the periodic potentials of the semiconductors making up the structure, also treated in the perturbation theory context]. In the case of a smooth heterojunction the correct procedure for deriving the one-band effective-mass equation near the bottom of the conduction band with all the above-indicated contributions taken into account was followed in Ref. \[28\].
1.2 Account of atomically sharp heterojunctions

The second problem requiring careful study is the non-smooth nature of actual heterojunctions, where the transition from one material to the other occurs over scales of the order of $a$. In this case, first, Leibler’s many-band $\mathbf{k} \cdot \mathbf{p}$ system [3], where smoothness of the potential was a necessary condition for validity of the system, is in need of refinement, and second, the problem of transforming to $\mathbf{r}$ space from the region of $\mathbf{k}$ space bounded by the first Brillouin zone is more complicated [1]. It is also necessary to analyze the consequences of the unitary transformation eliminating distant bands. It is important to estimate the error that enters at each step. An estimate of this error either gives us confidence in the absence of an excess of accuracy or it challenges the validity of the effective-mass approximation. In the works known to us which treat sharp heterojunctions, such an estimate is lacking. References [14] and [20], for example, only point to its smallness, and Ref. [19] made some approximations whose accuracy were not even estimated.

Thus, we can formulate the following steps in the construction of an effective-mass approximation for heterostructures: a) obtaining a many-band $\mathbf{k} \cdot \mathbf{p}$ system of equations for the envelope functions taking proper account of possible sharpness of the heterojunction; b) reducing this system to one-band equations with the help of the unitary transformation to $\mathbf{k}$ space, transforming to $\mathbf{r}$ space and transforming the resulting equation to differential form; c) estimating the accuracy of these transformations. Following this scheme, step a) is realized in Sec. 2. The equations include contributions associated with the non-smoothness of the heterojunction on scales of order $a$ which are treated within the framework of an approach similar to that used in Ref. [27] to describe the short-range part of the impurity potential. Section 3 shows that a common differential equation over all space for the envelope functions for sharp heterojunctions exists, and its accuracy is determined by the procedure of transforming to one-band equations in $\mathbf{r}$ space. One-band equations are considered in Sec. 4.1 (the conduction band) and in Sec. 4.2 (the valence band). Section 4.3 is devoted to heterostructures with super-thin layers. It is shown that additional contributions to the “standard” effective-mass equation can be classified by powers of the small parameter $\bar{k}a_m$, where $\bar{k}$ is a characteristic value of the quasi-momentum of the state and $a_m$ is of the order of the lattice constant. Section 5 constructs a hierarchical scheme of effective-mass equations, the $n$th level of which corresponds to taking account of these additional contributions up to $(\bar{k}a_m)^n$ inclusively. The zeroth order of the hierarchy ($n = 0$) corresponds to the “standard” effective-mass equation with position-independent parameters. At the first level of the hierarchy each heteroboundary gives an additional $\delta$-function contribution to the potential energy. Only at the second level of the hierarchy does spatial dependence of the effective mass appear, along with corrections associated with weak nonparabolicity of the spectrum and heterointerface terms of the spin-orbit interaction. At higher levels of the hierarchy nonlocal contributions arise, and the one-band differential effective-mass equations do not exist. Results are compared with the conclusions of other authors. Brief reports on the results obtained have been published elsewhere [29]-[31].
Many-band $k \cdot p$ system of equations for envelope functions in the case of a sharp (001) heterojunction

Let us consider a heterojunction formed from related lattice-matched semiconductors with zinc-blende structure. The Schrödinger equation without relativistic corrections, which will be taken into account below, and in the absence of external potentials has the usual form

$$ \left( \frac{p^2}{2m_0} + U(r) \right) \Psi (r) = \epsilon \Psi (r). $$

Here $U(r) \equiv U$ is the crystal potential of the heterostructure. To start with, we will use the following model of this potential:

$$ U = U_1 \left( z \right) U_2 - U_1 \right) \equiv U_1 \left( z \right) \delta U, \quad (1) $$

where $U_1 \equiv U_1 (r)$ and $U_2 \equiv U_2 (r)$ are periodic (with the same period) potentials, continued through the entire structure, of the left-hand and right-hand materials, respectively, the $z$ axis is directed perpendicular to the plane of the heterojunction, $G(z)$ is the form factor of the heterojunction

$$ G(z) \left| z < -d \right. = 0, \quad G(z) \left| z > d \right. = 1; $$

and the width of the transitional region of the heterojunction is $2d$ [non-one-dimensionality of $G(z)$ will be taken into account below].

It is natural to treat the potential $G(z) \delta U$ as a perturbation. As the basis for expanding the wave function we use the complete orthonormal set of Kohn-Luttinger functions $\{u_{n0}e^{ik \cdot r}\}$:

$$ \Psi (r) = \sum_{n'} \int F_{n'}(k') e^{ik' \cdot r} u_{n0} \, d^3k', \quad (2) $$

where $u_{n0} \equiv u_{n0}(r)$ is the periodic Bloch amplitude for the edge $\epsilon_{n0}$ of the $n$th band of the left-hand crystal at the $\Gamma$ point of the Brillouin zone (in the non-relativistic limit),

$$ \left( \frac{p^2}{2m_0} + U_1 \right) u_{n0} = \epsilon_{n0} u_{n0}. $$

The sum in Eq. (2) is over all bands, and the integral is over the Brillouin zone here and in what follows unless otherwise stated; $F_n(k)$ is the envelope function for the $n$ band in $k$ space. Following the standard procedure [1], we obtain a system of $k \cdot p$ equations [3]:

$$ \left( \epsilon_{n0} + \frac{\hbar^2 k^2}{2m_0} \right) F_n(k) + \sum_{n'} \frac{\hbar p_{n'n} \cdot k}{m_0} F_{n'}(k) + $$

$$ + \sum_{n'} \int \mathcal{M}_{nn'}(k, k') F_{n'}(k') \, d^3k' = \epsilon F_n(k); \quad (3) $$
\[ \mathcal{M}_{nn'}(k, k') = \sum_j C_j^{nn'} \mathcal{G}(k_z - k'_z + K_{\|^j}) \delta \left( k_{\|^j} - k'_{\|^j} + K_{\|^j} \right). \]

Here \( p_{nn'} = \langle n | p | n' \rangle \) and \( C_j^{nn'} = \langle n | \delta U e^{iK_j r} | n' \rangle \), and the matrix elements of a periodic operator \( f \) are defined as follows:

\[
\langle n | f | n' \rangle = \frac{(2\pi)^3}{\Omega} \int_{\text{cell}} u_{n0}^* f u_{n'0} \, d^3r,
\]

where \( \Omega \) is the volume of the unit cell; \( k_{\|^j} = (k_x, k_y, 0) \), and \( K_{\|^j} \) and \( K_{\|^j} \) are the components of the vector \( K_{\|^j} \) of the inverse lattice perpendicular and parallel to the plane of the heteroboundary, respectively; \( \mathcal{G}(k_z) \) is the Fourier transform of \( G(z) \). Let us analyze the expression for the matrix elements \( \mathcal{M}_{nn'}(k, k') \):

\[
\mathcal{M}_{nn'}(k, k') = \sum_j C_j^{nn'} \mathcal{G}(k_z - k'_z + K_{\|^j}) \delta \left( k_{\|^j} - k'_{\|^j} \right) + \sum_j C_j^{nn'} \mathcal{G}(k_z - k'_z + K_{\|^j}) \delta \left( k_{\|^j} - k'_{\|^j} + K_{\|^j} \right).
\]

The second sum in Eq. (4) describes transfer processes in the two-dimensional Brillouin zone, when the projections of any pair of vectors \( k \) and \( k' \) from the bulk Brillouin zone onto the plane of the heterojunction satisfy the condition \( k_{\|^j} - k_{\|^j} = K_{\|^j} \neq 0 \). For a heterojunction of arbitrary orientation such transfer processes exist. However, for the orientation of interest to us—the (001) orientation—their contribution to the desired equations for the envelope functions disappears (see Appendix B):

\[
\mathcal{M}_{nn'}(k, k') = \delta \left( k_{\|^j} - k'_{\|^j} \right) \left[ \mathcal{G}(k_z - k'_z) \delta U_{nn'} + \sum_{j \neq 0} C_j^{nn'} \mathcal{G}(k_z - k'_z + K_j) \right],
\]

where we have introduced the notation: \( K_j = (4\pi/a)j; j = \pm 1, \pm 2, \ldots; \) and \( \delta U_{nn'} = C_0^{nn'} \).

If \( G(z) \) is a sufficiently smooth function, \( a \ll d \), and we are interested in states with \( k_z \ll 2\pi/a \), where \( k_z \) is a characteristic value of the quasi-momentum of the state, we can neglect the second term inside the brackets in Eq. (5) and as a result obtain the well-known set of equations for the envelope functions \[3, 28\]. In the case of an atomically sharp heterojunction, on the other hand, it is possible to proceed in the spirit of the method used in Ref. 27 to describe a short-range impurity potential. We introduce the function \( G'(z) \equiv dG(z)/dz \), localized on the heteroboundary, \( |z| \leq d \). Then for \( j \neq 0 \) we have:

\[
\mathcal{G}(k_z - k'_z + K_j) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G(z) e^{-i(k_z - k'_z + K_j)z} \, dz =
\]

\[
\frac{1}{2\pi i k_z - k'_z + K_j} \int_{-\infty}^{+\infty} G'(z) e^{-i(k_z - k'_z + K_j)z} \, dz =
\]
and we can write the sum in Eq. (5) in the form of an expansion in powers of $(k_z - k'_z)$:

$$
\sum_{j \neq 0} C_{j}^{mn'} G (k_z - k'_z + K_j) = \sum_{s=0,1,2,...} \frac{(k_z - k'_z)^s}{2\pi} D_{snn'}.
$$

The constants in the expansion (7) have the form

$$
D_{0nn'} = \sum_{j \neq 0} C_{j}^{mn'} \frac{1}{iK_j} \int_{-d}^{d} G'(z)e^{-iK_j z} dz,
$$

$$
D_{1nn'} = \sum_{j \neq 0} C_{j}^{mn'} \frac{1}{iK_j} \int_{-d}^{d} G'(z)e^{-iK_j z} \left( -\frac{1}{K_j} - iz \right) dz,\ldots
$$

The present approach fundamentally allows one to treat even mathematically sharp heterojunctions, since the necessary convergence of the coefficients $D_{nn'}$ is ensured by the property $C_{j}^{mn'} \to 0$ as $K_j \to \infty$ [but a physically realizable heterojunction cannot be mathematically sharp].

