Analog of the WKB approximation for Bloch electrons

Robert Nyden Hill and Børge Oddvar Rosland*
Department of Physics, University of Delaware, Newark, Delaware 19711
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Bremmer's approach to the ordinary WKB approximation is used as the basis of a generalization to the one-dimensional Schrödinger equation with a perturbed periodic potential. Numerical comparisons of the proposed approximation with exact solutions are given for Kronig-Penney models with an external field and with slowly varying period.

I. INTRODUCTION AND SUMMARY

The ordinary WKB approximation[1] has been extremely useful for discussing the behavior of quantum-mechanical particles in slowly varying potentials. The present paper will develop a similar approximation for studying the single-particle Schrödinger equation with a perturbed periodic potential. To be precise, the equation of interest is

$$\{\nabla^2 + 2m\hbar^{-2}[E - U(\vec{r};\lambda)]\}\psi = 0, \tag{1}$$

where $U(\vec{r};\lambda)$ is periodic in $\vec{r}$ for fixed λ. We will be concerned with the case where λ varies slowly with $\vec{r}$. This includes as a special case the periodic potential with a superposed weak external field $[U(\vec{r};\lambda) = U(\vec{r}) + \lambda]$ which is of interest for interband tunneling calculations as in the theory of internal field emission (the Zener effect)[2] and the theory of tunneling across semiconductor junctions.[3] By considering a much more general dependence on λ, we will obtain results which also apply to graded band-gap systems, to some amorphous materials,[4] and to strained crystals where even the period may change with λ.

Zener's original treatment of internal field emission[2] has implicit in it an *ad hoc* generalization of the WKB approximation to Bloch electrons. As is well known, solutions of (1) for fixed λ have the Bloch form

$$\psi_{\vec{k},s}(\vec{r};\lambda) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k},s}(\vec{r};\lambda), \tag{2}$$

where $u_{\vec{k},s}(\vec{r};\lambda)$ is periodic in r with the same period as $U(\vec{r};\lambda)$. Here $\hbar\vec{k}$ is the crystal momentum and s is a band index. By analogy with the WKB approximation, Zener replaced, in the one-dimensional case, the prefactor e^{ikx} of the Bloch form (2) by $\exp(i\int k\,dx)$. A more careful treatment was given by James,[5] who constructed approximate solutions by joining together solutions valid for a single period of the unperturbed periodic potential. James's method was in turn improved by Butcher, Hum, and Pike,[6] who treated more carefully the polarization effects due to the variation of the perturbing potentials within individual cells of the periodic potential. The papers of James and of Butcher, Hum, and Pike treated only the case of a periodic potential with a superposed weak external field, but their method should admit of an extension to more general perturbations. Effective-mass theory,[7] derived by using Wannier functions rather than Bloch functions as a basis, provides an alternative approach to perturbations of periodic potentials, but appears to be of limited usefulness for discussing the more general perturbations which arise in graded band-gap systems and some amorphous materials. Calculations using a Wannier function basis have been carried out by Gora and Williams and by Inglis and Williams[4] for such systems, but are limited to the case in which the period remains unchanged.

One type of generalization of the WKB approximation, initiated by Langer[8] and leading to uniform asymptotic approximations, is based on the mathematical idea that approximately identical differential equations have approximately identical solutions. We shall, however, base our generalization on a more physical view of the WKB approximation first given by Bremmer.[9] Bremmer's analysis begins with the ordinary differential equation

$$\left(\frac{d^2}{dx^2} + k^2(x)\right)\psi = 0$$

and replaces a slowly and continuously varying $k(x)$ by the stepwise approximation

$$k(x) \approx k_n \equiv k(x_0 + n\Delta x), \quad x_0 + n\Delta x < x < x_0 + (n+1)\Delta x .$$

At each step, reflection and transmission coefficients can be calculated. The WKB approximation results from keeping only the transmitted wave at each step and then passing to the limit of continuous $k(x)$ by letting Δx tend to zero. Corrections result from summing all once-reflected waves, all twice-reflected waves, etc. From this point of view, the success of the WKB approximation is due to destructive interference among

the reflected waves. We will use Bremmer's idea as the basis for a generalization of the WKB approximation to Bloch electrons.

Section II presents the generalization of Bremmer's approach to Bloch electrons in one dimension. Section III presents numerical comparisons of the approximation scheme proposed in Sec. II with exact results for Kronig-Penney models with an external field and with a slowly varying period. Section IV discusses, but does not solve, the problems of treating the neighborhood of the band edge and of extending the approach to three dimensions.

II. ONE-DIMENSIONAL PROBLEM

The one-dimensional version of Eq. (1) is

$$\left(\frac{d^2}{dx^2} + 2m\hbar^{-2}[E - U(x, \lambda(x))]\right)\psi = 0 \tag{3}$$

where U is periodic for fixed[10] λ:

$$U(x + a(\lambda); \lambda) = U(x; \lambda)\,. \tag{4}$$

For fixed λ, the general solution of (3) is a linear combination of[11]

$$\psi_+(x; \lambda) \equiv e^{ikx} u_+(x; \lambda) \tag{5a}$$

and

$$\psi_-(x; \lambda) \equiv e^{-ikx} u_-(x; \lambda)\,, \tag{5b}$$

where

$$u_\pm(x + a(\lambda); \lambda) = u_\pm(x; \lambda)\,. \tag{6}$$

When k is real, we assume $k \geq 0$ so that ψ_+ is a wave traveling to the right and ψ_- a wave traveling to the left. The phases of ψ_+ and ψ_- are chosen so that $\overline{\psi}_+ = \psi_-$. When k is pure imaginary, we assume $ik \geq 0$, and choose the phases so that ψ_+ and ψ_- are both real. In general, E depends on both k and λ. Since we are interested in solutions of (3) for fixed E, we fix the dependence of k on λ by requiring that $E(k; \lambda) = E_0 = \text{const}$.

A. A physical approximation

We will now apply Bremmer's method[9] to our problem. Replace the continuously varying λ by

$$\lambda \approx \lambda_n \equiv \lambda(x_0 + n\Delta x), \quad x_0 + n\Delta x < x < x_0 + (n+1)\Delta x\,,$$

and suppose that there is only the wave ψ_+ moving to the right in $x_0 + (m-1)\Delta x \leq x \leq x_0 + m\Delta x$. The reflection and transmission coefficients R_m^+ and T_m^+ at $x = x_0 + m\Delta x$ can then be calculated by demanding continuity of ψ and of $\partial\psi/\partial x$ at $x_m \equiv x_0 + m\Delta x$:

$$\psi_+(x_m; \lambda_{m-1}) = R_m^+ \psi_-(x_m; \lambda_m) + T_m^+ \psi_+(x_m; \lambda_m)\,, \tag{7a}$$

$$\frac{\partial\psi_+(x_m; \lambda_{m-1})}{\partial x_m} = R_m^+ \frac{\partial\psi_-(x_m; \lambda_m)}{\partial x_m} + T_m^+ \frac{\partial\psi_+(x_m; \lambda_m)}{\partial x_m}\,. \tag{7b}$$

