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QUANTUM MECHANICS OF ELECTRONS IN CRYSTALS WITH GRADED COMPOSITION

by M. R. Geller and W. Kohn

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Quantum Mechanics of Electrons in Crystals with Graded Composition

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ABSTRACT:

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. The effective Hamiltonian, constructed from the band structures of uniform crystals, also includes the effects of a slowly varying applied scalar potential $U(\mathbf{r})$. Near the edges of a nondegenerate band, this effective Hamiltonian reduces to an effective mass Hamiltonian with position dependent mass (one of several forms previously appearing in the literature): $H_{\text{eff}} = \frac{1}{2}p_i\left(\frac{1}{m^*(\mathbf{r})}\right)_{ij}p_j + \mathcal{E}(\mathbf{r}) + U(\mathbf{r})$, where $\mathcal{E}(\mathbf{r})$ is the energy of the band edge as a function of position. The analogous effective mass Hamiltonian for degenerate bands is also derived. 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 non-periodic 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. In the future we hope to return to the effects of the deviation from near periodicity present in any particular sample, which causes electron scattering.

For simplicity, we consider a monatomic Bravais lattice $\mathbf{l} = \sum_{\alpha=1}^{3} l_\alpha \mathbf{b}^\alpha$, 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]:

$$\sum_{\mathbf{l}'n'\nu'} \Big(\langle a_{\mathbf{l}n\nu} | H | a_{\mathbf{l}'n'\nu'} \rangle + \langle a_{\mathbf{l}n\nu} | U | a_{\mathbf{l}'n'\nu'} \rangle \Big) \Phi_{\mathbf{l}'}^{n'\nu'} = E \; \Phi_{\mathbf{l}}^{n\nu}. \tag{1}$$

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

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 $a_{\mathbf{l}}^{n\nu}(\mathbf{r} - \mathbf{l})$ 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, $\langle a_{\mathbf{l}}^0; c | H_c | a_{\mathbf{l}'}^0; c \rangle = \frac{1}{v} \int d^3k \; E(\mathbf{k}, c) \; e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')}$. 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 $\mathbf{l}$ and $\mathbf{l}'$. Therefore, we can approximate the exact $\langle a_{\mathbf{l}} | H | a_{\mathbf{l}'} \rangle$ by

$$\mathcal{H}_{\mathbf{l}\mathbf{l}'} \equiv \frac{1}{v} \int_{\mathrm{BZ}} d^3k \; E\big(\mathbf{k}, c(\tfrac{\mathbf{l}+\mathbf{l}'}{2})\big) \; e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')}. \tag{2}$$

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 $\frac{1}{v}\int d^3k\ E\big(\mathbf{k}, \frac{c(\mathbf{l})+c(\mathbf{l}')}{2}\big)\ e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')}$, 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 $\langle a_\mathbf{l}|H|a_{\mathbf{l}'}\rangle$ are *real*, from which it follows that the $\langle a_\mathbf{l}|H|a_{\mathbf{l}'}\rangle$ have no parts of order ϵ; hence $\mathcal{H} = H\big(1 + \mathcal{O}(\epsilon^2)\big)$.

For a degenerate band n with branches ν, the effective Hamiltonian is defined similarly. First note that in a *uniform* crystal, the energy bands $E^\nu(\mathbf{k}, c)$ may be obtained from the matrix $D^{\nu\nu'}(\mathbf{k}, c) \equiv \sum_\mathbf{l} \langle a^0_{\mathbf{l}\nu}; c|H_c|a^0_{\mathbf{l}+\bar{\mathbf{l}},\nu'}; c\rangle\ e^{-i\mathbf{k}\cdot\bar{\mathbf{l}}}$, whose eigenvalues are $E^\nu(\mathbf{k}, c)$ [15]. Converesly, if $E^\nu(\mathbf{k}, c)$ 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 $E^\nu(\mathbf{k}, c)$. In practice a small number of *independent* matrix elements $\langle a^0_{\mathbf{l}\nu}; c|H_c|a^0_{\mathbf{l}+\bar{\mathbf{l}},\nu'}; c\rangle$ (on-site, nearest neighbor ...) in D will be sufficient. The matrix D is not unique, since the Wannier functions $|a^0_{\mathbf{l}\nu}; c\rangle$ 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

$$\mathcal{H}^{\nu\nu'}_{\mathbf{l}\mathbf{l}'} = \frac{1}{v}\int d^3k\ D^{\nu\nu'}\big(\mathbf{k}, c(\tfrac{\mathbf{l}+\mathbf{l}'}{2})\big)\ e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')}. \tag{3}$$