Let us consider the corrections associated with sharpness of the heterojunction. Simple estimates show that terms proportional to $D_{0nn'}, D_{1nn'}, \ldots$ can give corrections not greater in order of magnitude than $a\bar{k}_z$, $(a\bar{k}_z)^2$, $\ldots$, respectively. Our goal is to obtain one-band equations with position-dependent effective-mass parameters, which is achieved by taking account of corrections of order $(\lambda\bar{k}_z)^2$ to the standard approximation. Here we have introduced a characteristic “two-band” length $\lambda = \hbar(2mE_g)^{-1/2}$. For GaAs, for example, $\lambda \approx 6\Angstrom$. We will make use of the smallness of the parameter $d \cdot \bar{k}_z$, which will allow us to write down the final equation in quite simple form (see below).

Thus, three quantities having the dimensions of length, $a$, $d$, and $\lambda$, in combination with $\bar{k}_z$ form three parameters whose smallness is employed in the present method. In our view, the situation $a \ll d \ll \lambda$, is the most realistic, being realized in semiconductor heterostructures with sharp heteroboundaries. Thus, the parameter $\lambda\bar{k}_z$ can be taken as the main small parameter of the problem and the sum in Eq. (7) can be restricted to terms with $s = 0$ and $s = 1$.

As a result, the many-band system of $\mathbf{k} \cdot \mathbf{p}$ equations (3) takes the form

$$
0 = \left( \epsilon_{n0} - \epsilon + \frac{\hbar^2 k_z^2}{2m_0} \right) \mathcal{F}_n (\mathbf{k}) + \sum_{n'} \frac{\hbar p_{n'n'} \cdot \mathbf{k}}{m_0} \mathcal{F}_{n'} (\mathbf{k}) + \sum_{n'} \int \left[ G (k_z - k'_z) \delta U_{nn'} + \frac{1}{2\pi} D_{0nn'} + \frac{k_z - k'_z}{2\pi} D_{1nn'} \right] \mathcal{F}_{n'} (k'_z) \ d k'_z.
$$

Here we can distinguish different contributions of the perturbation potential: the contribution of the “smooth” part is represented by the first term inside the brackets, and the contribution of the “sharp” part is represented by the second and third terms.
2.1 Account of the 3D character of the form factor

Let us now consider instead of Eq. (1) a more realistic form of the heteropotential:

\[ U = U_1 + g \left( \mathbf{r}_\parallel, z \right) \delta U, \tag{9} \]

where \( \mathbf{r}_\parallel = (x, y, 0) \). By definition, \( g(\mathbf{r}_\parallel, z) \mid_{z < -d} = 0 \) and \( g(\mathbf{r}_\parallel, z) \mid_{z > d} = 1 \), and the function \( g(\mathbf{r}_\parallel, z) \) is periodic in \( \mathbf{r}_\parallel \). For our case of (001) heterostructure the unit translation vectors in the plane of the heteropotential are \( \mathbf{a}_1 = (1, 1, 0)a/2 \) and \( \mathbf{a}_2 = (-1, 1, 0)a/2 \). The sites of the two-dimensional inverse lattice with basis vectors \( \mathbf{b}_1 = (1, 1, 0)\pi/a \) and \( \mathbf{b}_2 = (-1, 1, 0)\pi/a \) are projections of the sites of the three-dimensional inverse lattice onto the (001) plane.

We expand \( g(\mathbf{r}_\parallel, z) \) in a 2D Fourier series:

\[ g \left( \mathbf{r}_\parallel, z \right) = \sum_l G_l(z) e^{i \mathbf{K}_l \mathbf{r}_\parallel}, \]

where the summation index \( l \) is defined so that the vectors \( \mathbf{K}_l \) determine the sites of the indicated two-dimensional inverse lattice, and

\[ G_l(z) = \frac{1}{\Omega_{\parallel}} \int_{\text{cell}} g \left( \mathbf{r}_\parallel, z \right) e^{-i \mathbf{K}_l \mathbf{r}_\parallel} d^2\mathbf{r}_\parallel; \]

The integration is over a unit cell of the 2D lattice with area \( \Omega_{\parallel} = a^2/2 \). Denoting \( G_l(z) \equiv G_0(z) \), we obtain for the perturbation potential

\[ g \left( \mathbf{r}_\parallel, z \right) \delta U = G(z) \delta U + \delta U \sum_{l \neq 0} G_l(z) e^{i \mathbf{K}_l \mathbf{r}_\parallel}. \tag{10} \]

It can be seen that the simple model (1) takes into account the first term in the sum (10). The functions \( G_l(z) \) for \( l \neq 0 \) are nonzero only for \( z \in [-d, d] \). Therefore, the left-hand side of Eq. (3) will include an additional sum of interface contributions:

\[ \sum_{n'} \int \mathcal{M}_{n'n'}(\mathbf{k}, \mathbf{k}') \mathcal{F}_{n'}(\mathbf{k}') d^3k', \]

where

\[ \mathcal{M}_{n'n'}(\mathbf{k}, \mathbf{k}') = \sum_{l \neq 0,j} \frac{C_{n'n'}^l}{(2\pi)^3} \int_{\text{all space}} G_l(z) e^{i \mathbf{K}_l \mathbf{r}} e^{-i (\mathbf{k} - \mathbf{k}') \mathbf{r}} d^3r. \]

For states with \( |k_x| + |k_y| < \pi/a \) (see Appendix B) we obtain

\[ \mathcal{M}_{n'n'}(\mathbf{k}, \mathbf{k}') = \delta \left( \mathbf{k}_\parallel - \mathbf{k}_\parallel' \right) \sum_{l \neq 0,j} \frac{C_{n'n'}^l}{2\pi} \delta_{\mathbf{K}_l, \mathbf{K}_l} \int_{-d}^{d} G_l(z) e^{-i (k_x k_x' + K_x z)} dz = \]

\[ = \delta \left( \mathbf{k}_\parallel - \mathbf{k}_\parallel' \right) \sum_{j(\mathbf{K}_l, j \neq 0)} \frac{C_{n'n'}^l}{2\pi} \int_{-d}^{d} d^2\mathbf{r}_\parallel \int_{\text{cell}} d^2\mathbf{r} g \left( \mathbf{r}_\parallel, z \right) e^{-i \mathbf{K}_l \mathbf{r}_\parallel} e^{-i (k_x k_x' + K_x z)}. \]
For a smooth heterojunction it is necessary to retain only terms with $K_{zj} = 0$ in the sum and develop the expression in the standard way \[3\], since the equations for the envelope functions in the $r$ representation will include an additional interface potential. Note that while the smooth part of $G(z)\delta U$ ensures mixing of states of the same crystal symmetry [i.e., the local symmetry of the smooth part of the perturbation potential $G(z)\delta U$ coincides with the symmetry of the bulk crystal], this additional potential also ensures mixing of states of different symmetry. We are interested in the case $d \cdot \vec{k}_z \ll 1$, and this obviates the necessity of separating effects of this additional potential into contributions of smooth and sharp parts and allows us to use the expansion

$$ \mathcal{M}_{nn'}(\mathbf{k}, \mathbf{k}') = \delta \left(\mathbf{k} - \mathbf{k}'\right) \sum_{s=0,1,2,...} \frac{(k_z - k'_z)^s}{2\pi} \mathcal{D}_{snn'}, $$

where

$$ \mathcal{D}_{0nn'} = \sum_{j(K_{||} \neq 0)} \frac{C_{nn'}^{mn'}}{\Omega_{||}} \int dz \int_{2D_{\text{cell}}} d^2r_{||} g \left(\mathbf{r}_{||}, z\right) e^{-i\mathbf{K}_j \cdot \mathbf{r}}, $$

$$ \mathcal{D}_{1nn'} = \sum_{j(K_{||} \neq 0)} \frac{C_{nn'}^{mn'}}{\Omega_{||}} \int dz \int_{2D_{\text{cell}}} d^2r_{||} g \left(\mathbf{r}_{||}, z\right) e^{-i\mathbf{K}_j \cdot \mathbf{r} (-iz)}, \ldots $$

In the expansion (11) it is necessary to keep only the first two terms; the terms proportional to $\mathcal{D}_{0nn'} \mathcal{D}_{1nn'}$ can give contributions of order $d \cdot \vec{k}_z$ and $(d \cdot \vec{k}_z)^2$, respectively.