The pair (7a), (7b) can be solved for R_m^+ and T_m^+; the result of Taylor expanding the solution in powers of Δx for Δx small is

$$R_m^+ = -[M_+(x_m; \lambda_m)/D(\lambda_m)]\,\lambda'(x_m)\Delta x + O((\Delta x)^2) \tag{8}$$

and

$$T_m^+ = 1 - [N_+(x_m; \lambda_m)/D(\lambda_m)]\,\lambda'(x_m)\Delta x + O((\Delta x)^2), \tag{9}$$

where

$$N_+(x; \lambda) \equiv \frac{\partial\psi_+}{\partial\lambda}\frac{\partial\psi_-}{\partial x} - \psi_- \frac{\partial^2\psi_+}{\partial x\,\partial\lambda}\,, \tag{10}$$

$$M_+(x; \lambda) \equiv -\frac{\partial\psi_+}{\partial\lambda}\frac{\partial\psi_+}{\partial x} + \psi_+ \frac{\partial^2\psi_+}{\partial x\,\partial\lambda}\,, \tag{11}$$

$$D(\lambda) \equiv \psi_+ \frac{\partial\psi_-}{\partial x} - \psi_- \frac{\partial\psi_+}{\partial x}\,. \tag{12}$$

The fact that $\partial D/\partial x = 0$ follows from the fact that D is the Wronskian of ψ_+ and ψ_- when λ is fixed. The reflection and transmission coefficients R_m^- and T_m^- at $x = x_m$ for a wave traveling to the left can be obtained by interchanging the subscripts $+$ and $-$ in the preceding calculation to obtain

$$R_m^- = -[M_-(x_m; \lambda_m)/D(\lambda_m)]\,\lambda'(x_m)\Delta x + O((\Delta x)^2) \tag{13}$$

and

$$T_m^- = 1 - [N_-(x_m; \lambda_m)/D(\lambda_m)]\,\lambda'(x_m)\Delta x + O((\Delta x)^2)\,, \tag{14}$$

where

$$N_-(x; \lambda) = -\frac{\partial\psi_+}{\partial x}\frac{\partial\psi_-}{\partial\lambda} + \psi_+ \frac{\partial^2\psi_-}{\partial x\,\partial\lambda} \tag{15}$$

and

$$M_-(x; \lambda) = \frac{\partial\psi_-}{\partial x}\frac{\partial\psi_-}{\partial\lambda} - \psi_- \frac{\partial^2\psi_-}{\partial x\,\partial\lambda}\,. \tag{16}$$

Making the approximation of keeping only the transmitted wave yields the approximate solutions

$$\psi_\pm \prod_m T_m^\pm = \psi_\pm \exp\left(\sum_m \ln T_m^\pm\right) \approx \psi_\pm \exp\left(-\sum_m \frac{N_\pm(x_m; \lambda_m)}{D(\lambda_m)}\,\lambda'(x_m)\Delta x\right)\,. \tag{17}$$

In the continuum limit $\Delta x \to 0$, the approximate equality in (17) becomes exact, yielding the approximate solutions

$$\phi_{\pm}(x) \equiv \psi_{\pm}(x;\lambda(x)) \exp\left(-\int_{x_0}^{x} \frac{N_{\pm}(x_1,\lambda(x_1))}{D(\lambda(x_1))}\,\lambda'(x_1)\,dx_1\right), \tag{18}$$

which are our generalizations of the WKB solutions. Here x_0 is some fixed reference point.

It follows from (10), (12) and (15) that

$$\frac{\partial D(\lambda)}{\partial \lambda} = N_+(x;\lambda) + N_-(x;\lambda). \tag{19}$$

By using (19) to integrate the combination $\frac{1}{2}(N_+ + N_-)D^{-1}\lambda'$, the approximate solutions $\phi_{\pm}$ given by (18) can be rewritten as

$$\phi_{\pm}(x) = \left(\frac{D(\lambda(x_0))}{D(\lambda(x))}\right)^{1/2} \psi_{\pm}(x;\lambda(x)) \exp\left(\mp\int_{x_0}^{x} \frac{N_+(x_1;\lambda(x_1)) - N_-(x_1;\lambda(x_1))}{2D(\lambda(x_1))}\,\lambda'(x_1)\,dx_1\right). \tag{20}$$

For the case of propagating waves, where $\overline{\psi}_+ = \psi_-$, it follows from (10), (12), and (15) that $\overline{N}_{\pm} = -N_{\mp}$ and $\overline{D} = -D$, so that the exponential in (20) is pure imaginary. The prefactor $[D(\lambda(x_0))/D(\lambda(x))]^{1/2}$, which is real, then gives the change in amplitude; it is the analog of the prefactor $k^{-1/2}$ in the ordinary WKB approximation, and guarantees current conservation to zeroth order in λ'.

B. An alternative derivation and an integral equation

Before analyzing further the result (20), we will derive a pair of integral equations which have (20) as the first term of their Neumann series solution. We begin by looking for a solution to the differential equation (3) in the form

$$\psi(x) = c_+(x)\psi_+(x;\lambda(x)) + c_-(x)\psi_-(x;\lambda(x)). \tag{21}$$

We fix c_+ and c_- by demanding, in analogy with the method of variation of constants,[12] that

$$\psi'(x) = c_+ \frac{\partial \psi_+}{\partial x} + c_- \frac{\partial \psi_-}{\partial x}. \tag{22}$$

Differentiating (21) with respect to x and using (22) yields

$$c_+'\psi_+ + c_-'\psi_- = -\left(c_+ \frac{\partial \psi_+}{\partial \lambda} + c_- \frac{\partial \psi_-}{\partial \lambda}\right)\lambda'. \tag{23}$$

Inserting the expression for the second derivative of ψ, obtained by differentiating (22) with respect to x, into (3) and using (21) yields

$$c_+' \frac{\partial \psi_+}{\partial x} + c_-' \frac{\partial \psi_-}{\partial x} = -\left(c_+ \frac{\partial^2 \psi_+}{\partial x\,\partial \lambda} + c_- \frac{\partial^2 \psi_-}{\partial x\,\partial \lambda}\right)\lambda'. \tag{24}$$

The solution of (23) and (24) for the derivatives c_+' and c_-' is

$$c_+' = -c_+(N_+/D)\lambda' - c_-(M_-/D)\lambda', \tag{25}$$

$$c_-' = -c_+(M_+/D)\lambda' - c_-(N_-/D)\lambda', \tag{26}$$

with $M_{\pm}$, $N_{\pm}$, and D given by Eqs. (10)–(12), (15), and (16). The physical interpretation of (25) is clear from the analysis which led to (9) and (13): the amplitude $c_+(x+\Delta x)$ of the wave moving to the right at $x+\Delta x$ is the sum of the amplitude T^+c_+ of the transmitted part of the wave moving to the right and the amplitude R^-c_- of the reflected part of the wave moving to the left. The interpretation of (26) is similar. The approximate solutions in the form (18) now follow from (25) and (26) by neglecting the cross terms proportional to $M_{\pm}$.[13] We will now work with ϕ_+ and ϕ_- instead of ψ_+ and ψ_-. Define $b_+(x)$ and $b_-(x)$ by

$$c_{\pm}(x)\psi_{\pm}(x;\lambda(x)) = b_{\pm}(x)\phi_{\pm}(x). \tag{27}$$

Then $b_{\pm}$ is given by

$$b_{\pm}(x) = c_{\pm}(x) \exp\left(\int_{x_0}^{x} \frac{N_{\pm}(x_1;\lambda(x_1))}{D(\lambda(x_1))}\,\lambda'(x_1)\,dx_1\right), \tag{28}$$

while (21) and (22) are replaced by

$$\psi(x) = b_+(x)\phi_+(x) + b_-(x)\phi_-(x) \tag{29}$$

and

$$\psi'(x) = b_+(x)\phi_+(x)\left(\frac{\partial}{\partial x}\ln\psi_+(x;\lambda)\right)_{\lambda=\lambda(x)} + b_-(x)\phi_-(x)\left(\frac{\partial}{\partial x}\ln\psi_-(x;\lambda)\right)_{\lambda=\lambda(x)}. \tag{30}$$

