Quantum Mechanics of Electrons in Crystals with Graded Composition

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We construct the effective Hamiltonian describing the motion of electrons in compositionally graded crystals which is *valid throughout a given energy band* and part way into the gaps. Near the edges of a simple or degenerate band this effective Hamiltonian reduces to an effective mass Hamiltonian with position dependent effective mass. Next, we examine more general states—not restricted to the vicinity of a band edge—in crystals with composition and applied potential variation in one direction. We obtain a WKB-type solution for the envelope functions, as well as the appropriate turning point connection rules.

In recent years, the ability to fabricate semiconductor nanostructures with highly controlled variable chemical composition has led to a renewed interest in the physics of electrons in nearly periodic fields and at interfaces. In this Letter we present some results of an ongoing investigation into this subject: (i) First, an effective Hamiltonian $\mathcal{H}$ is constructed that describes the behavior of electrons in a semiconductor whose composition has a slow spatial variation—slow enough so the concept of a local "band" is well defined. This will be the case when the length scale over which the composition varies is much larger than a lattice constant. The accuracy of this effective Hamiltonian depends only on the composition gradient—*it is valid throughout a given energy band* and part way into the gaps. (ii) Second, we use this effective Hamiltonian to (a) derive effective mass Hamiltonians valid near the edges of simple and degenerate bands (settling a controversy in the literature [1–11]), and (b) derive a WKB-type envelope function and associated turning point connection rules for states, not necessarily near a band edge, in crystals with composition and applied potential variation in one direction.

Consider first a random alloy A_cB_{1-c} with a spatially *uniform* composition characterized by c. Any particular sample, J, will have a nonperiodic single-particle potential $V_J(\mathbf{r},c)$ due to the particular positions of the type A and B atoms. We now define a *periodic* potential, $V(\mathbf{r},c) \equiv \langle V_J(\mathbf{r},c)\rangle$, where $\langle\ \rangle$ represents the ensemble average over all atomic configurations having a fraction c of type A atoms. This approximation is similar to the virtual crystal approximation [12], a linear interpolation between $V(\mathbf{r},0)$ and $V(\mathbf{r},1)$. We assume the knowledge of the band structures $E_n(\mathbf{k},c)$ associated with the periodic potentials $V(\mathbf{r},c)$. Next consider a sample with a composition $c(\mathbf{r})$ varying slowly on the scale of a lattice constant. We shall call $V(\mathbf{r},c(\mathbf{r}))$ the *nearly periodic potential* and $E_n(\mathbf{k},c(\mathbf{r}))$ the *local band structure* of the alloy.

For simplicity, we consider a monatomic Bravais lattice $l = \sum_{\alpha=1}^{3} l_\alpha \mathbf{b}^\alpha$, where the $\mathbf{b}^\alpha$ are the three smallest primitive lattice vectors. We assume that the primitive lattice vectors $\mathbf{b}^\alpha$ are independent of c. Most of the results we will present are valid for arbitrary crystal structures—the places where the Bravais lattice assumption is explicitly used will be noted.

I. Effective Hamiltonian.— Let H be the Hamiltonian for an electron in a crystal with a slowly varying composition $c(\mathbf{r})$, and let $U(\mathbf{r})$ be a slowly varying applied potential. We expand the Schrödinger equation in a generalized Wannier function (GWF) basis [13,14]:

$$\sum_{l'n'v'} (\langle a_{lnv}|H|a_{l'n'v'}\rangle + \langle a_{lnv}|U|a_{l'n'v'}\rangle)\Phi_{l'}^{n'v'} = E\Phi_l^{nv}. \quad (1)$$

The GWFs $|a_{lnv}\rangle$ in a nearly periodic potential are labeled by a band index n, a branch index v if the band is composite, and a lattice vector l about which the function is centered. They have the same completeness, orthonormality $\langle a_{lnv}|a_{l'n'v'}\rangle = \delta_{ll'}\delta_{nn'}\delta_{vv'}$, band diagonality $\langle a_{lnv}|H|a_{l'n'v'}\rangle = \delta_{nn'}\langle a_{lnv}|H|a_{l'nv'}\rangle$, and localization properties as the standard Wannier function (WF) in a periodic potential. The eigenvectors Φ_l^{nv} of (1) determine the eigenfunctions in the coordinate representation: $\psi(\mathbf{r}) = \sum_{lnv}\Phi_l^{nv}a_l^{nv}(\mathbf{r}-l)$, where $a_l^{nv}(\mathbf{r}-l) \equiv \langle\mathbf{r}|a_{lnv}\rangle$.