We have shown that taking the three-dimensionality of the form factor into account (see Eq. \[3\]), causes no special difficulty for analysis, and we now make an important observation which will allow us to use the simple model \[1\]. The function $g(\mathbf{r}_{||}, z)$ has lower symmetry than $G(z)$. Specifically, it is invariant under symmetry transformations from the point group $C_{2v}$. But the complete perturbation potential in both models, \[1\] and \[3\], possesses the same symmetry, both its point-group symmetry ($C_{2v}$) and translational symmetry in the plane of the heterojunction. Information about $C_{2v}$ symmetry will be preserved, however, only if the contribution of the sharp part of the potential $G(z)\delta U$ in model \[1\] is taken into account. Therefore, using model \[3\] instead of model \[1\] does not give anything qualitatively new, and only leads to renormalization of some parameters, namely those that are negligibly small for the smooth heterojunction in model \[1\]. The expressions for these parameters are very complicated, so in what follows we will stick with model \[1\].

### 2.2 Account of relativistic corrections

Let us now consider relativistic effects. We restrict the discussion to the spin-orbit interaction. The remaining relativistic contributions only influence the values of the constants that we will obtain. We assume that within the framework of perturbation theory the characteristic parameter of the spin-orbit interaction and also the difference of this parameter for the left-hand and right-hand crystals are less than or of the same order as the characteristic band offset. The expansion of the total wave function, as
before, is given by expression (2). Omitting intermediate manipulations, we give the resulting, quite lengthy $k \cdot p$ system of equations which take into account the spin-orbit interaction

$$
\left( \epsilon_{n_0} - \epsilon + \frac{\hbar^2 k^2}{2m_0} \right) \mathcal{F}_n(k) + \sum_{n'} \frac{\hbar p_{nn'} \cdot k}{m_0} \mathcal{F}_{n'}(k) +
$$

$$
+ \sum_{n'} \delta U_{nn'} \int \mathcal{G}(k_z - k'_z) \mathcal{F}_{n'}(k'_z, k||) \, dk'_z + \sum_{n'} \frac{\hbar \langle n | \mathbf{\nabla} \delta U \times \mathbf{p} | n' \rangle \cdot \sigma}{4m_0^2 c^2} \mathcal{F}_{n'}(k) +
$$

$$
+ \sum_{n'} \frac{\hbar \langle n | \mathbf{\nabla} \delta U \times \mathbf{p} | n' \rangle \cdot \sigma}{4m_0^2 c^2} \int \mathcal{G}(k_z - k'_z) \mathcal{F}_{n'}(k'_z, k||) \, dk'_z +
$$

$$
+ \sum_{n'} \int \frac{\hbar^2 \langle n | \mathbf{\nabla} \delta U \times \mathbf{p} | n' \rangle \cdot \sigma}{4m_0^2 c^2} \int i (k_z - k'_z) \mathcal{G}(k_z - k'_z) \mathcal{F}_{n'}(k'_z, k||) \, dk'_z +
$$

$$
+ \sum_{n'} \int \frac{\hbar}{2\pi} \left( D_{nn'} + \frac{k_z - k'_z}{2\pi} D_{1nn'} \right) \mathcal{F}_{n'}(k'_z, k||) \, dk'_z +
$$

$$
+ \sum_{n'} \int \left( \frac{1}{2\pi} \sigma \right) \mathcal{F}_{n'}(k'_z, k||) \, dk'_z +
$$

$$
+ \sum_{n'} \int \frac{1}{2\pi} \delta (k|| - k'||) [\hbar \mathbf{k} \times \sigma] \cdot \mathbf{B}_{0nn'} \mathcal{F}_{n'}(k') \, d^3k' = 0. \quad (12)
$$

The vectors $\mathbf{S}_{0nn'}$, $\mathbf{S}_{1nn'}$ and $\mathbf{B}_{0nn'}$ have the following form:

$$
\mathbf{S}_{0nn'} = \sum_{j \neq 0} \frac{\hbar \langle n | \mathbf{\nabla} \left( e^{iK_j z} \delta U \right) \times \mathbf{p} | n' \rangle}{4iK_j m_0^2 c^2} \int \frac{d}{-d} G'(z) e^{-iK_j z} \, dz;
$$

$$
\mathbf{S}_{1nn'} = -\sum_{j \neq 0} \frac{\hbar \langle n | \mathbf{\nabla} \left( e^{iK_j z} \delta U \right) \times \mathbf{p} | n' \rangle}{4iK_j m_0^2 c^2} \int \frac{d}{-d} G'(z) e^{-iK_j z} \, dz -
$$

$$
- \sum_{j \neq 0} \frac{\hbar \langle n | e^{iK_j z} \mathbf{\nabla} \delta U \times \mathbf{p} | n' \rangle}{4iK_j^2 m_0^2 c^2} \int \frac{d}{-d} G'(z) e^{-iK_j z} \, dz;
$$

$$
\mathbf{B}_{0nn'} = \sum_{j \neq 0} \frac{\hbar \langle n | \mathbf{\nabla} \left( e^{iK_j z} \delta U \right) | n' \rangle}{4iK_j m_0^2 c^2} \int \frac{d}{-d} G'(z) e^{-iK_j z} \, dz.
$$

Here $\mathbf{n}$ is the unit vector along the $z$ axis, $\mathbf{n} G'(z) \equiv \mathbf{\nabla} G(z)$, and $\sigma$ are the Pauli matrices. On the left-hand side of Eq. (12) the fourth term describes the spin-orbit interaction in the potential of the basis perturbation semiconductor; the fifth, sixth, and seventh terms are due to the smooth part of the perturbation potential. The terms proportional to $\mathbf{S}_{0nn'}$, $\mathbf{S}_{1nn'}$ and $\mathbf{B}_{0nn'}$ are due to the sharpness of the potential. In Ref. [23], in a consideration of
the state of the conduction band in heterostructures with smooth heteroboundaries, we neglected the sixth and seventh terms on the left-hand side of Eq. (12) as small. We noted that in second-order perturbation theory they, together with $\hbar \mathbf{k} \cdot \mathbf{p}_{nn'}/m_0$, give a correction only of order $(\lambda \bar{k}_z)^2 m/m_0$, which can be neglected as the effective mass is small in comparison with $m_0$. For the hole states, on the other hand, $m/m_0$ is able not to be a small parameter.

We do not consider $k$-linear contributions of the spin-orbit interaction due to the potential $U_1$. They give corrections of order $(\lambda \bar{k}_z)^3$ (third-order corrections, along with two terms of the form $\hbar \mathbf{k} \cdot \mathbf{p}_{nn'}/m_0$) similar to the contribution responsible for removing the spin degeneracy in the conduction band of the bulk semiconductor (we neglect terms of this order), and for the valence band it is well known that to first order the contribution of these terms is small, and to second order, along with $\hbar \mathbf{k} \cdot \mathbf{p}_{nn'}/m_0$ they only renormalize the effective-mass parameters.

As for the contributions from the sharpness of the heterojunction potential to the spin-orbit interaction, the terms proportional to $S_{0nn'}$ can give corrections of order $a \bar{k}_z$, while the terms $S_{1nn'}$ and $B_{0nn'}$ can give corrections of order $(a \bar{k}_z)^2$.

It is trivial to generalize to the case of many heterojunctions. In this case it is convenient to choose the coordinates of the heteroboundaries so that the distances between them be integer multiples of $a/2$, so that the phase factor of each of the expansions of the type (7) is equal to unity.

3 Problem of transformation of the effective-mass equations from quasi-momentum space to coordinate space

In the following section we obtain the one-band effective-mass equations for the conduction band and the valence band. But first of all, we must discuss a problem arising in the method of envelope functions and associated with the boundedness of $k$ space. Let us consider the following one-band equation for the envelope functions $f(k_z)$ in $k$ space:

$$\int \mathcal{H}(k_z, k_z') f(k_z') \, dk_z' = \epsilon f(k_z),$$  \hspace{1cm} (13)

where $k_z$ and $k_z'$ are bounded by the Brillouin zone. Transforming Eq. (13) to go over to the coordinate representation we obtain, generally speaking, an integral equation. The problem consists in the accuracy with which it is possible to obtain a differential equation in $r$ space. Let us consider an equation similar to Eq. (13), in which $k_z$ and $k_z'$ belong to the entire inverse space:

$$\int_{-\infty}^{+\infty} \mathcal{H}(k_z, k_z') g(k_z') \, dk_z' = \epsilon g(k_z).$$ \hspace{1cm} (14)

The Fourier transform of Eq. (14) with the system of equations (12) taken into account gives a differential equation in the $r$ representation. If the function $g(k_z)$ vanished for
$k_z$ not in the Brillouin zone, it would also be a solution of Eq. (13), and we would solve our problem exactly. In general this is not so. But in order for Eqs. (13) and (14) to be approximately equivalent, it is necessary that $g(k_z)$ be small for $k_z$ not in the Brillouin zone. In the theory of smooth perturbations this smallness is ensured by exponentially decaying envelope functions in the $k$ representation; however, in the case of discontinuous perturbations the envelope functions are decreasing functions of $k_z$ with only a power-law falloff. Thus, if the envelope function possesses one discontinuity, its Fourier transform satisfies $g(k_z) \propto (\delta \bar{g}/\bar{g}) \cdot (k_z)^{-1}$ for large $k_z$ (where the exponential contributions associated with the effects of smooth fields have decayed); where $(\delta \bar{g}/\bar{g})$ is a typical relative discontinuity of the function in $r$ space. If we consider, for example, the standard effective-mass equations [1] with discontinuous potentials, then the second derivatives of the corresponding envelope functions will be discontinuous with characteristic relative discontinuity of the order of unity [again, for states whose energies, measured from the band edge of the left-hand or right-hand material, is of the order of the band discontinuity], and the error incurred by using differential equations will be of order $(\bar{k}_z/K)^3$, where $K$ is the radius of the Brillouin zone along the $k_z$ axis.