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

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

$\gamma \equiv \frac{b|\nabla U|}{W}$ is a dimensionless small parameter characterizing the small gradient in $U(\mathbf{r})$, and $W(\mathbf{r})$ is the local band width. 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

$$\sum_{\mathbf{l}'\nu'} \mathcal{H}^{\nu\nu'}_{\mathbf{l}\mathbf{l}'}\ \Phi^{\nu'}_{\mathbf{l}'} + U(\mathbf{l})\Phi^{\nu}_{\mathbf{l}} = E\ \Phi^{\nu}_{\mathbf{l}}, \tag{4}$$

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 [16,17] with position dependent 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 $\Phi_{\mathbf{l}}$ are slowly varying in space. Let $F(\mathbf{r})$ be a smooth interpolating function passing exactly through the values $\Phi_{\mathbf{l}}$ at each site: $F(\mathbf{r})\big|_{\mathbf{l}} = \Phi_{\mathbf{l}}$. 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 $E\big(\mathbf{k}, c(\mathbf{l})\big) = \sum_{\bar{\mathbf{l}}} \mathcal{H}_{\mathbf{l},\mathbf{l}+\bar{\mathbf{l}}} \cos(\mathbf{k}\cdot\bar{\mathbf{l}}) + \mathcal{O}(\epsilon^2)$. This leads to

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

with errors $\mathcal{O}(\gamma^2) + \mathcal{O}(\epsilon\gamma) + \mathcal{O}(\epsilon^2) + \mathcal{O}(\epsilon\eta^3) + O(\eta^4)$, assuming a Bravais lattice. Here $\eta \equiv \frac{b|\nabla F|}{F}$ is a dimensionless small parameter characterizing the slow variation of F, 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 $\mathbf{l}$. It involves the continuous envelope function $F(\mathbf{r})$ only through its value and its first and second derivatives at $\mathbf{r} = \mathbf{l}$. $F(\mathbf{r})$ is now *defined* for all $\mathbf{r}$ by requiring it to satisfy $\left(H_{\text{eff}} - E\right)F = 0$ 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 the band—in this case $\mathcal{E}(\mathbf{r})$ corresponds to the energy of the local band maximum. Solving the eigenvalue problem $\left(H_{\text{eff}} - E\right)F = 0$ yields eigenfunctions $F(\mathbf{l})$ 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) $T_{\text{eff}} = \frac{1}{4}(p^2\frac{1}{m^*} + \frac{1}{m^*}p^2)$, $T_{\text{eff}} = \frac{1}{2}\frac{1}{\sqrt{m^*}}p^2\frac{1}{\sqrt{m^*}}$, 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 $F^\nu(\mathbf{r})$ for the νth branch of band n results in a set of coupled differential equations $\sum_{\nu'}\left(H_{\text{eff}}^{\nu\nu'} - E\delta^{\nu\nu'}\right)F^{\nu'} = 0$ for the $F^\nu(\mathbf{r})$. We find

$$H_{\text{eff}}^{\nu\nu'} \equiv -\hbar^2\nabla_i\left(\frac{\partial^2 D^{\nu\nu'}(\mathbf{k},c(\mathbf{r}))}{\partial k_i \partial k_j}\right)_{\mathbf{k}=0}\nabla_j + D^{\nu\nu'}(0,c(\mathbf{r})) + U(\mathbf{r})\delta^{\nu\nu'}, \tag{7}$$

with errors $\mathcal{O}(\gamma^2) + \mathcal{O}(\epsilon\gamma) + \mathcal{O}(\epsilon) + \mathcal{O}(\epsilon\eta^3) + \mathcal{O}(\eta^4)$. The quantity $\left(\frac{\partial^2 D^{\nu\nu'}(\mathbf{k},c(\mathbf{r}))}{\partial k_i \partial k_j}\right)_{\mathbf{k}=0}$ 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 $\Phi_l = e^{i\mathbf{k}_\perp \cdot \mathbf{l}_\perp} F_l$, where $\mathbf{k}_\perp$ is a constant, and (4) reduces to