The exact matrix elements in (1), of course, are unknown. We shall show that we can approximate the matrix elements of H by using the local band structure—the precise forms of the Hamiltonian H and GWFs $a_l^{nv}(\mathbf{r}-l)$ are not needed. Consider first the matrix elements of the Hamiltonian H_c for an electron in a crystal with a *uniform* composition c. For a nondegenerate band n, in the standard WF basis, $\langle a_l^0;c|H_c|a_{l'}^0;c\rangle = v^{-1}\int d^3k\, E(\mathbf{k},c) \times e^{i\mathbf{k}\cdot(l-l')}$. Here v is the Brillouin zone (BZ) volume and the integral is over the first BZ. The matrix elements in the *graded* crystal depend on the composition of the crystal near the sites l and l'. Therefore, we can approximate the exact $\langle a_l|H|a_{l'}\rangle$ by

$$\mathcal{H}_{ll'} \equiv \frac{1}{v}\int_{BZ} d^3k\, E\left(\mathbf{k}, c\left(\frac{l+l'}{2}\right)\right)e^{i\mathbf{k}\cdot(l-l')}. \quad (2)$$

This defines our effective Hamiltonian $\mathcal{H}$ for nondegenerate bands. Although band indices have been suppressed, (2) is to be understood to be exactly band diagonal. $\mathcal{H}$ is manifestly Hermitian, and since $E(\mathbf{k},c) = E(-\mathbf{k},c)$ for a given c, it is also real. The form we have chosen for $\mathcal{H}$ is not unique—alternate forms, for example,

$$\frac{1}{v}\int d^3k\, E\left(\mathbf{k}, \frac{c(l)+c(l')}{2}\right)e^{i\mathbf{k}\cdot(l-l')},$$

differ from (2) by terms of order ϵ^2. Here $\epsilon \equiv b|\nabla c|$ is a dimensionless small parameter characterizing the small gradient in $c(\mathbf{r})$, and b is the average magnitude of the three $\mathbf{b}^\alpha$. In general, the errors in (2) are of order ϵ, the change in c over a unit cell, in contrast to errors of the order of the change in c over the entire sample if a *single* mean composition were used. In a study to be published [14], we have shown that for a Bravais lattice the exact $\langle a_l|H|a_{l'}\rangle$ are *real*, from which it follows that the $\langle a_l|H|a_{l'}\rangle$ have no parts of order ϵ; hence $\mathcal{H} = H(1 + \mathcal{O}(\epsilon^2))$.

For a degenerate band n with branches v, the effective Hamiltonian is defined similarly. First note that in a *uniform* crystal, the energy bands $E^v(\mathbf{k},c)$ may be obtained from the matrix $D^{vv'}(\mathbf{k},c) \equiv \sum_{\bar{l}}\langle a_{l v}^0; c|H_c|a_{l+\bar{l},v'}^0; c\rangle e^{-i\mathbf{k}\cdot\bar{l}}$, whose eigenvalues are $E^v(\mathbf{k},c)$. Conversely, if $E^v(\mathbf{k},c)$ is known from experiment or from a band structure calculation, the matrix D can be determined by the requirement that its eigenvalues agree with the known $E^v(\mathbf{k},c)$. In practice a small number of *independent* matrix elements $\langle a_{l v}^0; c|H_c|a_{l+\bar{l},v'}^0; c\rangle$ (on-site, nearest neighbor, etc.) in D will be sufficient to fit the band structure. The matrix D is not unique, since the WFs $|a_{l v}^0; c\rangle$ are not unique; however, any matrix D yielding the correct energy bands is acceptable. In terms of the matrix D, the effective Hamiltonian for a degenerate band may be written as

$$\mathcal{H}_{ll'}^{vv'} = \frac{1}{v}\int d^3k\, D^{vv'}\left[\mathbf{k}, c\left(\frac{l+l'}{2}\right)\right]e^{i\mathbf{k}\cdot(l-l')}. \tag{3}$$

In general, $\mathcal{H} = H(1 + \mathcal{O}(\epsilon))$ for a degenerate band.