In the case of a quantum well of width $L$ it is possible to treat two cases: $\bar{k}_z L \gtrsim 1$ and $\bar{k}_z L \ll 1$. In the first case the error is of the same order as for a single heterojunction; in the second case it can be of the order $(\bar{k}_z L)^{-1}(\bar{k}_z/K)^3$. This is an upper estimate. For a symmetric quantum well in the conduction band, for example, the error depends on the sign of the product of the values of the envelope function on the heteroboundaries, and for states of the second 2D subband it is overestimated. In the limiting case of a narrow quantum well, $L \lesssim 1/K$, the potential can be replaced by a $\delta$-function. Then we obtain an envelope function with a discontinuous derivative and error of order $(\bar{k}_z/K)^2$.

Above, in Eq. (13), we tacitly assumed that the Hamiltonian $H(k_z, k'_z)$ is defined for all $k_z$ and $k'_z$, belonging to the Brillouin zone. Since our goal is to obtain the one-band equations, we must take one more circumstance into account. In $k$ space near the $\Gamma$ point there exists a region $\Lambda_1$ in which the spectrum of states of the conduction band of the bulk material can be written in the form of a series in powers of the quasi-momentum (for states of a degenerate band the spectrum is determined by a matrix whose elements are such series). The series converges for $|k| < 1/(2\lambda)$, as follows from the two-band approximation [again, such an estimate is valid if the effective mass is formed mainly by the $k \cdot p$ interaction]. This is the region described by a Hamiltonian of the one-band equation. There is also a region $\Lambda_2$, where the interaction of states of isolated bands with distant bands principally cannot be described by this series. In our case of sharp heterojunctions the envelope functions in the $k$ representation fall off according to a power law; therefore we should also provide a valid description of the region $\Lambda_2$, which will be done elsewhere in connection with the problem of inter-valley mixing of states in heterostructures. Here we only mention that if the ratio of the characteristic band offset to the energy gap between the states under study in the region $\Lambda_1$ and the states in the region $\Lambda_2$ is a small parameter $\omega \ll 1$, then the error incurred by neglecting the region $\Lambda_2$ will be less than or of order $\omega(a\bar{k}_z)^2$. Thus, the effective radius in $k$ space determining the accuracy of reducing the integral equation to a differential equation is
in fact not determined by the size of the Brillouin zone along the \( k_z \) axis, but depends on which bands are taken to be distant and are “eliminated” by the unitary transformation. In our case, this radius is of the order of \( 1/\lambda \).

Below we will obtain an equation for the conduction band, leaving out details of the unitary transformation to \( k \) space and at once carrying out the transformation to the \( r \) representation. Formally, the final equation is a fourth-order differential equation, and the envelope function satisfying it in the case of a discontinuous potential, the most unfavorable case for accuracy, has a discontinuous second derivative with characteristic discontinuity of the order of the second derivative itself. It is possible to proceed otherwise. Reducing the fourth-order differential equation to a physically equivalent second-order equation \[28\], we obtain a discontinuous envelope function with characteristic relative discontinuity of order \((\bar{k}_z \lambda)^2\). This means that for a single heterojunction or a wide quantum well the accuracy of the obtained effective-mass equation is limited as a result of having to take account of all terms up to order \((\bar{k}_z \lambda)^3\) (exclusively). In the case of a narrow quantum well, on the other hand, even for \( L \sim \lambda \) the effective-mass equation should include only first-order corrections associated with effects of sharpness of the heterojunction, and considering all remaining orders, including those leading to spatial dependence of the effective-mass parameters, will yield an excess of accuracy. In such a case the short-range potential formalism, already used above to obtain the expansion \( [11] \). This will be taken up in Sec. 4.3.

4 One-band equations

4.1 Conduction band

4.1.1 Smooth heterojunction

The transformation from a many-band system of equations for the envelope functions to a single-band equation is realized in the standard way \[1, 27\]. For smooth heterojunctions the one-band equation for the envelope functions for the \( c \) band (conduction band) was derived in Ref. \[28\]. In the \( r \) representation it has the form:

\[
\epsilon_{c0}F_c(r) + \frac{1}{2} m^{\alpha_1}(z) p m^{\beta_1}(z) p m^{\alpha_1}(z) F_c(r) + \Gamma(z) \Delta U_c F_c(r) +
\]

\[
+ \alpha_0 p^4 F_c(r) + \beta_0 \left( p_x^2 p_z^2 + p_y^2 p_z^2 \right) F_c(r) + \eta [p \times n] \cdot \sigma \Gamma'(z) F_c(r) = \epsilon F_c(r). \tag{15}
\]

The conduction band offset \( \Delta U_c \) and the modified form factor of the heterojunction \( \Gamma(z) \) are given by

\[
\Gamma(z) \Delta U_c = G(z) \delta U_{cc} + \sum_n \frac{|\delta U_{cn}|^2}{\epsilon_{c0} - \epsilon_n} G^2(z),
\]

so that in all small corrections \( G(z) \) can be replaced by \( \Gamma(z) \). The position-dependent effective mass is given by

\[
m(z) = m_1 [1 + m_1 (\mu_1 - \mu_2) \Gamma(z)],
\]

\[14\]
and \( m_1 \) is the effective mass of the edge of the conduction band of the left-hand material, and for \( m_2 \), which is the effective mass of the conduction band of the right-hand material, we have

\[
1/m_2 = 1/m_1 + \mu_2 - \mu_1.
\]

The parameters \( \alpha_1 \) and \( \beta_1 \) are defined as follows:

\[
\alpha_1 = \frac{\mu_1}{2(\mu_2 - \mu_1)}, \quad 2\alpha_1 + \beta_1 = -1.
\]

The parameters \( \mu_1 \) and \( \mu_2 \) are given by:

\[
\mu_1 = \sum_n r_2 \left[ \frac{|c| p_x |n|}{m_0^2 (\epsilon_{c0} - \epsilon_{n0})^2} \right] \frac{\delta U_{cc}}{\epsilon_{c0} - \epsilon_{0l}} + \frac{\sum_{n,l} r_4 \langle c | p_x |n| \langle n | p_x |l\rangle}{} \frac{\delta U_{lc}}{m_0^2 (\epsilon_{c0} - \epsilon_{n0}) (\epsilon_{c0} - \epsilon_{0l})}.
\]

\[
\mu_2 = \sum_{n,l} r_2 \frac{2 \langle c | p_x |n| \delta U_{nl} \langle l | p_x |c\rangle}{m_0^2 (\epsilon_{c0} - \epsilon_{n0}) (\epsilon_{c0} - \epsilon_{0l})}.
\]

In Eq. (15) \( \alpha_0 \) and \( \beta_0 \) are the nonparabolicity parameters of the bulk spectrum. Finally, the last parameter entering into the equation is

\[
\eta = \sum_{n,l} r_4 \frac{\langle c | p_z |n| \langle n | \nabla \delta U \times \mathbf{p} |l\rangle}{} \frac{\delta U_{nl}}{m_0^2 (\epsilon_{c0} - \epsilon_{n0}) (\epsilon_{c0} - \epsilon_{0l})}.
\]

In the Introduction it was pointed out that an invalid expression for the effective mass of the edge of the conduction band of a non-basis semiconductor was obtained in Ref. [14] by direct elimination of the small envelope functions. This corresponds to the absence in expression (16) of the second sum, and in expression (17) of the terms with \( n \neq l \). Thus it is necessary to be careful when using the method of direct elimination of small envelope functions.

The relation of the envelope function of the conduction band \( F_c(r) \) with the total wave function is given by

\[
\Psi(r) = u_{c0} \{ 1 + 2Rm_1 (\Gamma(z) \Delta U_c + \epsilon_{c0} - \epsilon) \} F_c(r) + \\
+ \sum_{n} \frac{u_{n0}}{(\epsilon_{c0} - \epsilon_{n0})} \left[ \frac{\hbar \langle n | \mathbf{p} |c\rangle}{im_0} \cdot \nabla + \delta U_{nc} \Gamma(z) + \sum_{l,\alpha,\beta} \langle n | p_{\alpha} |l\rangle \langle l | p_{\beta} |c\rangle \cdot p_{\alpha} p_{\beta} \right] F_c(r).
\]

Here

\[
R = \frac{1}{2} \sum_{n} \frac{|\langle c | p_x |n\rangle|^2}{m_0^2 (\epsilon_{c0} - \epsilon_{0n})^2},
\]

and the term \( 2Rm_1 (\Gamma(z) \Delta U_c + \epsilon_{c0} - \epsilon) \) inside the braces in expression (18) comes from the term \( -R \mathbf{p}^2 \) treated as a perturbation using the standard effective-mass equation. In the brackets in expression (18) we neglected the term

\[
\frac{\hbar \langle n | \nabla U_1 \times \mathbf{p} |c\rangle \cdot \sigma}{4m_0^2 c^2} + \Gamma(z) \frac{\hbar \langle n | \nabla \delta U \times \mathbf{p} |c\rangle \cdot \sigma}{4m_0^2 c^2},
\]

(19)
since the largest contribution to the matrix elements (19) comes from the region of the potential near the atomic nuclei in which the spin-orbit interaction operator can be written in the form of a product of operators of the electron spin and the orbital angular momentum, and the function \( u_{c0} \) is spherically symmetric (the orbital momentum is zero).

