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Application of a Variational Principle to the Calculation of Low-Energy Electron Diffraction Intensities. I. One-Dimensional Problems

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A variational principle for the reflectance is derived for elastic scattering from one-dimensional potentials. Using this principle, we show that the reflection coefficient is given by the ratio of two determinants without any subsidiary calculation of the wave field in the crystal and without any need to perform a matching on the boundary. The results are valid for crystals having variable lattice constants, including the possibility of impurity layers. For scattering from periodic potentials, the results are most conveniently obtained by employing Bloch's theorem with the wave number inside the crystal obtained from evaluating a Hill's determinant. The variational principle is also employed to obtain a modified Born approximation for the reflectance. We also compare the reflectance given by approximate wave functions with the exact reflectance for the Kronig-Penney model, the latter also having been obtained by the variational principle.

I. INTRODUCTION

RECENTLY there has been renewed interest in the use of low-energy electron diffraction (LEED) as a tool for the study both of surfaces and the interaction of electrons with solids.[1]

The most significant early work that related the experimental results to quantum theory was performed by Bethe,[2] who assumed the diffraction pattern was the result of elastic scattering of the incident electrons on the periodic crystal potential. He calculated the reflected intensities by matching the incident and the diffracted plane waves to a linear combination of waves with the same energy in a crystal having wave number parallel to the surface 2π times a reciprocal-lattice vector different from the incident wave. The latter requirement is a rigorous consequence of lattice periodicity parallel to the crystal surface. Bethe found that a qualitative understanding of the data could be obtained using only a two-beam model, this model leading to energy gaps in the allowed energy spectrum in the crystal and, consequently, to large reflection coefficients at these energies. He was also able to deduce that the Bragg peaks should be shifted from the positions derived from a simple geometric diffraction theory. Bethe's theory is in principle essentially correct for elastic scattering, but a two- or three-beam calculation is not capable of giving trustworthy quantitative results.

Boudreaux and Heine[3] have observed that the Bethe method may be more accurately employed if one uses a pseudopotential instead of the crystal potential. The advantage of the latter arises from the fact that only a few Fourier components of the pseudopotential will be large, and, consequently, the calculation of the allowed energy-band structure will be simplified. They have also pointed out the need to include at least a few of the infinite number of evanescent waves[4] allowed in the finite crystal in matching the wave functions on the surface.

Another technique used to obtain the energy eigenvalues and the corresponding Bloch waves in the crystal has been given by Marcus and Jepsen.[5] They truncate the potential by taking only a finite number of Fourier components in the direction parallel to the surface and treat the variation of these Fourier components in the perpendicular direction exactly. Since this method becomes rapidly more complicated as the number of Fourier components increases, it is useful only for low energies.

The above-mentioned techniques all have certain basic elements in common, i.e., the numerical calculation of the wave field in the crystal and the matching of the wave field to the incoming plane wave at the surface. The application of such an approach has certain inherent difficulties. Since the match on the surface is very sensitive to the precise values of the wave function at the boundary, a detailed calculation of the interior wave field is necessary in order to obtain reliable reflection coefficients.

Furthermore, these techniques are difficult to apply to anything but crystals having the same periodic potential right up to the boundary surface, followed by a sharp discontinuity into the vacuum. Thus, the variable interatomic distance near the surface is a significantly complicating factor, as is the change in potential in the last few layers and nearby "vacuum," because of the exponential tailing off of the electron-density distribution. Finally, it is possible in principle to take impurity layers into account but it is difficult in practice.

Methods for the calculation of LEED intensities that do not make explicit use of Bloch functions have also been proposed. McRae[6] has developed such a technique by applying Lax's[7] multiple-scattering theory

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[1] R. M. Stern, J. J. Perry, and D. S. Boudreaux, Rev. Mod. Phys. **41**, 275 (1969).

[2] H. Bethe, Ann. Physik **87**, 55 (1928).

[3] D. S. Boudreaux and V. Heine, Surface Sci. **8**, 426 (1967).

[4] V. Heine, Proc. Phys. Soc. (London) **81**, 300 (1963); J. B. Krieger, Phys. Rev. **156**, 776 (1967).

[5] P. M. Marcus and D. W. Jepsen, Phys. Rev. Letters **20**, 925 (1968).

[6] E. G. McRae, J. Chem. Phys. **45**, 3258 (1966).