Since the external potential $U(\mathbf{r})$ in (1) is assumed to be slowly varying, $\langle a_{lnv}|U|a_{l'n'v'}\rangle \approx U(l)\delta_{ll'}\delta_{nn'}\delta_{vv'}$. In general, the errors in this approximation are $\mathcal{O}(\gamma)$

$+\mathcal{O}(\epsilon\gamma)$, where $\gamma \equiv b|\nabla U|/W$ is a dimensionless small parameter characterizing the small gradient in $U(\mathbf{r})$, and $W(\mathbf{r})$ is the local bandwidth. To see this, note that the relation is exact when $\gamma = 0$, but has $\mathcal{O}(\gamma)$ errors even in a uniform crystal. However, in a Bravais lattice (and in other crystal structures with inversion symmetry about the midpoints between the lattice sites), there are no $\mathcal{O}(\gamma)$ errors, but rather $\mathcal{O}(\gamma^2)$ errors instead. Therefore, Eq. (1) for the nth band becomes

$$\sum_{l'v'}\mathcal{H}_{ll'}^{vv'}\Phi_{l'}^{v'} + U(l)\Phi_l^v = E\Phi_l^v, \tag{4}$$

with errors $\mathcal{O}(\gamma^2) + \mathcal{O}(\epsilon\gamma)$, plus $\mathcal{O}(\epsilon^2)$ errors for a simple band in a Bravais lattice or $\mathcal{O}(\epsilon)$ errors otherwise. Under the stated conditions of slowly varying $U(\mathbf{r})$ and $c(\mathbf{r})$, *the solutions of the discrete linear equations (4) provide a complete description of the behavior of electrons associated with a given band*. In what follows, we apply (4) to two special cases.

IIa. Effective mass Hamiltonians.— We now show that near a band edge, $\mathcal{H}$ reduces to an effective mass Hamiltonian [15,16] with position dependent effective mass. Consider first the case where E is near the minimum of a nondegenerate band, that minimum occurring at the center of the BZ of the local band structure, independent of composition. In this regime, the WF amplitudes Φ_l are slowly varying in space. Let $F(\mathbf{r})$ be a smooth interpolating function passing exactly through the values Φ_l at each site: $F(\mathbf{r})|_l = \Phi_l$. The definition of F for all $\mathbf{r}$ will be given below; for now we assume that F has continuous first and second derivatives. Equation (4) can then be extended to the continuum by using the definition (2) of $\mathcal{H}$ for nondegenerate bands, Taylor expanding F to second order, and noting that $E(\mathbf{k},c(l)) = \sum_{\bar{l}}\mathcal{H}_{l,l+\bar{l}}\cos(\mathbf{k}\cdot\bar{l}) + \mathcal{O}(\epsilon^2)$. This leads to

$$\left[-\frac{1}{2}\nabla_i\left[\frac{\partial^2 E(\mathbf{k},c(\mathbf{r}))}{\partial k_i \partial k_j}\right]_{\mathbf{k}=0}\nabla_j + E(0,c(\mathbf{r})) + U(\mathbf{r}) - E\right]F(\mathbf{r})\Bigg|_l \approx 0, \tag{5}$$

with errors $\mathcal{O}(\gamma^2) + \mathcal{O}(\epsilon\gamma) + \mathcal{O}(\epsilon^2) + \mathcal{O}(\epsilon\eta^3) + \mathcal{O}(\eta^4)$, assuming a Bravais lattice. Here $\eta = b|\nabla F|/F$ is a dimensionless small parameter characterizing the slow variation of $F(\mathbf{r})$, and the first term in (5) involves the *local effective mass tensor*

$$\left[\frac{1}{m^*(\mathbf{r})}\right]_{ij} \equiv \hbar^{-2}\left[\frac{\partial^2 E(\mathbf{k},c(\mathbf{r}))}{\partial k_i \partial k_j}\right]_{\mathbf{k}=0}.$$