In Ref. [28] it was shown that for \( d \cdot k_z \ll 1 \) Eq. (15) can be replaced by an equivalent equation where the Heaviside step function \( \Theta(z - z_0) \) replaces the function \( \Gamma(z) \), and the coordinate \( z_0 \) assigning the position of the mathematically sharp heterojunction can be chosen arbitrarily within the limits \(-d \leq z_0 \leq d\). The method used in Ref. [28] for this transformation is not the most convenient. There is a simpler way of transforming to a mathematically sharp heterojunction based on the following chain of identities, valid for operators acting on smooth functions:

\[
\Gamma(z) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk_z e^{ik_z z} \int_{-\infty}^{+\infty} \Gamma(z') e^{-ik_z z'} dz' = \Theta(z - z_0) + \\
\frac{1}{2} \int_{-\infty}^{+\infty} dk_z e^{ik_z (z - z_0)} \int_{-d}^{d} (\Gamma(z') - \Theta(z' - z_0)) e^{-ik_z (z' - z_0)} dz' \approx \Theta(z - z_0) + \\
+ \delta(z - z_0) \left[ \int_{-d}^{d} \Gamma(z) \ dz - (d - z_0) \right] + \delta'(z - z_0) \left[ \int_{-d}^{d} \Gamma(z) (z_0 - z) \ dz + \frac{(d - z_0)^2}{2} \right].
\]

Setting \( z_0 = 0 \), instead of Eq. (15) we obtain a more convenient form of the effective-mass equation for a smooth heterojunction:

\[
[\epsilon_{c0} - \epsilon + (z) \Delta U_c + \Delta U_c \rho_0 \delta(z)] F_c(r) + \frac{1}{2} m^{\alpha_2} (z) \mathbf{p} m^{\beta_2} (z) \mathbf{p} m^{\alpha_2} (z) F_c(r) + \\
\alpha_0 \mathbf{p} \cdot \mathbf{F}_c(r) + \beta_0 \left( p_x^2 + p_y^2 + p_z^2 \right) F_c(r) + \eta [\mathbf{p} \times \mathbf{n}] \cdot \mathbf{\sigma} \delta(z) F_c(r) = 0. \tag{20}
\]

Here

\[
m(z) = m_1 \left[ 1 + m_1 (\mu_1 - \mu_2) \Theta(z) \right],
\]

and the parameter \( \alpha_2 \) not only depends on the materials of the heterojunction but also takes into account its finite width through its dependence on \( \Gamma(z) \):

\[
\alpha_2 = \frac{\mu_1 + 2 \Delta U_c \hbar^{-2} \left[ d^2 - \int_{-d}^{d} \Gamma(z) \ dz \right]}{2 (\mu_2 - \mu_1)}.
\]

The relation \( 2\alpha_2 + \beta_2 = -1 \) is preserved, and

\[
\rho_0 = \int_{-d}^{d} \Gamma(z) \ dz - d.
\]

The transformation to a mathematically sharp heterojunction described above is dictated only by arguments of convenience, and the explicit form of the function \( \Gamma(z) \) appears only in integral form in the expressions for the two parameters \( \alpha_2 \) and \( \rho_0 \).
4.1.2 Sharp heterojunction

To include corrections associated with the sharpness of the heterojunction in Eq. (20), it is necessary in the standard procedure [1, 27] to take into account the contributions of the terms \( D_{0mn'} \), \( D_{1mn'} \) and \( B_{0mn'} \) in the first-order perturbation theory [\( S_{0cc} = S_{1cc} = 0 \), as follows from zinc-blende symmetry], and the contributions of the terms \( D_{0mn'} \) and \( S_{0mn'} \) should still be treated in the second-order theory along with the terms \( \hbar \mathbf{k} \cdot \mathbf{p}_{mn'}/m_0 \).

Utilizing symmetry properties, it is not hard to obtain the following additional term \( H_{abr} \) to the Hamiltonian of Eq. (13):

\[
H_{abr} = D_{0cc} \delta(z) + \rho \delta'(z) + \tilde{\eta} [\mathbf{p} \times \mathbf{n}] \cdot \mathbf{\sigma} \delta(z). \quad (21)
\]

Here

\[
D_{0cc} = -\sum_{j \neq 0} \frac{\langle c | \delta U \cos(K_j z) | c \rangle}{K_j} \int_{-d}^{d} G'(z) \sin(K_j z) \, dz,
\]

\[
\rho = \sum_{n,j \neq 0} \frac{\hbar \langle c | p_x | n \rangle \langle n | \delta U \sin(K_j z) | c \rangle}{iK_j m_0 (\epsilon_{c0} - \epsilon_{n0})} \int_{-d}^{d} G'(z) \cos(K_j z) \, dz + \sum_{j \neq 0} \langle c | \delta U \cos(K_j z) | c \rangle \int_{-d}^{d} G'(z) \left( \frac{\cos(K_j z)}{K_j} + z \sin(K_j z) \right) \, dz,
\]

\[
\tilde{\eta} = \sum_{n,j \neq 0} \left( \sum_{c} \frac{\hbar \langle c | \nabla (\sin(K_j z) \delta U) \times \mathbf{p} \rangle_c | n \rangle \langle n | p_y | c \rangle}{2K_j m_0^2 c^2 (\epsilon_{c0} - \epsilon_{n0})} - \frac{\hbar \langle c \nabla_z (\sin(K_j z) \delta U) | c \rangle}{4K_j m_0^2 c^2} \right) \int_{-d}^{d} G'(z) \cos(K_j z) \, dz.
\]

Comparing expression (21) with the Hamiltonian of Eq. (20) we see that for the conduction band taking the sharpness of the heterojunction into account does not alter the form of the one-band equation and simply renormalizes the constants used in it. If we take Eqs. (20) and (21) into account, the desired equation for the conduction band takes the form

\[
(\epsilon_{c0} - \epsilon + \Theta(z) \Delta U_c + d_1 \delta(z)) F_c(r) + \frac{1}{2} m^\alpha(z) \mathbf{p} m^\beta(z) \mathbf{p} m^\gamma(z) F_c(r) + \alpha_0 \mathbf{p}^4 F_c(r) + \beta_0 \left( \mathbf{p}_x^2 + \mathbf{p}_y^2 \right) F_c(r) + d_2 [\mathbf{p} \times \mathbf{n}] \cdot \mathbf{\sigma} \delta(z) F_c(r) = 0. \quad (22)
\]

The term \( \rho \delta'(z) \) in expression (21) was absorbed by the kinetic-energy operator; as a result, for \( \alpha \) we obtain

\[
\alpha = \frac{\mu_1 + 2 \Delta U_c \hbar^{-2} \int_{-d}^{d} \Gamma(z) \, dz}{2 (\mu_2 - \mu_1)} + 4 \rho \hbar^{-2}.
\]
(here the error incurred in Ref. [29] has been corrected), and $2\alpha + \beta = -1$, with $d_1 = D_0 + \Delta U_c \rho_0$ and $d_2 = \eta + \tilde{\eta}$.

Let us discuss the Hamiltonian of Eq. (22). The first term represents the potential energy of an electron in the $c$ band. The possible existence of a heterointerface term proportional to $d_1$ was discussed in Ref. [5]; it is clear that this contribution disappears for a mathematically discontinuous heterojunction (in this rather unrealistic case models (1) and (9) are identical). The second term is the position-dependent kinetic-energy operator, which is quadratic in the momentum; such a form was proposed in Ref. [6] more generally. Note that the parameter $\alpha$ is not a universal constant but depends both on the materials and on the shape of the transitional region of the heterojunction, as seems natural even intuitively (see also Ref. [8]). If it happens that $m(z) = \text{const}$, i.e., $\mu_1 = \mu_2$, indeterminate expressions of the form $1^{\infty}$ arise in the form of the kinetic-energy operator used here which are easily evaluated. Such indeterminate forms do not arise if we use a different, equivalent form of this operator where we separate out a term analogous to the relativistic Darwin term (see Ref. [28]):

$$T_2 = \mathbf{p} \frac{1}{2m(z)} \mathbf{p} + \left( \frac{\mu_1 \hbar^2}{4} + \Delta U_c \left[ \frac{d^2}{2} - \int_{-d}^{d} \Gamma(z) zdz \right] + \rho \right) \delta'(z).$$

The third and fourth terms in the Hamiltonian of Eq. (22) describe corrections to the weak nonparabolicity and depend only on the bulk parameters. The fifth term describes the interface spin-orbit interaction (see, e.g., Ref. [32]), whose strength ($d_2$) depends not only on the materials of the heterojunction but also on the shape of the transitional region. The relation between the total wave function and the envelope functions of the conduction band is given by Eq. (18), where we can set $\Gamma(z) = \Theta(z)$.

### 4.1.3 Boundary conditions on the envelope function

From Eq. (22) it is not hard to obtain boundary conditions imposed on the envelope function at the heterojunction; to this end it is necessary to reduce Eq. (22) to a second-order differential equation by employing the smallness of the contribution proportional to $\mathbf{p}^4$ (see Ref. [28]). We present only the result:

$$\left. \begin{pmatrix} F_c(r) \\ F'_c(r) \end{pmatrix} \right|_{z=+0} = \left( \begin{pmatrix} d_{11} & 0 \\ d_{21} & d_{22} \end{pmatrix} \begin{pmatrix} F_c(r) \\ F'_c(r) \end{pmatrix} \right) \left|_{z=-0} \right.,$$

where

$$d_{11} = 1 + 4m_2^2 \alpha_0 \Delta U_c + m_1 \alpha \left( \frac{1}{m_2} - \frac{1}{m_1} \right),$$

$$d_{21} = \frac{2m_1}{\hbar^2} (d_1 + d_2 [\mathbf{p} \times \mathbf{n}] \cdot \mathbf{\sigma}),$$

and

$$d_{22} = \frac{m_2}{m_1} + 4m_1^2 \alpha_0 \Delta U_c - m_1 \alpha \left( \frac{1}{m_2} - \frac{1}{m_1} \right).$$
In the approximation of the standard effective-mass method we have a position-independent effective mass and a discontinuous (step-function) potential. Corrections which are first order in the small parameter of the problem are taken into account by including in the standard equation a δ-function potential proportional to \( \delta_z \) (formally, this is a correction of order \( \lambda k_z^2 \)). The complete equation (22) also includes all corrections of order \( (\lambda k_z^2)^2 \). It is not possible to take into account smaller contributions in the one-band version of the method of envelope functions because the unavoidable error arising in the transformation from the many-band system of integral equations to the one-band differential equation is of the same order.