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

where $h_{l,l+\bar{l}}(\mathbf{k}_\perp) \equiv \sum_{\bar{\mathbf{l}}_\perp} \mathcal{H}_{l,l+\bar{\mathbf{l}}}\, e^{i\mathbf{k}_\perp \cdot \bar{\mathbf{l}}_\perp}$. The local band structure may be written as $E\big(k, c(l)\big) = \sum_{\bar{l}} h_{l,l+\bar{l}}\, e^{ik\bar{l}}$, where we have suppressed the dependence on $\mathbf{k}_\perp$. Now define a local wavenumber $k(z)$ by

$$E\big(k(z), c(z)\big) + U(z) = E. \tag{9}$$

There may be more than one solution $k(z)$ to (9); the following analysis applies to each solution. The z component of the local velocity is defined as $v(z) \equiv \left(\frac{\partial E(\mathbf{k}, c(z))}{\partial k}\right)_{k=k(z)}$. A WKB solution to (8) is $F_l = \frac{1}{\sqrt{v(l)}}\, e^{i\int_{l_0}^{l} k(z)dz}$, with $\mathcal{O}(\epsilon^2) + \mathcal{O}\big((b^2k')^2\big) + \mathcal{O}(b^2k'\epsilon)$ errors, as can be verified by direct substitution. When written in terms of the continuous variable z, the envelope function is

$$F(z) = \frac{1}{\sqrt{\partial E/\partial k}}\, e^{i\int_{z_0}^{z} k(z')dz'}, \tag{10}$$

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. $\mathbf{k}_\perp$ is a fixed parameter and will not be written. 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 of 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:

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

For definiteness, we consider the case where $V_0' > 0$; the case where $V_0' < 0$ is analogous. Combining (12) 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 $\tilde{\gamma} \equiv \frac{2m_0^*}{\hbar^2} V_0'$. Next we introduce a stretched coordinate $\xi \equiv \tilde{\gamma}^{\frac{1}{3}} z$; then

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

where $\lambda \equiv \beta\tilde{\gamma}^{-\frac{1}{3}}$.

In the following we shall assume that $\lambda \ll 1$, which can be shown to be equivalent to the assumption that the fractional change of $\frac{1}{m^*}$ is small over the turning point region $L \approx \tilde{\gamma}^{-\frac{1}{3}}$. Also, as in conventional WKB theory, the condition $\frac{V_0''}{V_0'} L \ll 1$ must be satisfied.

We first 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 formulae. The solution to (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, $g(s) = e^{-\frac{1}{3}s^3}[1 - \lambda(\frac{1}{2}s^2 - \frac{1}{5}s^5)] + \mathcal{O}(\lambda^2)$, and the endpoints s_i and s_f of Γ satisfy $\frac{7\pi}{6} \le \arg(s_i) \le \frac{3\pi}{2}$ and $\frac{\pi}{2} \le \arg(s_f) \le \frac{5\pi}{6}$ as $|s| \to \infty$ [18]. Saddlepoint approximations then yield the following asymptotic solutions (to order λ):

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

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

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

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

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

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

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

for *each* solution $k(z)$ of (9). Here n is a nonnegative integer labeling the bound state, and $p(z) = \hbar k(z)$ is given by $E\big(k(z), \mathbf{k}_\perp, c(z)\big) + U(z) = E$.

Equation (15) provides an efficient means to calculate energy levels—*including high lying ones*—in a slowly graded (e.g. parabolic) quantum well. Let $S(E) \equiv \frac{1}{2\pi}\oint k(z)\,dz$ 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 $\mathbf{k}_\perp$. Simple numerical integration yields $S(E)$ for each E, for any local band structure and confining potential. A plot of S versus 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 $k(z)$ [19].

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 [20], 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 we use consists of a linear interpolation between the band structure of GaAs and that of AlAs, and we have chosen

$\mathbf{k}_\perp = 0$. The dashed line results from the application of the effective mass approximation (6) with *uniform* effective mass $m^* = 0.067\ m_e$ of GaAs; it shows the expected uniform level spacing throughout the quantum well. The solid curve deviates from the dashed curve because (15) uses the true band structure of the material and accounts for the composition gradient [19].