The use of (28) in (25) and (26) followed by an integration with respect to x yields the pair of integral equations

$$b_+(x) = b_+(x_0) + \int_{x_0}^{x} dx_1\, S_-(x_1)b_-(x_1), \tag{31a}$$

$$b_-(x) = b_-(x_0) + \int_{x_0}^{x} dx_1\, S_+(x_1)b_+(x_1), \tag{31b}$$

where

$$S_{\pm}(x) \equiv -\exp\left(\mp\int_{x_0}^{x} dx_1\,\lambda'(x_1)\frac{N_+(x_1;\lambda(x_1)) - N_-(x_1;\lambda(x_1))}{D(\lambda(x_1))}\right) \times \frac{M_{\pm}(x;\lambda(x))}{D(\lambda(x))}\lambda'(x). \tag{32}$$

Specification of $\psi(x_0)$ and $\psi'(x_0)$ determines $b_\pm(x_0)$ as a consequence of (21), (22), and the fact that $b_\pm(x_0)=c_\pm(x_0)$ from (28). The first term of the Neumann series (iterative) solution of the pair of integral equations (31a) and (31b), that is to say the approximations $b_+(x)\cong b_+(x_0)$ and $b_-(x)\cong b_-(x_0)$, yields the approximation of Sec. II A. Because this pair of integral equations is of Volterra type, it has a Neumann series solution which converges under rather weak conditions.[14] Thus, for example, $M_\pm$, $N_\pm$, and D bounded and D different from zero on the path of integration is sufficient to guarantee convergence. When k is real, the exponential in (32) is pure imaginary as a consequence of $\bar{\psi}_+=\psi_-$; the resulting oscillations, which correspond physically to destructive interference among the reflected waves, tend to make corrections to the approximate solutions ϕ_+ and ϕ_- small. Error bounds on the approximate solutions can be obtained by bounding the absolute values of the kernels $S_\pm$ in (31) and summing the Neumann series with the true kernels replaced by their bounds; the reader is referred to Froman and Froman,[1] who carry out such a program for the ordinary WKB approximation, for details. Our generalization of the WKB approximation fails at band edges, where $D=0$ because ψ_+ and ψ_- are no longer linearly independent; this is the same difficulty which arises at turning points in the ordinary WKB approximation.

C. The usual WKB approximation

As should be anticipated, the ordinary WKB approximation can be recovered as a special case of our method. If

$$2m\hbar^{-2}[E-U(x;\lambda)]=\lambda^2, \tag{33}$$

the solutions to the unperturbed problem are

$$\psi_\pm(x)=e^{\pm i\lambda x}. \tag{34}$$

The use of (34) in (10)–(12), (15), and (16) yields

$$N_+=-i+2\lambda x, \tag{35a}$$

$$N_-=-i-2\lambda x, \tag{35b}$$

$$M_+=ie^{2i\lambda x}, \tag{35c}$$

$$M_-=ie^{-2i\lambda x}, \tag{35d}$$

and

$$D=-2i\lambda. \tag{35e}$$

The use of (35) in (20) produces

$$\phi_\pm(x)=\left(\frac{\lambda(x_0)}{\lambda(x)}\right)^{1/2}\exp\left[\pm i\left(x_0\lambda(x_0)+\int_{x_0}^{x}\lambda(x_1)\,dx_1\right)\right], \tag{36}$$

which, except for the unimportant constant factors $[\lambda(x_0)]^{1/2}\exp[\pm ix_0\lambda(x_0)]$, are the usual WKB solutions.

D. Variation of the period

A naive approach to variation of the period with x would begin by assuming (4) to hold when the period varies. Application of our approximation scheme then leads to difficulties, however, as can be seen by looking more closely at the kernels $S_\pm$ of the integral equations (31) in this case. Differentiation of (6) with respect to λ yields

$$\frac{\partial u_\pm(x+a(\lambda);\lambda)}{\partial\lambda}-\frac{\partial u_\pm(x;\lambda)}{\partial\lambda}=-a'(\lambda)\frac{\partial u_\pm(x+a(\lambda);\lambda)}{\partial x}.$$

This is a difference equation for $\partial u_\pm/\partial\lambda$; its solutions have the form

$$\frac{\partial u_\pm(x;\lambda)}{\partial\lambda}=-x\frac{a'(\lambda)}{a(\lambda)}\frac{\partial u_\pm(x;\lambda)}{\partial x}+v_\pm(x;\lambda), \tag{37}$$

where both $\partial u_\pm/\partial x$ and $v_\pm$ are periodic in x with period a. By using (5) and (37) to calculate $\partial\psi_\pm/\partial\lambda$, it can be shown that

$$M_+=e^{2ikx}\Bigg\{x\frac{a'}{a}\Bigg[\left(\frac{\partial u_+}{\partial x}\right)^2+[2m\hbar^{-2}(E-U)-k^2]u_+^2+2iku_+\frac{\partial u_+}{\partial x}\Bigg]-\frac{a'}{a}u_+\frac{\partial u_+}{\partial x}+u_+\frac{\partial v_+}{\partial x}-v_+\frac{\partial u_+}{\partial x}+ik'u_+^2\Bigg\}. \tag{38}$$

Because M_+/D is a reflection coefficient, the presence of terms linear in x in (38) is an unphysical result: a given fractional change a'/a of the period should not reflect more strongly for large $|x|$ than for small $|x|$.

The difficulty arises from a poor formulation of the problem. Let us suppose for the moment that $U(x)$ is representable as a Fourier series

$$U(x;\lambda)=\sum_{m=-\infty}^{\infty}U_m\exp\{2\pi im[x/a(\lambda)]\}. \tag{39}$$

From (39) it is clear that a given fractional change a'/a of the period changes the phase of the exponential more for large $|x|$ than for small $|x|$; this is the origin of the unphysical result (38).

The cure for the difficulty lies in the recognition that the phase of the exponential should be changed into $\exp[2\pi im\int_0^x d\xi/a(\xi)]$ when the period changes (as in the ordinary WKB approximation). Thus, when the period changes, we replace Eq. (3) by

$$\left(\frac{d^2}{dx^2}+2m\hbar^{-2}[E-U(z(x,x);\lambda(x))]\right)\psi=0, \tag{40}$$

where $U(z;\lambda)$ is periodic with unit period for fixed λ

$$U(z+1;\lambda)=U(z;\lambda) \tag{41}$$

and

$$z(x,y)\equiv\frac{x-y}{a(y)}+\int_0^y\frac{d\xi}{a(\xi)}\ . \tag{42}$$

The analysis of Sec. IIA can now be repeated. The results have the same form as before [Eqs. (8), (9), (13), and (14)], except that the old $\psi_\pm(x;\lambda)$ is replaced by a $\psi_\pm(x,y;\lambda)$ which satisfies the equation

$$\left(\frac{\partial^2}{\partial x^2}+2m\hbar^{-2}[E-U(z(x,y);\lambda)]\right)\psi_\pm(x,y;\lambda)=0\,, \tag{43}$$

and the quantities $\lambda' N_\pm$, $\lambda' M_\pm$, and D are replaced by

$$\lambda' N_+=\left[\frac{\partial\psi_-(x,y;\lambda)}{\partial x}\left(\frac{\partial\psi_+(x,y;\lambda)}{\partial y}+\frac{\partial\psi_+(x,y;\lambda)}{\partial\lambda}\lambda'\right)-\psi_-(x,y;\lambda)\left(\frac{\partial^2\psi_+(x,y;\lambda)}{\partial x\,\partial y}+\frac{\partial^2\psi_+(x,y;\lambda)}{\partial x\,\partial\lambda}\lambda'\right)\right]_{y=x,\lambda=\lambda(x)}\,, \tag{44}$$