Note that we have not performed an *ad hoc* symmetrization in (5). Equation (5) holds at each lattice site l. It involves the continuous *envelope function* $F(\mathbf{r})$ only through its value and its first and second derivatives at $\mathbf{r} = l$. $F(\mathbf{r})$ is now *defined* for all $\mathbf{r}$ by requiring it to satisfy $(H_{\text{eff}} - E)F = 0$ exactly, where

$$H_{\text{eff}} \equiv \frac{-\hbar^2}{2}\nabla_i\left[\frac{1}{m^*(\mathbf{r})}\right]_{ij}\nabla_j + \mathcal{E}(\mathbf{r}) + U(\mathbf{r}), \tag{6}$$

along with the boundary conditions of the original problem. Here $\mathcal{E}(\mathbf{r})$ is the energy of the local band edge. The

effective mass Hamiltonian (6) also applies to states near the top of a nondegenerate band—in this case $\mathcal{E}(\mathbf{r})$ corresponds to the energy of the local band maximum. Solving the eigenvalue problem $(H_{\text{eff}} - E)F = 0$ yields eigenvectors $F(l)$ and eigenvalues E equal to the exact values apart from the errors quoted in (5). Alternative forms of the kinetic energy term in H_{eff}, differing by $\mathcal{O}(\epsilon^2)$ terms, are (in one dimension)

$$T_{\text{eff}} = \frac{1}{4}\left[p^2\frac{1}{m^*} + \frac{1}{m^*}p^2\right], \quad T_{\text{eff}} = \frac{1}{2}\frac{1}{\sqrt{m^*}}p^2\frac{1}{\sqrt{m^*}},$$

and so forth. *These kinetic terms are all equivalent when their accuracy is considered*, a point which seems to have been overlooked in the literature [1-11].

An effective mass Hamiltonian for degenerate bands may be derived similarly. For simplicity, we again assume that the extremum occurs at the BZ center. Defining a continuous envelope function $F^v(\mathbf{r})$ for the vth

branch of band n results in a set of coupled differential equations $\sum_{v'}(H_{\text{eff}}^{vv'} - E\delta^{vv'})F^{v'} = 0$ for the $F^v(\mathbf{r})$. We find

$$H_{\text{eff}}^{vv'} \equiv -\frac{1}{2}V_i \left[\frac{\partial^2 D^{vv'}(\mathbf{k}, c(\mathbf{r}))}{\partial k_i \partial k_j} \right]_{k=0} V_j$$
$$+ D^{vv'}(0, c(\mathbf{r})) + U(\mathbf{r})\delta^{vv'}, \qquad (7)$$

with errors $\mathcal{O}(\gamma^2) + \mathcal{O}(\epsilon\gamma) + \mathcal{O}(\epsilon) + \mathcal{O}(\epsilon\eta^3) + \mathcal{O}(\eta^4)$. The quantity $[\partial^2 D^{vv'}(\mathbf{k}, c)/\partial k_i \partial k_j]_{k=0}$ has a well known form given in Ref. [15]. Our results (6) and (7) agree with perturbative calculations in the $c \ll 1$ limit [3–5]; however, the present derivations are free of this assumption.

IIb. WKB approximation for crystals.— We now obtain a WKB-type solution to (4) for a nondegenerate band, whose validity is not limited to the vicinity of a band edge. We assume that the composition and external potential vary in the z direction only. Then, in obvious notation, the WF amplitudes may be written as $\Phi_l = e^{i\mathbf{k}_\perp \cdot l_\perp}F_l$, where $\mathbf{k}_\perp$ is a constant, and (4) reduces to

$$\sum_{\bar{l}} h_{l,l+\bar{l}}F_{l+\bar{l}} + U(l)F_l = EF_l, \qquad (8)$$

where $h_{l,l+\bar{l}}(\mathbf{k}_\perp) \equiv \sum_{\bar{l}_\perp} \mathcal{H}_{l,l+\bar{l}}e^{i\mathbf{k}_\perp \cdot \bar{l}_\perp}$. Now define a local wave number $k(z)$ by

$$E(k(z), c(z)) + U(z) = E, \qquad (9)$$

suppressing the dependence on $\mathbf{k}_\perp$. There may be more than one solution $k(z)$ of (9); the following analysis applies to each solution. The z component of the local velocity is defined as $v(z) \equiv [\partial E(\mathbf{k}, c(z))/\partial k]_{k=k(z)}$. A WKB-type solution of (8) is

$$F_l = \frac{1}{\sqrt{v(l)}} \exp\left[i\int_{l_0}^{l} k(z)dz \right],$$

with $\mathcal{O}(\epsilon^2) + \mathcal{O}((b^2 k')^2) + \mathcal{O}(b^2 k'\epsilon)$ errors, as can be verified by direct substitution. When written in terms of the continuous variable z, the envelope function is

$$F(z) = \frac{1}{\sqrt{\partial E/\partial k}} \exp\left[i\int_{z_0}^{z} k(z')dz' \right], \qquad (10)$$

where k and E are related through the band structure and $\partial E/\partial k$ is understood to be a function of position.