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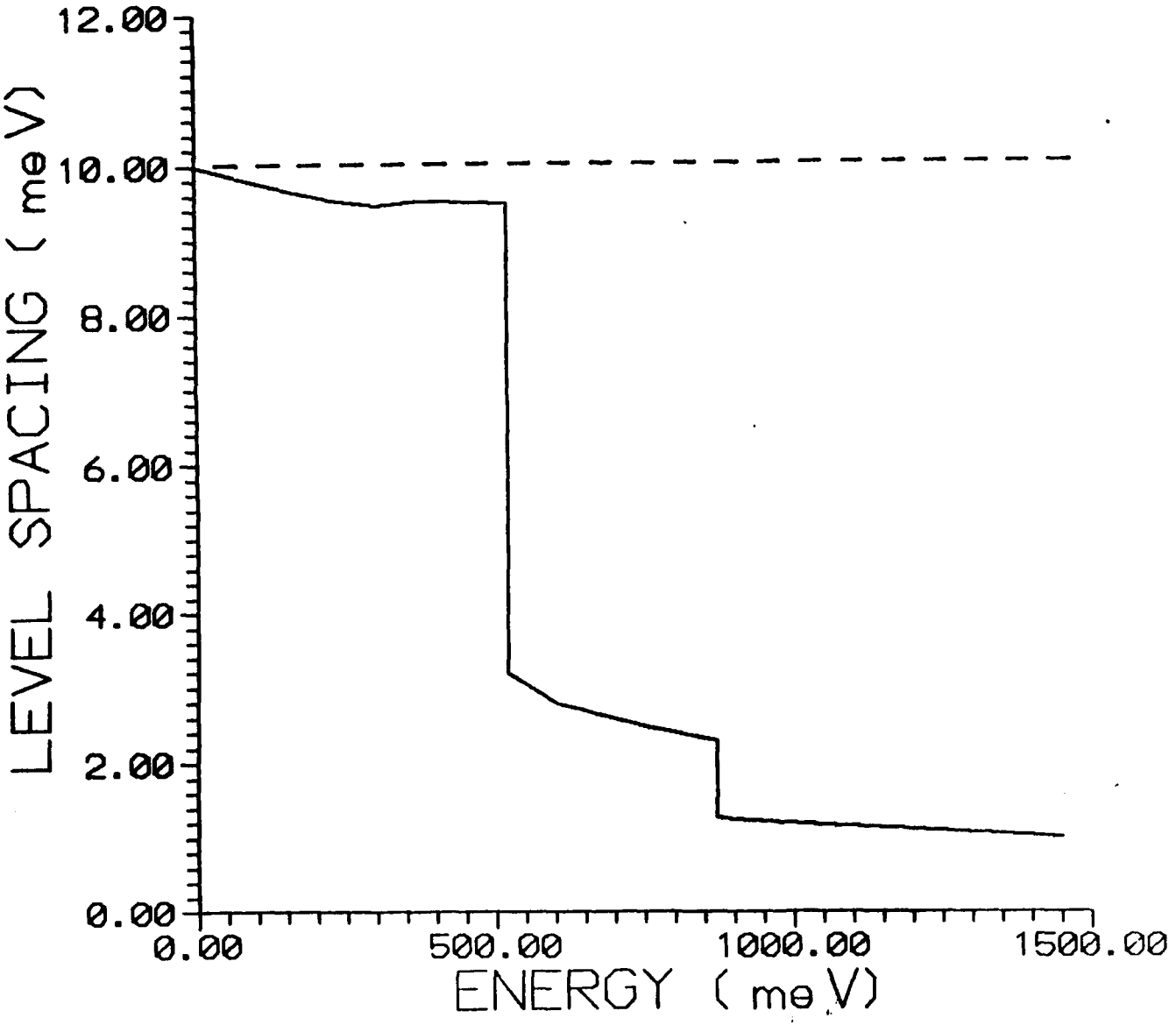
FIGURE CAPTION

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 $c = 1$ at the edges. The depth of the quantum well is 1.45 eV, and the width has been chosen to that the energy level spacing at the bottom of the well is 10 meV. The level spacing abruptly decreases at 520 meV due to the presence of the X-valley, and again decreases at 870 meV due to the appearance of the next band.


12.00
10.00
8.00
6.00
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LEVEL SPACING (meV)
0.00
500.00
1000.00
1500.00
ENERGY (meV)