$$\lambda' M_+=\left[-\frac{\partial\psi_+(x,y;\lambda)}{\partial x}\left(\frac{\partial\psi_+(x,y;\lambda)}{\partial y}+\frac{\partial\psi_+(x,y;\lambda)}{\partial\lambda}\lambda'\right)+\psi_+(x,y;\lambda)\left(\frac{\partial^2\psi_+(x,y;\lambda)}{\partial x\,\partial y}+\frac{\partial^2\psi_+(x,y;\lambda)}{\partial x\,\partial\lambda}\lambda'\right)\right]_{y=x,\lambda=\lambda(x)}\,, \tag{45}$$

$$\lambda' N_-=\left[-\frac{\partial\psi_+(x,y;\lambda)}{\partial x}\left(\frac{\partial\psi_-(x,y;\lambda)}{\partial y}+\frac{\partial\psi_-(x,y;\lambda)}{\partial\lambda}\lambda'\right)+\psi_+(x,y;\lambda)\left(\frac{\partial^2\psi_-(x,y;\lambda)}{\partial x\,\partial y}+\frac{\partial^2\psi_-(x,y;\lambda)}{\partial x\,\partial\lambda}\lambda'\right)\right]_{y=x,\lambda=\lambda(x)}\,, \tag{46}$$

$$\lambda' M_-=\left[\frac{\partial\psi_-(x,y;\lambda)}{\partial x}\left(\frac{\partial\psi_-(x,y;\lambda)}{\partial y}+\frac{\partial\psi_-(x,y;\lambda)}{\partial\lambda}\lambda'\right)-\psi_-(x,y;\lambda)\left(\frac{\partial^2\psi_-(x,y;\lambda)}{\partial x\,\partial y}+\frac{\partial^2\psi_-(x,y;\lambda)}{\partial x\,\partial\lambda}\lambda'\right)\right]_{y=x,\lambda=\lambda(x)}\,, \tag{47}$$

and

$$D=\left(\psi_+(x,y;\lambda)\frac{\partial\psi_-(x,y;\lambda)}{\partial x}-\psi_-(x,y;\lambda)\frac{\partial\psi_+(x,y;\lambda)}{\partial x}\right)_{y=x,\lambda=\lambda(x)}\ . \tag{48}$$

The relation (19) is replaced by

$$\frac{dD}{dx}=(N_++N_-)\lambda'\ . \tag{49}$$

Making the approximation of keeping only the transmitted wave again yields approximate solutions of the form (20).

The analysis of Sec. IIB also goes through as before. We look for a solution to (40) in the form

$$\psi(x)=c_+(x)\psi_+(x,x;\lambda(x))+c_-(x)\psi_-(x,x;\lambda(x))\,, \tag{50}$$

and fix $c_\pm$ by demanding that

$$\psi'(x)=\left(c_+(x)\frac{\partial\psi_+(x,y;\lambda)}{\partial x}+c_-(x)\frac{\partial\psi_-(x,y;\lambda)}{\partial x}\right)_{y=x,\lambda=\lambda(x)} \tag{51}$$

The coefficients $c_\pm$ can be shown to satisfy equations of the same form as before [Eqs. (25) and (26)] except that now the $\lambda' N_\pm$, $\lambda' M_\pm$, and D which appear are given by Eqs. (44)–(48). The remainder of Sec. IIB also goes through as before with the replacement of the old $\psi_\pm$, $N_\pm$, $M_\pm$, and D by the new.

Additional insight into the above modifications used to deal with a varying period can be obtained by using z instead of x as an independent variable. The approximate equation (43) goes over into

$$\left(\frac{\partial^2}{\partial z^2}+2m\hbar^{-2}a^2[E-U(z;\lambda)]\right)\psi_\pm(z;a,\lambda)=0\,, \tag{52}$$

which is to be integrated with a and λ fixed. Under this change of variables,

$$\frac{\partial}{\partial x}\to\frac{1}{a(y)}\frac{\partial}{\partial z}\,,\quad \frac{\partial}{\partial y}\to\frac{(y-x)a'(y)}{[a(y)]^2}\frac{\partial}{\partial z}+\frac{\partial}{\partial y}\,,$$

and

$$\frac{\partial^2}{\partial x\,\partial y}\to\frac{(y-x)a'(y)}{[a(y)]^3}\frac{\partial^2}{\partial z^2}+\frac{1}{a(y)}\frac{\partial^2}{\partial y\,\partial z}-\frac{a'(y)}{[a(y)]^2}\frac{\partial}{\partial z}\ .$$

With the aid of these formulas it can be shown that the terms of $\lambda' M_\pm$ and $\lambda' N_\pm$ are proportional either to a' or to λ', and that the unphysical increase of the reflection coefficient with increasing x has been eliminated. As an example, we take $\lambda' M_+$ which goes over from the form (45) into

$$\lambda' M_+ = \frac{1}{a(x)}\left[-\frac{\partial\psi_+(z;a,\lambda)}{\partial z}\left(\frac{\partial\psi_+(z;a,\lambda)}{\partial a}a'(x)+\frac{\partial\psi_+(z;a,\lambda)}{\partial\lambda}\lambda'(x)\right)\right.$$
$$\left.+\psi_+(z;a,\lambda)\left(\frac{\partial^2\psi_+(z;a,\lambda)}{\partial x\,\partial a}a'(x)-\frac{\partial\psi_+(z;a,\lambda)}{\partial z}\frac{a'(x)}{a(x)}+\frac{\partial^2\psi_+(z;a,\lambda)}{\partial x\,\partial\lambda}\lambda'(x)\right)\right]. \quad (53)$$

The right-hand side of (53) is to be evaluated at $z=z(x,x)$, $a=a(x)$, and $\lambda=\lambda(x)$. The solutions to (43) have the form

$$\psi_\pm(x,y;\lambda)=\exp[\pm ik(y;\lambda)x]\,u_\pm(x,y;\lambda), \quad (54)$$

where $u_\pm(x,y;\lambda)$ is periodic with period $a(y)$ for y and λ fixed. The argument which led to (37) goes through as before to yield

$$\frac{\partial u_\pm(x,y;\lambda)}{\partial y}=-x\frac{a'(y)}{a(y)}\frac{\partial u_\pm(x,y;\lambda)}{\partial x}+v_\pm(x,y;\lambda), \quad (55)$$

where both $\partial u_\pm/\partial x$ and $u_\pm$ are periodic with period $a(y)$ for y and λ fixed. However, the change to the variable z shows that

$$\left(\frac{\partial u_\pm}{\partial x}\right)_{y,\lambda}=\frac{1}{a(y)}\left(\frac{\partial u_\pm}{\partial z}\right)_{a,\lambda} \quad (56)$$

and

$$\left(\frac{\partial u_\pm}{\partial y}\right)_{x,\lambda}=\frac{(y-x)a'(y)}{[a(y)]^2}\left(\frac{\partial u_\pm}{\partial z}\right)_{a,\lambda}+\left(\frac{\partial u_\pm}{\partial a}\right)_{z,\lambda}a'(y). \quad (57)$$

By comparing (56) and (57) with (55), it is clear that

$$v_\pm(x,y;\lambda)=\frac{ya'(y)}{[a(y)]^2}\left(\frac{\partial u_\pm}{\partial z}\right)_{a,\lambda}+\left(\frac{\partial u_\pm}{\partial a}\right)_{z,\lambda}a'(y). \quad (58)$$

Thus, $v_\pm$ now contains a term linear in y which cancels the term linear in x in (55) when y is set equal to x and eliminates the unphysical increase of the reflection coefficient with increasing x.