This is the appropriate generalization of the conventional WKB wave function to electrons in uniform or slowly graded crystals.

In analogy with conventional WKB theory, we now calculate the *connection rules* by solving Eq. (4) near a turning point where the energy E is equal to the total energy of the band edge. Since we are interested in the regime near the band edge, we may use the effective mass Hamiltonian with position dependent effective mass (6), in one dimension. Let $V(z) \equiv \mathcal{E}(z) + U(z)$ be the total energy at a band minimum, the turning point z_0 defined by $V(z_0) = E$. We then shift the z origin to the turning point and expand the inverse effective mass and V linearly about the turning point:

$$\frac{1}{m^*(z)} \approx \frac{1}{m_0^*}(1 - \beta z), \quad V(z) \approx V_0 + V_0'z. \qquad (11)$$

For definiteness, we consider the case where $V_0' > 0$; the case where $V_0' < 0$ is analogous. Combining (11) with (6) yields

$$\left[-\frac{d^2}{dz^2} + \tilde{\gamma}z + \beta\left[z\frac{d^2}{dz^2} + \frac{d}{dz} \right] \right]F(z) = 0,$$

where $\tilde{\gamma} \equiv (2m_0^*/\hbar^2)V_0'$. Next we introduce a stretched coordinate $\xi \equiv \tilde{\gamma}^{1/3}z$; then

$$\left[-\frac{d^2}{d\xi^2} + \xi + \lambda\left[\xi\frac{d^2}{d\xi^2} + \frac{d}{d\xi} \right] \right]F(\xi) = 0, \qquad (12)$$

where $\lambda \equiv \beta\tilde{\gamma}^{-1/3}$. We first assume that $\lambda \ll 1$, which can be shown to be equivalent to the assumption that the fractional change of $(m^*)^{-1}$ is small over the turning point region $L \approx \tilde{\gamma}^{-1/3}$. Also, as in conventional WKB theory, the condition $(V_0''/V_0')L \ll 1$ must be satisfied.

We now solve (12) for the usual case, where λ is small. Asymptotic expansions of $F(\xi)$ as $\xi \to \pm\infty$ will be used to infer the connection rules. The solution of (12) may be written as a contour integral $F(\xi) = c\int_\Gamma e^{\xi s}g(s)ds$ in the complex s plane, where c is a constant, $g(s) = e^{-(1/3)s^3}[1 - \lambda(\frac{1}{2}s^2 - \frac{1}{5}s^5)] + \mathcal{O}(\lambda^2)$, and the end points s_i and s_f of Γ satisfying $7\pi/6 \leq \arg(s_i) \leq 3\pi/2$ and $\pi/2 \leq \arg(s_f) \leq 5\pi/6$ as $|s| \to \infty$. Saddle-point approximations then yield the following asymptotic solutions (to order λ):

$$F(\xi) \sim \frac{1}{2}\xi^{-1/4}e^{-(2/3)\xi^{3/2}}\left[1 - \frac{1}{5}\lambda\xi^{5/2} \right] \quad \text{as } \xi \to +\infty, \qquad (13a)$$

$$F(\xi) \sim |\xi|^{-1/4}\sin\left(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4} \right)\left[1 - \frac{1}{5}\lambda|\xi|^{5/2}\cot\left(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4} \right) \right] \quad \text{as } \xi \to -\infty, \qquad (13b)$$

where we have used $c = (2\pi^{1/2}i)^{-1}$. Near the turning point, $k = \tilde{\gamma}^{1/3}[-\xi/(1 - \lambda\xi)]^{1/2}$. Then (13) implies the connection rules

$$\left| \frac{\partial E}{\partial k} \right|^{-1/2}\cos\left(\int |k|dz - \frac{\pi}{4} \right) \leftarrow \frac{1}{2}\left| \frac{\partial E}{\partial k} \right|^{-1/2}\exp\left(-\int |k|dz \right), \qquad (14)$$