[7] M. Lax, Rev. Mod. Phys. **23**, 287 (1951); Phys. Rev. **85**, 621 (1952).

to the LEED problem. But this method appears to be difficult to apply to any problem involving more than *s*-wave scattering from the individual atoms. Kambe[8] has also considered the problem of scattering from a periodic array of muffin-tin potentials and has given formulas for the reflection coefficients. These formulas, however, contain the expansion coefficients of the wave field in the crystal, which leads to the necessity of calculating hundreds of unknowns for the case of diffraction from a thick crystal. Finally, more recently, McRae[9] has generalized Darwin's dynamical theory of x-ray diffraction to the *n*-beam case and thus has constructed a technique that is suitable for LEED calculations. This method requires a knowledge of the scattering amplitudes of a single layer (which can be obtained from Kambe's work) and thereby eliminates the necessity of numerical integration of the Schrödinger equation. Calculations of this type, however, do involve the inversion of large matrices.

The enormous amount of numerical calculations necessitated by these methods leads one to look for simpler techniques for the calculation of LEED intensities. The fact that the energy-band structure essentially determines the position and width of the diffraction maxima for elastic scattering suggests the use of a variational principle, which has been so useful in atomic binding-energy problems and in solid-state physics. Furthermore, variational principles have been successfully employed in scattering theory both in nuclear and atomic physics. Moreover, a significant simplification occurs when such a principle is applied to scattering from periodic potentials because the conservation of $\mathbf{k}_{\parallel}$ mod 2π times reciprocal-lattice vectors means we do not require the scattering amplitude for all angles but only for those discrete angles corresponding to a given energy and a discrete finite set of $\mathbf{k}_{\parallel}$. Thus, the scattering from a crystal resembles in some ways a one-dimensional scattering problem in that one is interested in a set of reflection coefficients (in a one-dimensional problem there is only one reflection coefficient) instead of a continuous scattering amplitude that would represent an infinite set of reflection coefficients as one would have in nuclear or atomic scattering.

In this paper, we report on the use of a variational principle for the calculation of the reflection coefficient for elastic scattering from a one-dimensional periodic potential. The generalization to three-dimensional problems will be presented later. We show that for one-dimensional problems the reflection coefficient is given by the ratio of two determinants without any subsidiary calculation of the wave field in the crystal. For scattering from periodic potentials, the results are most conveniently found by employing Bloch's theorem with k obtained from evaluating a Hill's determinant. A modified Born approximation is also obtained. Furthermore, we compare the reflectance given by approximate wave functions to the exact reflectance for the Kronig-Penney model, the latter also having been obtained by the variational principle.

II. FORMULATION OF VARIATIONAL PRINCIPLE

We consider one-dimensional elastic scattering by nonrelativistic electrons that have a definite energy and are incident from $x=-\infty$. A variational principle for the transmission coefficient has been previously given for the case by Morse and Feshbach.[10] We shall adapt their discussion for the calculation of the reflection coefficient.

The Schrödinger equation for a particle with potential energy $U(x)$ and energy $\epsilon=\hbar^2k^2/2m$ may be written

$$\frac{d^2}{dx^2}\psi(x)+[k^2-V(x)]\psi(x)=0\,, \tag{1}$$

where

$$V(x)=\frac{2m}{\hbar^2}U(x)\,. \tag{2}$$

It is convenient to write Eq. (1) as the integral equation

$$\psi(x)=\phi_0(x)+\int G(x,x')V(x')\psi(x')dx'\,, \tag{3}$$

where

$$\phi_0(x)=e^{ikx} \tag{4}$$

is the incident plane wave and $G(x,x')$ is the one-dimensional free-electron Green's function.

$$G(x,x')=-\frac{i}{2k}e^{ik|x-x'|}\,, \tag{5}$$

where G satisfies

$$\frac{d^2}{dx^2}G(x,x')+k^2G(x,x')=\delta(x-x')\,.$$

The reflection coefficient R is obtained directly by letting $x\rightarrow-\infty$ in the integral equation. Then (assuming $V(x)\rightarrow 0$ for $x\rightarrow-\infty$)

$$\psi(x)=e^{ikx}+Re^{-ikx}\,,$$

$$R=-\frac{i}{2k}\int e^{ikx'}V(x')\psi(x')dx'\,, \tag{6}$$

$$1=-\frac{i}{2kR}\int e^{ikx'}V(x')\psi(x')dx'\,.$$

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[8] K. Kambe, Z. Naturforsch. **22A**, 322 (1967); **22A**, 422 (1967); **23A**, 1280 (1968).