III. COMPARISON OF APPROXIMATE AND EXACT RESULTS FOR A KRONIG-PENNEY MODEL

The present section applies the approximation proposed in Sec. II to a Kronig-Penney model and compares the result with Zener's *ad hoc* approximation and with exact results. Both application of an external field and variation of the period are considered. The potential is introduced in the form contemplated in Eq. (40):

$$U(z;\lambda)=\begin{cases}(-V_0+\lambda), & n<z<n+\frac{1}{2}\\ \lambda, & n+\frac{1}{2}<z<n+1\end{cases} \quad (59)$$

$n=\ldots,-2,-1,0,1,2,\ldots$.

The method used to obtain the exact results for this model is outlined in the Appendix.

The parameters are chosen to have values which are reasonable for a crystalline solid. The mass m is the electron mass, the unperturbed well depth V_0 is 5 eV, and the unperturbed constant period a, introduced via $z=x/a_0$ [see Eq. (40) and (42)], is chosen to be 2 Å. With these parameters, the first allowed band extends from -2.636 to 5.274 eV.

The initial conditions used to calculate the values of ψ shown in the tables correspond to a Bloch wave traveling to the right in the unperturbed lattice at $x=0$ [$c_-(0)=0$ in Eq. (21) and (22) or in (50) and (51)]. The normalization of ψ is arbitrary.

A. An applied external field

Data for a constant external field, introduced via

$$\lambda(x)=-e\mathcal{E}x, \quad (60)$$

are presented in Table I. The value $\mathcal{E}=-5\times10^6$ V/cm chosen for the field is of the order of magnitude of the breakdown field in real solids, and is, therefore, an approximate upper limit to the field strengths of interest. Because the approximation method is most accurate in the middle of the band, initial conditions have been specified in the middle of the band and the Schrödinger equation integrated in both directions until the band edges are reached. The columns in Table I labeled "neglecting polarization" are for an approximating potential which is constant between discontinuities instead of slanted with slope $-e\mathcal{E}$. The column labeled "Zener" is the result of using Zener's *ad hoc* replacement of $\exp(ikx)$ by $\exp(i\int k\,dx)$ to approximate the phase change in ψ. The columns labeled "WKB" are the results of using the approximation, proposed in Sec. II, of keeping only the transmitted wave.

It will be noticed that neglecting polarization is a poor approximation for cells 64 through 78. The reason for this is that the argument of the Airy functions which appear in the exact solutions [see the Appendix, especially Eq. (A14)] is small for these cells; Airy functions of small argument are not well approximated by the trigonometric and/or

TABLE I. Comparison for a linearly varying external field with $\mathcal{E} = -5.0 \times 10^6$ V/cm and $E = 5.225$ eV.

		Magnitude of ψ			Phase of ψ			
Cell no.	Value of X_N	Exact	Neglecting polarization	WKB	Exact	Neglecting polarization	WKB	Zener
0	0.00	0.4449	0.4467	0.7057	−98.57	−98.80	−100.13	−99.16
1	2.00	0.4347	0.4359	0.5481	−95.61	−95.83	−97.00	−96.11
2	4.00	0.4263	0.4272	0.4945	−92.68	−92.90	−93.94	−93.12
3	6.00	0.4195	0.4203	0.4657	−89.77	−89.98	−90.93	−90.15
4	8.00	0.4141	0.4150	0.4475	−86.88	−87.08	−87.96	−87.22
5	10.00	0.4100	0.4111	0.4350	−84.01	−84.21	−85.03	−84.32
6	12.00	0.4069	0.4083	0.4261	−81.17	−81.36	−82.12	−81.45
8	16.00	0.4030	0.4042	0.4144	−75.54	−75.72	−76.40	−75.78
10	20.00	0.4000	0.3999	0.4077	−70.01	−70.17	−70.77	−70.20
12	24.00	0.3973	0.3966	0.4039	−64.56	−64.72	−65.25	−64.73
14	28.00	0.3970	0.3976	0.4019	−59.20	−59.35	−59.82	−59.35
16	32.00	0.3985	0.3986	0.4011	−53.93	−54.07	−54.49	−54.06
18	36.00	0.3981	0.3971	0.4013	−48.75	−48.88	−49.25	−48.86
20	40.00	0.4000	0.4004	0.4023	−43.67	−43.78	−44.10	−43.75
22	44.00	0.4024	0.4019	0.4038	−38.66	−38.76	−39.05	−38.74
24	48.00	0.4035	0.4032	0.4057	−33.76	−33.85	−34.09	−33.82
26	52.00	0.4077	0.4075	0.4081	−28.94	−29.02	−29.22	−28.99
28	56.00	0.4091	0.4084	0.4109	−24.22	−24.29	−24.45	−24.26
30	60.00	0.4139	0.4136	0.4141	−19.59	−19.65	−19.78	−19.63
32	64.00	0.4162	0.4158	0.4176	−15.07	−15.11	−15.21	−15.09
34	68.00	0.4209	0.4200	0.4214	−10.63	−10.66	−10.73	−10.65
36	72.00	0.4255	0.4256	0.4256	−6.30	−6.32	−6.36	−6.31
38	76.00	0.4288	0.4277	0.4302	−2.07	−2.08	−2.09	−2.08
40	80.00	0.4350	0.4342	0.4351	2.05	2.06	2.07	2.05
42	84.00	0.4408	0.4408	0.4405	6.07	6.09	6.12	6.07
44	88.00	0.4455	0.4447	0.4463	9.97	10.01	10.06	9.99
46	92.00	0.4514	0.4500	0.4526	13.77	13.82	13.88	13.79
48	96.00	0.4590	0.4577	0.4595	17.45	17.51	17.58	17.47
50	100.00	0.4674	0.4665	0.4670	21.01	21.09	21.16	21.03
52	104.00	0.4760	0.4754	0.4752	24.44	24.54	24.62	24.47
54	108.00	0.4852	0.4863	0.4844	27.75	27.85	27.94	27.78
56	112.00	0.4952	0.4966	0.4945	30.92	31.04	31.12	30.96
58	116.00	0.5059	0.5074	0.5059	33.96	34.10	34.16	34.00
60	120.00	0.5166	0.5171	0.5187	36.83	37.02	37.04	36.90
62	124.00	0.5451	0.5221	0.5335	39.45	39.79	39.77	39.64
64	128.00	0.8005	0.5251	0.5507	42.16	42.38	42.82	42.23
66	132.00	0.6651	0.5478	0.5712	44.56	44.77	44.69	44.64
68	136.00	0.7506	0.5954	0.5962	46.51	47.03	46.85	46.86
70	140.00	0.9663	0.6090	0.6280	48.73	49.12	48.80	48.89
72	144.00	0.7483	0.6445	0.6707	50.52	50.90	50.49	50.69
73	146.00	0.9728	0.6597	0.6987	51.44	51.76	51.23	51.49
74	148.00	1.1309	0.7151	0.7338	52.01	52.54	51.89	52.23
75	150.00	1.0620	0.7662	0.7799	52.54	53.19	52.45	52.89
76	152.00	0.9527	0.8005	0.8457	53.19	53.78	52.91	53.47
77	154.00	1.0429	0.8488	0.9540	53.87	54.32	53.23	53.94
78	156.00	1.3307	0.9447	1.2151	54.35	54.78	53.33	54.28

exponential functions which appear when polarization is neglected.