for the envelope functions. The derivation of (14) is valid for small λ. A derivation of the connection rules up to $\lambda \approx 1$ is also possible, by performing an analytic continuation and passing *around* the turning point in the complex z plane, remaining everywhere in the region where (10) is valid. We have also carried out this calculation and have obtained
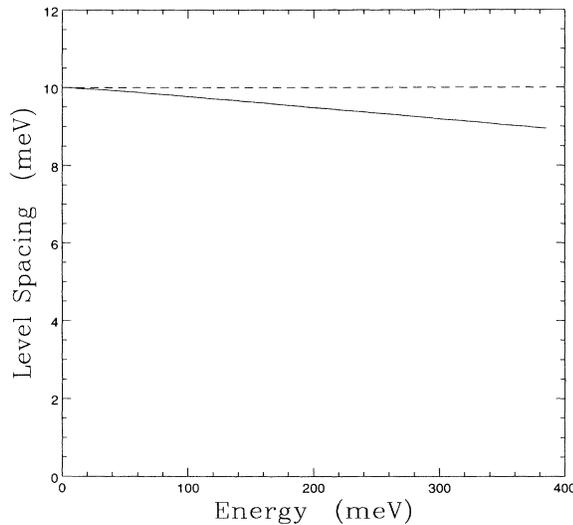
FIG. 1. Energy level spacing in a $Al_cGa_{1-c}As$ parabolic quantum well, slowly graded from $c = 0$ at the center of the well to $c = 0.5$ at the edges. The depth of the quantum well is 385 meV, and the width has been chosen so that the energy level spacing at the bottom of the well is 10 meV.

precisely the same connection rules (14). *Therefore, the envelope function connection rules take the form* (14), which are similar to the standard WKB connection rules

$$|k|^{-1/2}\cos\left[\int |k|dz - \frac{\pi}{4}\right] \leftarrow \frac{1}{2}|k|^{-1/2}\exp\left(-\int |k|dz\right).$$

The WKB envelope functions and the turning point connection rules immediately yield the bound state quantization condition

$$\frac{1}{2\pi}\oint k(z)dz = n + \frac{1}{2}. \tag{15}$$

Here n is a non-negative integer labeling the bound state, and $k(z)$ is a solution of $E(k(z),k_\perp,c(z)) + U(z) = E$.

Equation (15) provides an efficient means to calculate energy levels—*including high lying ones*—in a slowly graded (e.g., parabolic) quantum well. Let $S(E) \equiv (2\pi)^{-1}\oint k(z)dz$ be the dimensionless action associated with the classical trajectory of an electron of energy E, the z component of that trajectory forming a closed path, for some fixed value of $k_\perp$. Simple numerical integration yields $S(E)$ for each E, for any local band structure and confining potential. A plot of S vs E yields eigenvalues E_n, when $S(E_n) = n + \frac{1}{2}$, and the density of levels $(\partial S/\partial E)^{-1}$. The complete spectrum is obtained by including the energy levels corresponding to each $k(z)$ [17].

In Fig. 1, we apply (15) to the calculation of single-electron energy levels in a slowly graded $Al_cGa_{1-c}As$ parabolic quantum well [18], with the growth axis in the (100) direction. The curvature of the parabolic band edge has been chosen so that the energy level spacing at

the bottom of the well is 10 meV. The band structure $E(k,c)$ we use consists of a linear interpolation between the band structure of GaAs and that of AlAs [19], the gap becoming indirect at $c \approx 0.5$. We have also chosen $k_\perp = 0$. The dashed curve results from the application of the effective mass approximation (6) to the infinite well with a *uniform* effective mass $m^* = 0.067m_e$ of GaAs; it shows the expected uniform level spacing. The solid curve deviates from the dashed curve because (15) uses the true band structure of the material and accounts for the composition gradient.

In conclusion, we have constructed an effective Hamiltonian which describes the motion of electrons in compositionally graded crystals throughout a local nondegenerate or degenerate energy band. As special applications we have derived effective mass Hamiltonians with position dependent effective mass (valid near band edges), and a WKB-type approximation for crystals with inhomogeneity in one direction. In the future, we plan to include the effects of magnetic fields varying slowly in space, and time-dependent fields.

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