It is not hard to generalize the above results to the case of an arbitrary heterostructure. It is easy to do this proceeding from symmetry arguments for a symmetric quantum well with two equivalent heterojunctions with coordinates \( z = 0 \) and \( z = L \), where \( L = Na/2 \), and \( N \) is an integer. The effective Hamiltonian is

\[
H_{\text{el}} = \epsilon_{c0} + \Delta U_c \{ \Theta (z) - \Theta (z - L) \} + \frac{1}{2} m^\alpha (z) p m^\beta (z) p m^\alpha (z) + \alpha_0 p^4 +
\]

\[
+ \beta_0 \left( p_x^2 \right) + d_1 \{ \delta (z) + \delta (z - L) \} + d_2 \{ \delta (z) - \delta (z - L) \} [p \times n] \cdot \sigma.
\]

### 4.2 Valence band

The distinction between the effective-mass method for the valence band and the effective-mass method for the conduction band consists, in principle, simply of the necessity of considering more elaborate equations in the case of the valence band. The main points of the problem of deriving the equation for the hole states with position-dependent effective-mass parameters were noted in Ref. [29]. The equation for the \( c \) band already contains three new parameters which depend on the bulk properties of the materials of the heterostructure and on the properties of the heteroboundary. For the valence band, there is a larger number of such parameters, which may be seen as rendering such an equation of little practical value. Therefore we limit ourselves here to a derivation of first-order corrections to the standard equation in the above small parameter.

In the basis \( \{|J,j_z\rangle\} \) of eigenfunctions of the total angular momentum \( J \) and its projection \( j_z \), with these eigenfunctions being combinations of the Bloch functions \( \mathcal{X} \), \( \mathcal{Y} \) and \( \mathcal{Z} \) of the top of the valence band (transforming according to the representation \( \Gamma_{15} \)) and the spin, the matrix of the effective Hamiltonian for the valence band \( \mathbf{H} \) in this approximation is a sum of the \( 6 \times 6 \) matrix of the standard kinetic energy operator \( \mathbf{T} \) (we neglect the small contribution of \( \mathbf{k} \)-linear bulk terms from the spin-orbit interaction) and the \( 6 \times 6 \) matrix of the potential energy operator \( \mathbf{V} \):

\[
\mathbf{H} = \mathbf{T} + \mathbf{V}.
\]

Of course, in the standard approximation \( \mathbf{V} \) contains only diagonal discontinuous (step-function) potentials. Additional terms appear in the approximation that follows which are diagonal and non-diagonal δ-function potentials.
It is convenient first to find the elements of the potential energy matrix $\tilde{V}$ in the basis $\{X, Y, Z\}$, and then compose from them the necessary linear combinations and transform to $V$.

$$
\tilde{V}_{ZZ} = \tilde{V}_{XX} = \epsilon_{x0} + \delta U_{XX}G(z) + D_{0XX}\delta(z) \approx \\
\approx \epsilon_{x0} + \delta U_{XX}\Theta(z) + (D_{0XX} + \rho_0\delta U_{XX})\delta(z); \\
\tilde{V}_{XY} = \frac{1}{3i}(\Delta + \delta G(z))\sigma_z + D_{0XY}\delta(z) + S_{0XY}^z\delta(z)\sigma_z \approx \\
\approx \frac{1}{3i}(\Delta + \delta \Delta \Theta(z))\sigma_z + D_{0XY}\delta(z) + \left(S_{0XY}^z + \frac{\rho_0\delta \Delta}{3i}\right)\delta(z)\sigma_z,
$$

where

$$
\Delta = \frac{3\hbar i}{4m_0 c^2} \langle X | [\nabla U_1 \times \mathbf{p}|_z | Y]\rangle , \quad \delta \Delta = \frac{3\hbar i}{4m_0 c^2} \langle X | [\nabla \delta U \times \mathbf{p}|_z | Y]\rangle.
$$

Analogously,

$$
\tilde{V}_{XZ} = i\frac{1}{3} (\Delta + \delta G(z))\sigma_y + S_{0XZ}^y\delta(z)\sigma_y \approx \\
\approx i\frac{1}{3} (\Delta + \delta \Delta \Theta(z))\sigma_y + \left(S_{0XZ}^y + \frac{i\rho_0\delta \Delta}{3}\right)\delta(z)\sigma_y.
$$

The remaining elements of $\tilde{V}$ can be obtained from those shown above by cyclic permutation of the indices.

The contribution of the sixth and seventh terms on the left-hand side of Eq. (12), as can be seen, is not included in $\tilde{V}$, since it is negligibly small for the following reason:

$$
\langle X | \nabla_z U_1 | Y\rangle = 0
$$

(see Ref. [27], Sec. 21). This means that the matrix element

$$
\langle X | \nabla_z \delta U | Y\rangle = \langle X | \nabla_z U_2 | Y\rangle.
$$

For the Bloch functions of the $n$th band at the $\Gamma$ point of the right-hand crystal in the non-relativistic limit ($\tilde{u}_{n0}$) we have:

$$
\tilde{u}_{n0} = u_{n0} + \sum_{n'} \frac{\delta U_{n'n}u_{n'n0}}{\epsilon_{n'} - \epsilon_{n'0}}, \quad (23)
$$

and for the corresponding functions of the edge of the valence band of the right-hand crystal $\tilde{X}$ and $\tilde{Y}$ the relation $\langle \tilde{X} | \nabla_z U_2 | \tilde{Y}\rangle = 0$ holds. That is, the seventh term on the left-hand side of Eq. (12) gives corrections only of order $(\lambda \bar{k}_z)^3$, not $\lambda \bar{k}_z$. In our approximation it is necessary in general to neglect the difference between the Bloch functions $\tilde{u}_{n0}$ and $u_{n0}$. Hence it follows from invariance of the equation under time reversal that the contribution from the sixth term on the left-hand side of Eq. (12) is negligibly small.
It is not difficult now to obtain the elements of $V$. We choose the phases the same as was done in Ref. [1] and write

$$
|1\rangle \equiv \left| \frac{3}{2}, \frac{3}{2} \right\rangle, \quad |2\rangle \equiv \left| \frac{3}{2}, -\frac{3}{2} \right\rangle, \quad |3\rangle \equiv \left| \frac{3}{2}, \frac{1}{2} \right\rangle, \\
|4\rangle \equiv \left| \frac{3}{2}, -\frac{1}{2} \right\rangle, \quad |5\rangle \equiv \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \quad |6\rangle \equiv \left| \frac{1}{2}, -\frac{1}{2} \right\rangle
$$

(pairs of states of heavy holes, light holes, and states of the split-off band). Thus, the desired potential-energy matrix takes the form

$$
V = \begin{pmatrix}
V_{\Gamma s} & V_0 \sigma_y & -i\sqrt{2}V_0 \sigma_y \\
V_0^\dagger \sigma_y & V_{\Gamma s} & 0 \\
i\sqrt{2}V_0^\dagger \sigma_y & 0 & V_{\Gamma s}
\end{pmatrix}, \quad (24)
$$

where

$$
V_{\Gamma s} = E_{\Gamma s} + \Delta U_{\Gamma s} \Theta (z) + \chi_1 \delta (z), \\
V_{\Gamma s} = E_{\Gamma s} + \Delta U_{\Gamma s} \Theta (z) + \chi_2 \delta (z), \\
V_0 = \frac{D_{0xy}}{\sqrt{3}} \delta (z).
$$

Here we have introduced the notation

$$
E_{\Gamma s} = \epsilon \chi_0 + \frac{1}{3} \Delta, \quad \Delta U_{\Gamma s} = \delta U \chi \chi + \frac{1}{3} \delta \Delta, \\
E_{\Gamma s} = \epsilon \chi_0 - \frac{2}{3} \Delta, \quad \Delta U_{\Gamma s} = \delta U \chi \chi - \frac{2}{3} \delta \Delta, \\
\chi_1 = D_{0xx} + \rho_0 \delta U \chi \chi + \frac{1}{3} \rho_0 \delta \Delta, \\
\chi_2 = D_{0xx} + \rho_0 \delta U \chi \chi - 2i S_{0xy}^z - \frac{2}{3} \rho_0 \delta \Delta.
$$

The expressions for $D_{0xx}$, $D_{0xy}$ and $S_{0xy}^z$ have the following form:

$$
D_{0xx} = -\sum_{j \neq 0} \frac{\langle \chi | \delta U \cos (K_j z) | \chi \rangle}{K_j} \int_{-d}^{d} G'(z) \sin (K_j z) \, dz,
$$

$$
D_{0xy} = \sum_{j \neq 0} \frac{\langle \chi | \delta U \sin (K_j z) | \chi \rangle}{K_j} \int_{-d}^{d} G'(z) \cos (K_j z) \, dz, \quad (25)
$$

$$
S_{0xy}^z = -\sum_{j \neq 0} \frac{\hbar}{4K_j m_0^2 c^2} \langle \chi | \nabla (\cos (K_j z) \delta U) \cdot p | \chi \rangle \int_{-d}^{d} G'(z) \sin (K_j z) \, dz.
$$

Thus, within the framework of the $k \cdot p$ method we have shown that in (001) III-V heterostructures mixing of heavy (hh) and light (lh) holes takes place at the center of the
2D Brillouin zone (see Ref. [33] and the references cited therein) which bears no relation to the \( k_z \)-linear bulk terms from the spin-orbit interaction. This mixing is governed by the parameter \( D_{0XZ} \), which was estimated in Ref. [33] on the basis of experimental data for GaAs/AlAs heterostructures: \( D_{0XZ} \approx 500 \text{ meV } \AA \).