B. A varying period

Both a linearly varying period, introduced via Eq. (42) with

$$a(x) = a_0 + x\Delta a, \quad \lambda(x) = 0 \tag{61}$$

and a sinusoidally varying period, introduced via

$$a(x) = a_0 + \Delta a \cos(Cx), \quad \lambda(x) = 0 \tag{62}$$

were considered. Because the top of the band

changes quite rapidly with the period, the number of cells through which the Schrödinger equation can be integrated before arriving at the band edge varies considerably with energy in the linear case. For this reason, only data for the sinusoidally varying period, which are believed to give a better picture of the way the accuracy of the approximation changes with energy, are presented. Table II presents data for an energy near the top edge of the band, and Table III presents data for an energy in the middle of the band. Table IV lists the root-mean-square fractional error δ in magnitude and in phase as a function of energy for three different choices of the parameters C [determined by n; see Eq. (64)] and Δa. It is defined by

$$\delta = \left(\sum_i \frac{(x_i - y_i)^2}{x_i^2} \right)^{1/2}, \tag{63}$$

where x_i is the exact value at the end of the ith

TABLE II. Comparison for a sinusoidally varying period with $\Delta a = 0.2$ Å, $n = 20$, and $E = 3.55$ eV.

		Magnitude of ψ		Phase of ψ		
Cell no.	Value of X_N	Exact	WKB	Exact	WKB	Zener
0	0.00	0.7363	0.7363	0.00	0.00	0.00
1	2.20	0.7313	0.6323	3.03	3.04	3.01
2	4.37	0.6905	0.5334	6.04	6.05	5.95
3	6.50	0.5721	0.4855	8.98	8.96	8.78
4	8.57	0.3659	0.4626	11.69	11.74	11.51
5	10.58	0.2903	0.4512	13.55	14.40	14.13
6	12.53	0.5518	0.4453	15.90	16.95	16.66
7	14.43	0.7103	0.4421	18.72	19.41	19.11
8	16.28	0.5526	0.4404	21.51	21.79	21.49
9	18.10	0.2687	0.4396	23.45	24.14	23.83
10	19.90	0.5542	0.4393	25.33	26.45	26.14
11	21.70	0.7170	0.4396	28.11	28.77	28.46
12	23.52	0.5109	0.4404	30.86	31.10	30.80
13	25.37	0.2761	0.4421	32.73	33.48	33.18
14	27.27	0.5314	0.4453	34.82	35.91	35.63
15	29.22	0.7342	0.4512	37.66	38.42	38.15
16	31.23	0.7662	0.4626	40.61	41.02	40.78
17	33.30	0.7027	0.4855	43.59	43.71	43.50
18	35.43	0.6233	0.5334	46.55	46.49	46.34
19	37.60	0.5689	0.6323	49.50	49.35	49.27
20	39.80	0.5449	0.7363	52.44	52.29	52.29
21	42.00	0.5370	0.6323	55.36	55.33	55.30
22	44.17	0.5222	0.5334	58.27	58.34	58.23
23	46.30	0.4776	0.4855	61.10	61.25	61.07
24	48.37	0.4016	0.4626	63.76	64.03	63.80
25	50.38	0.3624	0.4512	66.13	66.68	66.42
26	52.33	0.4412	0.4453	68.48	69.23	68.95
27	54.23	0.5223	0.4421	71.04	71.69	71.39
28	56.08	0.4719	0.4404	73.61	74.08	73.78
29	57.90	0.3663	0.4396	75.82	76.42	76.11
30	59.70	0.4441	0.4393	77.91	78.74	78.43
31	61.50	0.5301	0.4396	80.40	81.05	80.75
32	63.32	0.4602	0.4404	82.93	83.39	83.08
33	65.17	0.3724	0.4421	85.17	85.76	85.47
34	67.06	0.4425	0.4453	87.43	88.20	87.91
35	69.01	0.5400	0.4512	90.06	90.71	90.44
36	71.03	0.5755	0.4626	92.86	93.31	93.06
37	73.10	0.5716	0.4855	95.72	96.00	95.79
38	75.23	0.5684	0.5334	98.62	98.78	98.62
39	77.40	0.5873	0.6323	101.55	101.64	101.56
40	79.60	0.6285	0.7363	104.53	104.57	104.57

TABLE III. Comparison for a sinusoidally varying period with $\Delta a = 0.2$ Å, $n = 20$, and $E = 0.5$ eV.

		Magnitude of ψ		Phase of ψ		
Cell no.	Value of X_N	Exact	WKB	Exact	WKB	Zener
0	0.00	0.8771	0.8771	0.00	0.00	0.00
1	2.20	0.8753	0.8766	2.04	2.04	2.04
2	4.37	0.8696	0.8754	4.04	4.05	4.05
3	6.50	0.8694	0.8740	6.00	6.01	6.02
4	8.57	0.8683	0.8728	7.90	7.92	7.93
5	10.58	0.8667	0.8719	9.73	9.76	9.77
6	12.53	0.8695	0.8713	11.51	11.54	11.56
7	14.43	0.8672	0.8710	13.23	13.26	13.29
8	16.28	0.8708	0.8708	14.91	14.94	14.97
9	18.10	0.8687	0.8708	16.56	16.59	16.63
10	19.90	0.8720	0.8708	18.20	18.23	18.27
11	21.70	0.8703	0.8708	19.84	19.87	19.90
12	23.52	0.8733	0.8708	21.50	21.53	21.56
13	25.37	0.8725	0.8710	23.19	23.21	23.25
14	27.27	0.8748	0.8713	24.92	24.95	24.97
15	29.22	0.8762	0.8719	26.72	26.74	26.76
16	31.23	0.8765	0.8728	28.57	28.59	28.60
17	33.30	0.8806	0.8740	30.49	30.50	30.51
18	35.43	0.8790	0.8754	32.47	32.48	32.48
19	37.60	0.8796	0.8766	34.49	34.49	34.49
20	39.80	0.8786	0.8771	36.53	36.53	36.53
21	42.00	0.8726	0.8766	38.57	38.57	38.57
22	44.17	0.8714	0.8754	40.57	40.58	40.58
23	46.30	0.8695	0.8740	42.53	42.54	42.55
24	48.37	0.8666	0.8728	44.43	44.45	44.46
25	50.38	0.8692	0.8719	46.26	46.29	46.30
26	52.33	0.8668	0.8713	48.04	48.07	48.09
27	54.23	0.8697	0.8710	49.76	49.79	49.82
28	56.08	0.8686	0.8708	51.44	51.47	51.50
29	57.90	0.8706	0.8708	53.09	53.12	53.16
30	59.70	0.8704	0.8708	54.74	54.76	54.80
31	61.50	0.8717	0.8708	56.37	56.40	56.44
32	63.32	0.8724	0.8708	58.03	58.06	58.09
33	65.17	0.8729	0.8710	59.72	59.75	59.78
34	67.06	0.8753	0.8713	61.46	61.48	61.51
35	69.01	0.8747	0.8719	63.25	63.27	63.29
36	71.03	0.8791	0.8728	65.10	65.12	65.14
37	73.10	0.8781	0.8740	67.03	67.03	67.04
38	75.23	0.8801	0.8754	69.00	69.01	69.01
39	77.40	0.8808	0.8766	71.02	71.02	71.02
40	79.60	0.8760	0.8771	73.07	73.06	73.06

cell and y_i is the value calculated from the "WKB" or "Zener" approximations. In all cases the Schrödinger equation was integrated for two periods of the periodic perturbation (for a distance $4\pi/C$).

The parameter C was chosen to have values given by

$$C = 2\pi[a_0^2 - (\Delta a)^2]^{-1/2} n^{-1}, \tag{64}$$

where n is an integer; this is done so that one period of the perturbation would correspond to n of the original cells [Eq. (64) is obtained by putting $x = y = 2\pi/C$ and $z = n$ in Eq. (42)]. With n an integer, the perturbed potential is then periodic with the "superperiod" $2\pi/C$. The presence of this superperiod implies the existence of additional gaps (minigaps) in the spectrum. These minigaps show up in our exact solutions. The accuracy of our approximation method is unaffected by the presence of the minigaps.