[9] E. G. McRae, Surface Sci. **11**, 479 (1968); **11**, 492, (1968).

[10] P. M. Morse and H. Feshbach, in *Methods of Theoretical Physics* (McGraw-Hill Book Co., New York, 1953), p. 1128.

Equation (3) may now be written as a homogeneous equation in which R appears explicitly. Using Eq. (6), we obtain

$$\psi(x)=-\frac{i}{2kR}\int e^{ikx'}V(x')\psi(x')dx'e^{ikx}+\int G(x,x')V(x')\psi(x')dx'. \tag{7}$$

Multiplying Eq. (7) by $\psi(x)V(x)$ and integrating over all space, we obtain

$$R=-\frac{i}{2k}\left(\int e^{ikx}V(x)\psi(x)dx\right)^2\Big/\int dx\psi(x)V(x)\times\left(\psi(x)-\int G(x,x')V(x')\psi(x')dx'\right). \tag{8}$$

Equation (8) is an exact expression for R, in terms of the exact solution $\psi(x)$ of the Schrödinger equation. It is shown in Appendix A that when the exact $\psi(x)$ is substituted into Eq. (8), R is an extremum, and, hence, we obtain the variational principle $\delta R=0$.

A similar expression may be constructed for the transmission coefficient, which may also be shown to be an extremum for small variations about the exact wave function.[10]

The exact wave function may always be expanded in terms of a complete set of functions. We take a linear combination of a finite subset of these functions as a trial wave function. Thus,

$$\psi(x)=\sum_{i=1}^{n}C_i\phi_i(x), \tag{9}$$

where the C_i are complex parameters that are chosen such that R is an extremum. Substituting Eq. (9) into Eq. (8), we obtain

$$R=-(i/2k)\sum_{i,j}D_iD_jC_iC_j/\sum_{i,j}F_{ij}C_iC_j, \tag{10}$$

where

$$D_i\equiv\int\phi_i(x)V(x)e^{ikx}dx,$$

$$F_{ij}\equiv\int\phi_i(x)V(x)\times\left(\phi_j(x)-\int G(x,x')V(x')\phi_j(x')dx'\right)dx. \tag{11}$$

The requirement that R is an extremum is equivalent to

$$\frac{\partial R}{\partial C_i}=0,\quad i=1,\ldots,n$$

which yields the set of equations

$$\sum_{j=1}^{n}\left(F_{ij}+\frac{i}{2kR}D_iD_j\right)C_j=0,\quad i=1,\ldots,n \tag{12}$$

where we have used $F_{ij}=F_{ji}$, which follows from $G(x,x')=G(x',x)$.

The necessary and sufficient condition required so that not all C_i are zero in Eq. (12) is that the determinant of the coefficients is zero, i.e.,

$$\det(\Delta_{ij})=0, \tag{13}$$

where

$$\Delta_{ij}\equiv F_{ij}+(i/2kR)D_iD_j. \tag{14}$$

In his work on nuclear-collision theory, Kohn[11] has proved that an equation of the form of Eq. (13), with elements given by Eq. (14), constitutes a linear equation for R and hence determines R uniquely. This is different from the usual secular equation for the energy, where the degree of the equation in the unknown energy equals the number of wave functions summed in Eq. (9).

The transformation Kohn[11] used is

$$\begin{aligned}f_1&=\sum_{i=1}^{n}C_iD_i,\\ f_i&=C_i,\qquad i\neq1.\end{aligned} \tag{15}$$

Equation (10) then may be written

$$\sum_{i,j=1}^{n}H_{ij}f_if_j+\frac{i}{2kR}f_1^2=0, \tag{16}$$

with

$$\begin{aligned}H_{11}&=\frac{F_{11}}{D_1^2},\\ H_{1j}=H_{j1}&=\frac{F_{1j}}{D_1}-\frac{F_{11}D_j}{D_1^2},\qquad j\neq1\\ H_{ij}&=F_{ij}-\frac{D_iF_{1j}}{D_1}+\frac{F_{11}D_iD_j}{D_1^2}-\frac{F_{i1}D_j}{D_1},\quad i,j\neq1.\end{aligned} \tag{17}$$