In Ref. [29] it was concluded that the strength of the mixing of the heavy and light holes at the center of the 2D Brillouin zone is greater for sharp heterojunctions than for heterojunctions with smoothly varying chemical composition. But this is valid only in model (1). Generally speaking, one can draw conclusions only about the dependence of the strength of this mixing on the structure of the transitional region of the heterojunctions.

For a symmetric quantum well with boundaries \( z = 0 \) and \( z = L \) the elements of the potential energy matrix can be easily obtained from symmetry arguments:

\[
V_{\Gamma_8} = E_{\Gamma_8} + \Delta U_{\Gamma_8} \left( \Theta (z) - \Theta (z - L) \right) + \chi_1 \left( \delta (z) + \delta (z - L) \right),
\]

\[
V_{\Gamma_7} = E_{\Gamma_7} + \Delta U_{\Gamma_7} \left( \Theta (z) - \Theta (z - L) \right) + \chi_2 \left( \delta (z) + \delta (z - L) \right),
\]

\[
V_0 = \frac{D_{0XZ}}{\sqrt{3}} \left( \delta (z) - \delta (z - L) \right).
\]

### 4.3 Equation for the envelope function for a narrow quantum well in the conduction band

We will devote separate attention to the problem of electron states in narrow quantum wells because at present it is widely held that the effective-mass method is inapplicable in such case. Here we treat only states of the \( c \) band in a III-V (001) heterostructure consisting of related semiconductors of isolated-quantum-well-type (or narrow-barrier-type) for the case when its width satisfies \( L \lesssim \lambda \). Hole states are easily treated in an analogous way. Now the contributions from the sharpness of the potential begin to play a much greater role than in the case of a wide quantum well. In fact, the estimate \( \bar{k}_z^2/2m \sim \delta U_{cc} \) is valid only when the width of the quantum well is greater than or of the order of the characteristic localization length of the states. For states in a narrow quantum well, on the other hand, of course \( \bar{k}_z^2/2m \sim \delta U_{cc} \bar{k}_z a \), and the contribution to the energy eigenvalue from the terms associated with sharpness of the potential can be estimated to first order as \( \delta U_{cc} \bar{k}_z a \), which implies that they must be taken into account even in the zeroth approximation.

Thus, the potential of the heterostructure under consideration can be written as

\[
U = U_1 + P[U_2 - U_1] \equiv U_1 + P(z) \delta U,
\]

where \( U_1 \) and \( U_2 \) are the periodic crystal potentials of the “barrier” (basis) and “well” semiconductor, respectively, and \( P(z) \) is the form factor of the heterostructure. We choose \( L \) so that \( P(z < -L/2) = P(z > L/2) = 0 \). It is natural to consider \( P(z) \) as a local function on the scale of variation of the envelope function of the conduction band.
since $L \bar{k}_z \ll 1$. The one-band equation has the following form:

$$\left[ \epsilon_{c0} - \epsilon + \frac{p^2}{2m} + b_1 \delta(z) + b_2 \delta'(z) + b_3 \delta(z) \right] [p \times n] \cdot \sigma \ F_c(r) = 0,$$  \hspace{1cm} (26)

where $m$ is the position-independent effective mass, and we have the following expressions for the three parameters $b_i$ ($i = 1, 2, 3$):

$$b_1 = \sum_j \langle c | \delta U \cos (K_j z) | c \rangle \int_{-L/2}^{L/2} P(z) \cos(K_j z) \ dz; \hspace{1cm} (27)$$

$$b_2 = \sum_{n,j} \frac{\hbar \langle c | p_z | n \rangle \langle n | \delta U \sin (K_j z) | c \rangle}{im_0 (\epsilon_{c0} - \epsilon_{n0})} \int_{-L/2}^{L/2} P(z) \sin(K_j z) \ dz -$$

$$- \sum_j \langle c | \delta U \cos (K_j z) | c \rangle \int_{-L/2}^{L/2} P(z) \cos(K_j z) \ dz;$$

$$b_3 = \sum_j \left( \sum_n \frac{\hbar \langle c | \nabla (\sin(K_j z) \delta U) \times p_z | n \rangle \langle n | p_y | c \rangle}{2m_0^2 c^2 (\epsilon_{c0} - \epsilon_{n0})} - \right.$$

$$\left. - \frac{\hbar \langle c | \nabla_z (\sin(K_j z) \delta U) | c \rangle}{4m_0^2 c^2} \right) \int_{-L/2}^{L/2} P(z) \sin(K_j z) \ dz,$$

in which the summation index $j$ includes zero (the terms with $j = 0$ represent the contribution of the smooth part of the potential). The term in the potential energy proportional to $b_1$ gives the main contribution, and the two remaining terms are corrections of order $\lambda \bar{k}_z$. For a symmetric structure, $P(z) = P(-z)$, the equation simplifies: $b_2 = b_3 = 0$.

Strictly speaking, Eq. (26) is invalid from a mathematical point of view (it does not have a rigorous nontrivial solution); therefore, it needs to be put into a different form using the smallness of the term proportional to $b_2$, and discarding corrections of order $(\lambda \bar{k}_z)^2$. It is necessary to invoke the approximate relation

$$b_1 \delta(z) + b_2 \delta'(z) \approx b_1 \delta \left( z + \frac{b_2}{b_1} \right), \hspace{1cm} (28)$$

and in the term proportional to $b_3$, $\delta(z)$ can be replaced by $\delta(z + b_2/b_1)$ for simplicity. We obtain the valid equation

$$\left[ \epsilon_{c0} - \epsilon + \frac{p^2}{2m} + b_1 \delta \left( z + \frac{b_2}{b_1} \right) + b_3 \delta \left( z + \frac{b_2}{b_1} \right) \right] [p \times n] \cdot \sigma \ F_c(r) = 0.$$  \hspace{1cm} (29)

Note that for states of one band (if we are not interested, for example, in inter-band transitions) in a heterostructure with one narrow layer the value of $b_2$ does not play a role: in Eq. (26) we can shift the origin $z' = z + b_2/b_1$.
Assume now that we are dealing with a structure containing two narrow layers lying near one another, such that the distance between them is of the order of $\lambda$. In this case, an upper estimate on the error arising from the transformation to a one-band differential equation is $\lambda \bar{k}_z$ (this is valid, in particular, in the case when the constant $b_1$ describing the potential of the first layer is equal to the constant describing the potential of the second layer taken with opposite sign). Then we should remove from consideration those terms containing $b_2$ and $b_3$ in Eq. (26).

One could probably treat both layers as one local perturbation, thereby decreasing the error, and obtain Eq. (26) with one set of parameters of the local perturbation. But in the situation for which we obtained an upper estimate of the error, however, one could not then guarantee the smallness of the parameter $\bar{k}_z b_2 / \bar{b}_1$ on which Eq. (28) is based. If it is not small, then one could not say that Eq. (28) is mathematically correct, which would imply the inapplicability of such an approach.

Thus, taking the above modification into account, we can also apply the effective-mass method to electron states in heterostructures with super-thin layers. In this regard the situation can arise in which the potential of a thick layer of some semiconductor plays the role of a barrier for the electron states while a thin layer of the same material will couple states and vice versa, depending on the sign of the parameter $b_1$. The sign of this parameter, as can be seen from Eq. (27), can be different from the sign of the parameter $\langle c | \delta U | c \rangle$, which defines the conduction band offset at the heterojunction.

5 Hierarchy of effective-mass equations and discussion of results

We have derived a many-band $\mathbf{k} \cdot \mathbf{p}$ system of integral equations (12) which can be used to describe electron states in heterostructures with atomically sharp variation of their chemical composition. The system contains contributions in the form of converging power series in $(k_z - k'_z)$ which are due to the sharpness of the heterojunction. For example, such terms were discarded in Refs. [14], [19], and [20] so that the effects of a discontinuous change in the crystal potential of the structure near a heterojunction were in fact neglected. It is specifically the presence of these terms that distinguishes the many-band system of $\mathbf{k} \cdot \mathbf{p}$ equations derived here from the system obtained by Leibler [3] for heterostructures with smooth heterojunctions. All of the papers known to us which use one-band or many-band schemes of the method of envelope functions to describe electron states in heterostructures apply the $\mathbf{k} \cdot \mathbf{p}$ system of Leibler. Very often the distinction between the Bloch functions for the component semiconductors of the heterostructure is also neglected, which gives, in particular, $\delta U_{nn'} = 0$ for $n \neq n'$. Taking into account the terms due to sharpness of the heterojunction, the $\mathbf{k} \cdot \mathbf{p}$ method can also be used to describe inter-valley mixing of states in heterostructures, including the problem of $\Gamma$-$X_d$ mixing of states in (001) heterostructures.

The main limitation on the accuracy of the method of envelope functions employing differential equations is the procedure of transforming from $\mathbf{k}$ to $\mathbf{r}$ space. The one-band
A differential equation (of fourth order) with position-dependent effective mass is valid for structures with characteristic width of layers much greater than $\lambda$, where the length $\lambda$ was defined in Sec. 2.