Examination of Tables II and III shows that the approximate "WKB" magnitude is periodic with the superperiod while the exact solution is not. This is a consequence of the initial conditions, which correspond to a wave traveling to the right *in "WKB" approximation.* The exact solution for these initial conditions contains an admixture of left-traveling wave, which spoils the periodicity of the exact magnitude.

C. Comments and conclusions

Examination of the data shows that the approximation is best in the middle of the band, as should be expected from the fact that the approximation neglects the reflections which become increasingly important as the band edge is approached. The simple "Zener" approximation to the phase is clearly superior when the perturbation is a constant external field; the "Zener" and "WKB" approximations to the phase are of comparable accuracy when the perturbation is a varying period. The derivative ψ', for which the data were omitted, is approximated with about the same accuracy as ψ.

IV. TURNING-POINT PROBLEMS AND EXTENSION TO THREE DIMENSIONS

At a band edge, the solutions $\psi_+(x;\lambda)$ and $\psi_-(x;\lambda)$ defined by Eq. (5) and (6) are no longer linearly independent and their Wronskian $D(\lambda)$ [defined by (12)] vanishes. As a consequence, the approximation (20) fails. This failure is due to the fact that the band edge is a turning point. Unfortunately, there is no comparison equation which can be used to solve the turning-point problem in the way that Airy's equation is used to solve the problem of an isolated turning point in ordinary WKB theory.

Several possible methods of handling the turning-point problem are currently under investigation and will be discussed quantitatively in a subsequent publication. One method is to take the next term in the analog of the Bremmer series and sum up all the once-reflected waves. This has been shown to be an effective alternative to the use of Airy's equation in ordinary WKB theory.[15]

TABLE IV. Comparison for a sinusoidally varying period. Root-mean-square deviation of the magnitude and phase of the wave function.

	$\Delta a = 0.2$ Å, $n = 20$			$\Delta a = 1.0$ Å, $n = 20$			$\Delta a = 1.0$ Å, $n = 100$		
E		Phase			Phase			Phase	
(eV)	Magnitude	WKB	Zener	Magnitude	WKB	Zener	Magnitude	WKB	Zener
3.55	1.6215	0.1266	0.0903						
3.50	1.3759	0.1152	0.0801						
3.00	0.8551	0.0623	0.0438						
2.50	0.3032	0.0396	0.0304						
2.00	0.0927	0.0265	0.0232						
1.50	0.0553	0.0181	0.0186						
1.00	0.0367	0.0121	0.0154						
0.50	0.0257	0.0076	0.0130						
−0.10	0.0181	0.0036	0.0180	2.9923	0.1751	0.2062	2.5090	0.0634	0.0848
−0.50	0.0144	0.0019	0.0097	0.7606	0.0676	0.1205	0.1755	0.0282	0.0571
−1.00	0.0113	0.0033	0.0086	0.2288	0.0340	0.0914	0.0569	0.0103	0.0421
−1.50	0.0090	0.0072	0.0076	0.1109	0.0377	0.0726	0.0333	0.0148	0.0337
−2.00	0.0076	0.0154	0.0066	0.0679	0.0858	0.0592	0.0219	0.0377	0.0288
−2.45	0.0297	0.0597	0.0152	0.5021	0.3384	0.1304	0.0285	0.1366	0.0300
−2.50	0.0625	0.0859	0.0297						
−2.55	0.4390	0.1667	0.0945						

A second possibility is to try to go around the turning point in the complex plane. This approach reproduces the usual connection formulas for an isolated turning point in ordinary WKB theory[16]; it can be expected to work if the necessary analyticity can be established and if there are no more than three Stokes lines emanating from the turning point. A third possibility is based on the observation that the two Bloch solutions $e^{ikx}u_k(x)$ and $e^{-ikx}u_{-k}(x)$ are no longer linearly independent at the band edge. It may be possible to get through the band edge by taking linear combinations (with slowly varying coefficients) which remain linearly independent at the band edge and reduce to the Bloch solutions well away from the band edge. The slowly varying coefficients could presumably be chosen to be solutions of a suitably averaged Schrödinger equation which still has the turning point, but whose potential has had the fluctuating periodic variations averaged out.

The extension to three dimensions also remains to be carried out. The essential difficulty in extending the Bremmer series approach to three dimensions is that it is necessary to consider surfaces of discontinuity rather than points of discontinuity in the potential. ψ and its normal derivative must then be matched along a whole surface, not just at a point. Doing this requires introducing, in addition to the traveling-wave Bloch solutions, the exponentially increasing and decreasing solutions which are normally rejected. ψ need not have—and in general will not have—the same analytic form on either side of the discontinuity; for this reason those solutions which decrease exponentially as one moves away from the discontinuity become admissable, just as in the theory of surface states.

APPENDIX: EXACT SOLUTIONS FOR A PERTURBED KRONIG-PENNEY MODEL

Solutions to the Schrödinger equation for a sequence of (not necessarily identical) cells can be obtained with the aid of a transfer matrix. Suppose $\phi_1(x)$ and $\phi_2(x)$ are two linearly independent solutions of a one-dimensional Schrödinger equation. The general solution then has the form

$$\psi(x) = c_1\phi_1(x) + c_2\phi_2(x), \tag{A1}$$

with the derivative given by

$$\psi'(x) = c_1\phi_1'(x) + c_2\phi_2'(x) \tag{A2}$$

where c_1 and c_2 are constants. If ψ and ψ' are given at some point x_{n-1}, then (A1) and (A2) can be solved for c_1 and c_2 to obtain

$$c_1 = \frac{1}{W}\begin{vmatrix} \psi(x_{n-1}) & \phi_2(x_{n-1}) \\ \psi'(x_{n-1}) & \phi_2'(x_{n-1}) \end{vmatrix} \tag{A3}$$

and

$$c_2 = \frac{1}{W}\begin{vmatrix} \phi_1(x_{n-1}) & \psi(x_{n-1}) \\ \phi_1'(x_{n-1}) & \psi'(x_{n-1}) \end{vmatrix}, \tag{A4}$$

where W is the Wronskian

$$W = \begin{vmatrix} \phi_1(x_{n-1}) & \phi_2(x_{n-1}) \\ \phi_1'(x_{n-1}) & \phi_2'(x_{n-1}) \end{vmatrix}. \tag{A5}$$

Because ϕ_1 and ϕ_2 are linearly independent, W is not zero. It can be easily shown from Schrödinger's equation that the value of W is independent of the particular point x_{n-1} at which (A5) is evaluated. The solutions (A3) and (A4) can be inserted back in (A1) and (A2) to give the values of ψ and ψ' at any point x. In particular, the values of ψ and ψ' at the point x_n are given by

$$\begin{pmatrix} \psi(x_n) \\ \psi'(x_n) \end{pmatrix} = T(x_n, x_{n-1})\begin{pmatrix} \psi(x_{n-1}) \\ \psi'(x_{n-1}) \end{pmatrix}, \tag{A6}$$

where the *transfer matrix* $T(x_n, x_{n-1})$ has the elements

$$T_{11}(x_n, x_{n-1}) = \frac{1}{W}\begin{vmatrix} \phi_1(x_n) & \phi_1'(x_{n-1}) \\ \phi_2(x_n) & \phi_2'(x_{n-1}) \end{vmatrix}, \tag{A7}$$

$$T_{12}(x_n, x_{n-1}) = -\frac{1}{W}\begin{vmatrix} \phi_1(x_n) & \phi_1(x_{n-1}) \\ \phi_2(x_n) & \phi_2(x_{n-1}) \end{vmatrix}, \tag{A8}$$

$$T_{21}(x_n, x_{n-1}) = \frac{1}{W}\begin{vmatrix} \phi_1'(x_n) & \phi_1'(x_{n-1}) \\ \phi_2'(x_n) & \phi_2'(x_{n-1}) \end{vmatrix}, \tag{A9}$$

$$T_{22}(x_n, x_{n-1}) = -\frac{1}{W}\begin{vmatrix} \phi_1'(x_n) & \phi_1(x_{n-1}) \\ \phi_2'(x_n) & \phi_2(x_{n-1}) \end{vmatrix}. \tag{A10}$$