The requirement that R is an extremum subject to variations in the f_i leads to a set of homogeneous equations whose compatibility condition is

$$\det(H_{ij}+(i/2kR)\delta_{1i}\delta_{1j})=0, \tag{18}$$

which is evidently linear in R, and the solution for R is the ratio of two determinants, i.e.,

$$(2k/i)R=|M|/|H_{ij}|, \tag{19}$$

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[11] W. Kohn, Phys. Rev. **74**, 1763 (1948).

where $|M|$ is the (1,1) minor of H_{ij} and is given by

$$|M|=|H_{ij}|\ i,j=2,\ldots,n.$$

By adding D_i times the first row of H_{ij} to the ith row and D_j times the resulting first column to the jth column, we find

$$|H_{ij}|=|F_{ij}|/D_1^2,$$

and hence

$$R=\frac{i}{2k}D_1^2\frac{|H_{ij}|\ i,j=2,\ldots,n}{|F_{ij}|}. \tag{20}$$

Thus far, the derivation has been entirely general and has made no assumptions about the form of the potential. However, if the potential is perfectly periodic inside the one-dimensional crystal and goes to zero abruptly at the boundary, we may make use of Bloch's[12] theorem, which states that the eigenfunctions in the crystal for a given energy may be written

$$\phi(x)=e^{ik'x}U_{k'}(x), \tag{21}$$

where k' is the wave number of the Bloch wave having energy $\hbar^2k^2/2m$ and $U_{k'}(x)$ is periodic in the lattice. If the energy is in a band gap, k' will be complex. There are always two solutions corresponding to $\pm k'$, and since the energy must be even in k', the two waves have equal and opposite velocity. For a semi-infinite crystal filling the positive axis, only the wave with velocity in the positive x direction in the crystal is allowed the other wave representing current incident from $x\rightarrow+\infty$. Thus, instead of including all known components in our set of basis functions, we can write

$$\psi(x)=e^{ik'x}U_{k'}(x), \tag{22}$$

where

$$U_{k'}(x)=\sum_n U_n e^{i2\pi nx/a} \tag{23}$$

and a is the lattice constant. Hence, we can take a linear combination of functions of the type $e^{i[k'+(2\pi n/a)]x}$ as our trial wave function and obtain the reflection amplitude as a function of k', the wave number of the electron in the crystal. The appropriate k' can be obtained by evaluating a Hill's determinant for the one-dimensional energy-band structure problem. The solution given by Morse[13] is