Above we considered in detail how taking account of contributions of the sharpness of the interface potential modifies the equation for states of the conduction band in (001) heterostructures of related, lattice-matched III-V semiconductors, derived in Ref. [28]. Formally, the resulting equation for a sharp heterojunction differs from that for a smooth heterojunction only by renormalization of the parameters entering into it. In the case of the valence band, on the other hand, taking account of the sharpness of the heterojunction leads to qualitatively new effects (mixing of heavy and light holes for $k_z = 0$).

For heterostructures with wide layers it is possible to construct a hierarchy of approximations of the one-band method of envelope functions according to the parameter $\bar{k}_z$, where $\bar{k}_z$ is the characteristic value of the quasi-momentum of the state. For example, for an isolated heterojunction we have the following:

0) Zeroth level of the hierarchy for electrons. In the effective-mass approximation in which small corrections in the order parameter have been neglected, we have the usual equation with position-independent effective mass and a discontinuous (step-function) potential:

$$\left( \epsilon_{c0} + \Theta (z) \Delta U_c + \frac{p^2}{2m} \right) F_c (r) = \epsilon F_c (r).$$  \hspace{1cm} (30)

1) First level of the hierarchy. First-order corrections are taken into account (here, in fact, the small parameter $d \cdot \bar{k}_z$ plays a role; $2d$ is the width of the transitional region of the heterojunction) by including a $\delta$-function potential in Eq. (30), which is localized at the heteroboundary:

$$\left( \epsilon_{c0} + \Theta (z) \Delta U_c + d_1 \delta (z) + \frac{p^2}{2m} \right) F_c (r) = \epsilon F_c (r),$$

where $d_1$ is given by the complicated expression in Sec. 4.1.

2) Second level of the hierarchy. Equation (22) includes all corrections of order $(\lambda \bar{k}_z)^2$. Smaller contributions, of third order and higher, cannot be taken into account correctly in a one-band version of the method.

For hole states we obtained, see Eq. (24), the first-order corrections to the standard equation [that is, the first step of the hierarchy of effective-mass equations for the holes] and showed that for (001) heterostructures mixing of heavy and light holes at the center of the 2D Brillouin zone does indeed take place and that contributions from the sharpness of the heterojunction potential determine the strength of this mixing so that it depends on the microscopic structure of the heteroboundaries. In Ref. [20] it is asserted, in particular, that such mixing of heavy and light holes is caused by a difference in the Bloch functions for the component semiconductors of the heterostructure and it is absent, if one neglects such a difference, or, what should be equivalent, if the Bloch functions of all the bulk semiconductors comprising the structure are the same set of functions. If this is indeed the case, then the contribution of these terms [even without taking symmetry
arguments into account] would be only of order \((\lambda \tilde{k}_z)^2\), as can be seen from Eq. (23). In fact, however, the difference in the Bloch functions does not play a substantial role.

To prove this, consider the idealized situation of a (001) homojunction—the problem of hole states in a weak but not smooth external potential, say, \(W(z) = G(z)W_0\), where \(W_0\) is a constant assigning the jump of the potential, small in comparison with the band gap. In this case the point symmetry of the structure, \(C_{2v}\), also admits the existence of mixing of heavy and light holes at the center of the 2D Brillouin zone [33], and for the coefficient governing this mixing, \(D_{0XY}\), instead of formula (25) we have

\[
D_{0XY} = \sum_{j \neq 0} W_0 \frac{\langle X | \sin (K_j z) | Y \rangle}{K_j} \int_{-d}^{d} G'(z) \cos (K_j z) \, dz.
\]

This is direct proof of our assertion.

The independent parameters \(\alpha, d_1\) and \(d_2\) introduced in the present work and appearing in Eq. (22), and also \(\chi_1, \chi_2\) and \(D_{0XY}\) entering into the effective potential energy operator for the valence-band states, depend not only on the bulk properties of the materials of the heterojunction, but also on its microscopic structure. All these parameters determine the heterointerface contribution to the potential energy. At the same time, it is well known [34], that as a consequence of the possible appearance of an electric dipole moment at the interface of two materials the magnitude of the potential jump at the interface can also depend on the microscopic structure of the boundary. This is not described in our model of a heterojunction because we do not take into account the effect of such a dipole. Including the corresponding discontinuous electrostatic potential in Eq. (1) and developing it according to the scheme laid out above also yields the desired effect.

The electron states in heterostructures consisting of thin layers whose thickness is less than or of the order of \(\lambda\) can be treated only in the approximation quadratic in the momentum operator. In this case an account of terms due to the sharpness of the potential becomes necessary already in the zeroth approximation. This is clear from Eqs. (27). In this regard, the following situation is possible: as the width of the quantum well is decreased, the bound state can disappear or conversely, a thin layer—nominally a “barrier” layer—of some semiconductor can create an attractive potential and form a bound state. It is possible that just such a situation was observed in Ref. [35] and then modeled in Ref. [36].

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Appendix A: The Dirac equation with position-variant gap

Let us consider a model Dirac equation with a position-dependent gap $2m(r)c^2$

$$\begin{bmatrix} m(r)c^2 & c\sigma \cdot p \\ c\sigma \cdot p & -m(r)c^2 \end{bmatrix} \begin{pmatrix} \varphi_e \\ \varphi_p \end{pmatrix} = \epsilon \begin{pmatrix} \varphi_e \\ \varphi_p \end{pmatrix},$$

where $\varphi_e$ and $\varphi_p$ are the electron and positron components of the wave function, respectively. Let $m(r)$ vary weakly in space, i.e., $m(r) = \tilde{m} + \delta m(r)$, so that $\delta m(r)/\tilde{m} \ll 1$. With the help of a Foldy-Wouthuysen unitary transformation it is quite simple, for example, following the scheme laid out in Ch. 20, Sec. 33 of Ref. [24], to obtain a one-band equation describing the states of the electron. Thus, the equation in which all small terms have been discarded is the ordinary Schrödinger equation

$$\left( m(r)c^2 + \frac{P^2}{2\tilde{m}} \right) \tilde{\varphi}_e = \epsilon \tilde{\varphi}_e,$$

where $\tilde{\varphi}_e$ is the transformed electron wave function. The equation, on the other hand, in which all terms of higher order than $\delta m(r)/\tilde{m}$ have been neglected has the form

$$H \tilde{\varphi}_e = \epsilon \tilde{\varphi}_e,$$

$$H = m(r)c^2 + \frac{P^2}{2\tilde{m}} - \frac{p\delta m(r)p}{2m^2} + \frac{\hbar^2 \nabla^2 \delta m(r)}{8\tilde{m}^2} - \frac{P^4}{8\tilde{m}^3c^2} - \frac{\hbar [\nabla \delta m(r) \times p] \cdot \sigma}{4\tilde{m}^2}. \quad (A1)$$

All terms in Eq. (A1) with the exception of the third which describes the position-dependent mass can be taken as “ordinary.” The second, third, and fourth terms (the fourth is the Darwin term) can either be written in the following form:

$$T_2 = \frac{1}{2} \frac{1}{m(r)} \frac{1}{P} + \frac{\hbar^2 \nabla^2 \delta m(r)}{8\tilde{m}^2},$$

or combined into one, quadratic in the momentum, kinetic energy operator:

$$T_2 = \frac{1}{2} \frac{1}{\sqrt{m(r)}} \frac{1}{P} \frac{1}{\sqrt{m(r)}},$$

or some other equivalent form can be used. For example, Ref. [21] uses the following form for $T_2$:

$$T_2 = \frac{1}{4} \left[ P \frac{1}{\sqrt{m(r)}} \frac{1}{P} + \frac{1}{\sqrt{m(r)}} \frac{1}{P} \right].$$

Thus, in the model Dirac equation with position-dependent gap the concept of a position-dependent effective mass shows up only beyond the frames of the non-relativistic (quadratic) approximation.
Appendix B: Regarding transfer processes in the two-dimensional Brillouin zone for a (001) heterostructure

Let us consider the second sum in Eq. (4) describing transfer processes in the two-dimensional Brillouin zone and prove that it does not contribute in the case of interest to us of states near the Brillouin zone center in (001) heterostructures. Since the function $G(q)$ is nonzero for any $q$, there also exist nonzero vectors of the inverse lattice $K_j$ for which $k'_\parallel - k_\parallel = K_j$. Here $k'_\parallel$ and $k_\parallel$ are components of vectors belonging to the Brillouin zone. There exits a finite number of vectors $K_j$ possessing this property. Therefore, in general we should also retain the second sum in expression (4). Let us now consider the interesting case of a (001) heterostructure. The octagon in Fig. 1 represents the projection of the bulk Brillouin zone onto the (001) plane, and projections of sites of the lattice are denoted by asterisks. The function $F'_n(k'_x,k'_y)$ on which the operator $M_{nn'}(k,k')$ acts in Eq. (3) is defined only for $k'_\parallel$ belonging to the projection of the bulk Brillouin zone onto the (001) plane. But since all sites $K_{||j}$ for $j \neq 0$ lie outside this projection, there exists a region of $k_\parallel$ for which $|k'_\parallel - k_\parallel| < K_\parallel j$, $j \neq 0$. This region is defined by the inequality $|k_x| + |k_y| < \pi/a$ and is indicated in the figure by the square with diagonal $2\pi/a$. The area of this region is one-fourth that of the area of the first 2D Brillouin zone (the square with diagonal $4\pi/a$). In the region $|k_x| + |k_y| < \pi/a$ the second sum in expression (4) does not contribute to the equations for the envelope functions. Its larger dimensions ensure satisfaction of the conditions of applicability of...
the derived equations for the envelope functions describing states near the Γ point.

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