It is easy to show that the elements $T_{ij}(x_n, x_{n-1})$ do not depend on which pair of linearly independent solutions ϕ_1, ϕ_2 of the given Schrödinger equation is used to compute them, and that

$$T(x_{n+1}, x_{n-1}) = T(x_{n+1}, x_n)T(x_n, x_{n-1}). \tag{A11}$$

If the transfer matrix T which transfers ψ and ψ' across a single cell can be calculated for each member of a sequence of cells, the transfer matrix which transfers ψ and ψ' across the whole sequence of cells can be constructed by multiplying together the transfer matrices for each cell in accordance with the rule (A11). If all the cells are the same, this matrix multiplication can be easily carried out by diagonalizing the single-cell transfer matrix. Even if the cells are different, so that the single-cell transfer matrices cannot be simultaneously diagonalized, the matrix multiplication can still be easily carried out on a com-

puter. The transfer matrix method outlined above is equivalent to the one introduced by Kerner[17] from a somewhat different point of view.

The potential for the (perturbed or unperturbed) Kronig-Penney model is a piecewise continuous function. A transfer matrix for each subinterval in which the potential is continuous is easily constructed. In particular, the transfer matrix for an interval of length a in which the potential has the constant value U_0 is

$$T(x+a,x)=\begin{pmatrix}\cos(\kappa a) & \kappa^{-1}\sin(\kappa a)\\ -\kappa\sin(\kappa a) & \cos(\kappa a)\end{pmatrix}, \tag{A12}$$

where

$$\kappa=[2m\hbar^{-2}(E-U_0)]^{1/2} \tag{A13}$$

with E the energy. The transfer matrix for an interval from x_{n-1} to x_n in which the potential is $U_0-e\mathcal{E}x$ is

$$T(x_n,x_{n-1})=\begin{pmatrix}\pi[\mathrm{Ai}(y_n)\,\mathrm{Bi}'(y_{n-1})-\mathrm{Bi}(y_n)\,\mathrm{Ai}'(y_{n-1})] & \pi\alpha^{-1}[\mathrm{Ai}(y_n)\,\mathrm{Bi}(y_{n-1})-\mathrm{Bi}(y_n)\,\mathrm{Ai}(y_{n-1})]\\ -\pi\alpha[\mathrm{Ai}'(y_n)\,\mathrm{Bi}'(y_{n-1})-\mathrm{Bi}'(y_n)\,\mathrm{Ai}'(y_{n-1})] & -\pi[\mathrm{Ai}'(y_n)\,\mathrm{Bi}(y_{n-1})-\mathrm{Bi}'(y_n)\,\mathrm{Ai}(y_{n-1})]\end{pmatrix}, \tag{A14}$$

where $\alpha=(2me\mathcal{E}/\hbar^2)^{1/3}$, $y_k=\alpha\{[(U_0-E)/e\mathcal{E}]-x_k\}$ and Ai and Bi are the Airy functions as defined by Magnus, Oberhettinger, and Soni[18] and by Abramowitz and Stegun.[19]

The transfer matrix (A14) was used to calculate the exact results (including polarization) for a constant external field in Table I. The transfer matrix (A13) was used to calculate the results for a constant external field neglecting polarization in Table I and the exact results for a varying period in Tables II–IV. Because the polarization is small for physically realistic field strengths, transfer matrices for nonconstant external fields, which can no longer be constructed from Airy functions, can be readily calculated to any desired accuracy by treating the variation in potential due to the external field across a single cell as a perturbation and applying standard perturbation methods.

*Work done in partial fulfillment of the requirements for the M.S. degree.

[1]Brief (and mathematically incomplete) accounts may be found in most quantum-mechanics textbooks. A careful treatment is given by N. Froman and P. O. Froman, in *JWKB Approximation Contributions to the Theory* (North-Holland, Amsterdam, 1965). Useful reviews can be found in R. E. Langer, Bull. Amer. Math. Soc. 40, 545 (1934); Phys. Rev. 51, 669 (1937); E. R. Pike, Quart. J. Mech. Appl. Math. 17, 105 (1964); 17, 369 (1964).

[2]C. Zener, Proc. R. Soc. Lond. 145, 523 (1934). More recent references and a brief review can be found in R. T. Shuey, Phys. Rev. 137, A1268 (1965).

[3]D. J. Ben Daniel and C. B. Duke, Phys. Rev. 152, 683 (1966); 160, 679 (1967); R. T. Shuey, Ref. 2.

[4]Application of the virtual-crystal approximation to such systems results in a Schrödinger equation of the type considered here. See T. Gora and F. Williams, in *II-VI Semiconducting Compounds* (Benjamin, New York, 1967); Phys. Rev. 177, 1179 (1969); G. B. Inglis and F. Williams, Phys. Rev. Lett. 25, 1275 (1970); J. Non-Crystalline Solids 5, 313 (1971); Bull. Am. Phys. Soc. 19, 361 (1974); and unpublished. Furthermore, there is evidence for intermediate-range order in some amorphous materials. See the articles by F. Williams and by M. B. Myers and J. S. Berkes, in *Proceedings of the Fourth International Conference on Amorphous and Liquid Semiconductors at Ann Arbor, Michigan, August 1971* (North-Holland, Amsterdam, 1972).

[5]H. M. James, Phys. Rev. 76, 1602; 76, 1611 (1949).

[6]P. N. Butcher, D. M. Hum, and E. R. Pike, Proc. R. Soc. Lond. A280, 185 (1964).

[7]A complete discussion of effective mass theory is given by E. I. Blount in *Solid State Physics, Advances in Research and Applications*, Vol. 13, edited by F. Seitz and D. Turnbull (Academic, New York, 1955).

[8]R. E. Langer, Trans. Amer. Math. Soc. 33, 23 (1931); 34, 447 (1932). See E. R. Pike, Ref. 1 for details and further references.

[9]H. Bremmer, in *Symposium on the Theory of Electromagnetic Waves* (Interscience, New York, 1951), p. 169. For a brief account and further references, see R. Bellman, *Perturbation Techniques in Mathematics, Physics, and Engineering* (Holt, Rinehart and Winston, New York, 1964), pp. 99–103.

[10]For reasons to be discussed later (in Sec. II D), Eq. (4) will not hold when the period varies with x.

[11]Except at band edges, where ψ_+ and ψ_- become linearly dependent. The second solution then has the form $u_1(x)+xu_2(x)$ where u_1 and u_2 are both periodic with a period a and can be obtained from ψ_+ and ψ_- by an appropriate limiting process, for which see H. M. James, Phys. Rev. 76, 1602 (1949), Sec. III.

[12]This is the route followed by Froman and Froman, Ref. 1, in discussing the ordinary WKB approximation.

[13]This route to WKB-like approximations has been discussed by H. B. Keller and J. B. Keller, J. Soc. Indust.

Appl. Math. 10, 246 (1962).
[14]The advantage of formulating the approximation scheme as an initial value problem, which leads to Volterra equations, rather than as a boundary value problem (as in Bremmer's original paper, Ref. 9) has been emphasized by Keller and Keller, Ref. 13.
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[17]E. H. Kerner, Proc. Phys. Soc. A 69, 234 (1956).
[18]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics, 3rd ed.* (Springer-Verlag, Berlin, 1966), pp. 75–76.
[19]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1965), pp. 446–450.