$$\sin^2(\tfrac{1}{2}k'a)=\sin^2(\tfrac{1}{2}ka)\cdot\Delta(0), \tag{24}$$

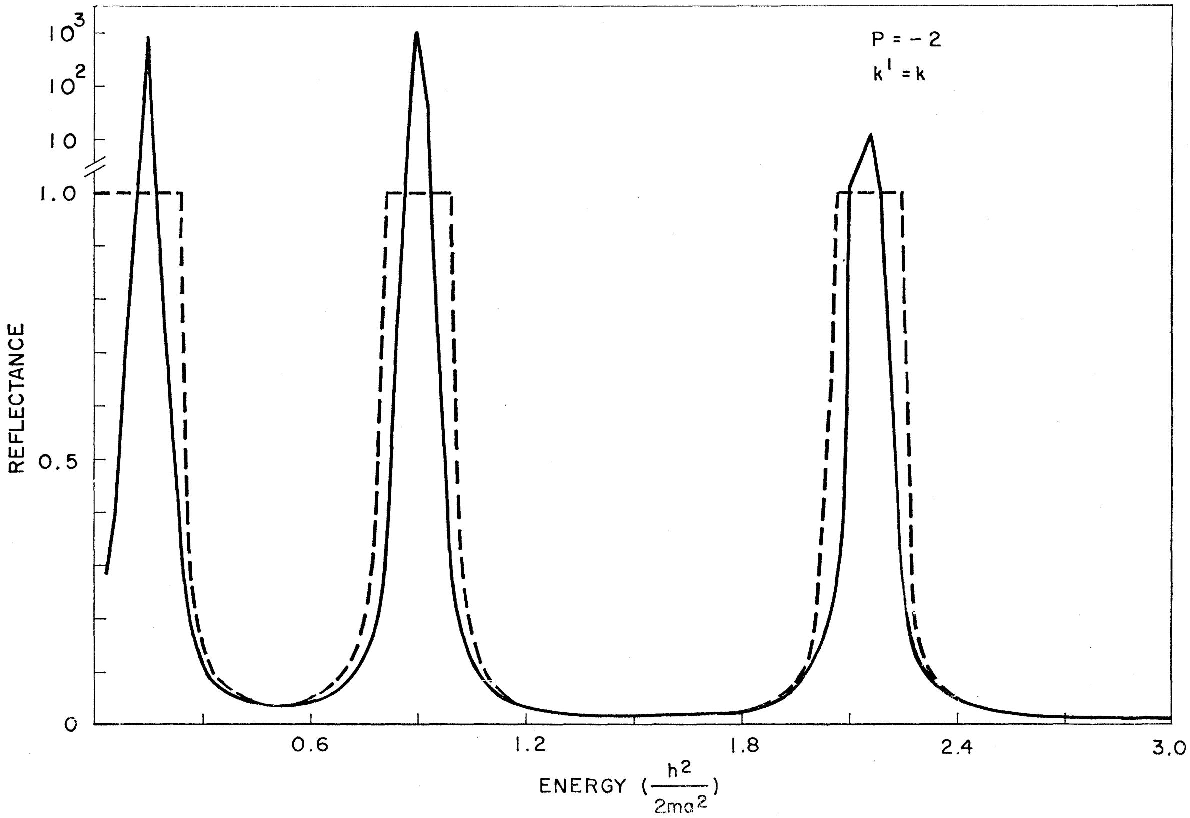

FIG. 1. Reflectance $|R|^2$ versus incident electron energy E for $P=-2$. The energy scale is in units of $h^2/2ma^2$. The dotted curve is the exact solution. The solid curve is obtained by putting e^{ikx} as the trial wave function.

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[12] F. Bloch, Z. Physik **52**, 555 (1928).
[13] P. M. Morse, Phys. Rev. **35**, 1310 (1930).

where Δ is

$$\left|\begin{array}{cccccccc}
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \frac{-A_{-1}}{1-W} & 1 & \frac{-A_1}{1-W} & \frac{-A_2}{1-W} & \frac{-A_3}{1-W} & \frac{-A_4}{1-W} & \cdots \\
\cdots & \frac{-A_{-2}}{-W} & \frac{-A_{-1}}{-W} & 1 & \frac{-A_1}{-W} & \frac{-A_2}{-W} & \frac{-A_3}{-W} & \cdots \\
\cdots & \frac{-A_{-3}}{1-W} & \frac{-A_{-2}}{1-W} & \frac{-A_{-1}}{1-W} & 1 & \frac{-A_1}{1-W} & \frac{-A_2}{1-W} & \cdots \\
\cdots & \frac{-A_{-4}}{2^2-W} & \frac{-A_{-3}}{2^2-W} & \frac{-A_{-2}}{2^2-W} & \frac{-A_{-1}}{2^2-W} & 1 & \frac{-A_1}{2^2-W} & \cdots \\
\cdots & \frac{-A_{-5}}{3^2-W} & \frac{-A_{-4}}{3^2-W} & \frac{-A_{-3}}{3^2-W} & \frac{-A_{-2}}{3^2-W} & \frac{-A_{-1}}{3^2-W} & 1 & \cdots \\
\cdots & \frac{-A_{-6}}{4^2-W} & \frac{-A_{-5}}{4^2-W} & \frac{-A_{-4}}{4^2-W} & \frac{-A_{-3}}{4^2-W} & \frac{-A_{-2}}{4^2-W} & \frac{-A_{-1}}{4^2-W} & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{array}\right| \tag{25}$$

with

$$V(x)=\left(\frac{2\pi}{a}\right)^2 \sum_n A_n e^{i(2\pi n/a)x}, \quad A_0=0$$

$$W=[(a/2\pi)k]^2.$$

Thus, by including enough Fourier components in the trial wave function and using k' obtained from the Hill's determinant, the reflection coefficient for one-dimensional problems may be obtained with as much accuracy as desired without the necessity to actually calculate the coefficients U_n or perform the matching on the surface of the crystal, as originally done by Morse.

III. APPLICATION TO KRONIG-PENNEY MODEL

In Sec. II, we made use of linear variational parameters to obtain the reflection coefficient, with k' determined by the solution of a Hill's determinant. It is possible to derive a more general variational principle that is valid for three-dimensional problems and to obtain the reflection coefficients by expanding the wave function in the crystal in terms of the set of Bloch waves in the crystal having the same energy and the same $\mathbf{k}_{\parallel}$ mod 2π times a reciprocal-lattice vector. However, the

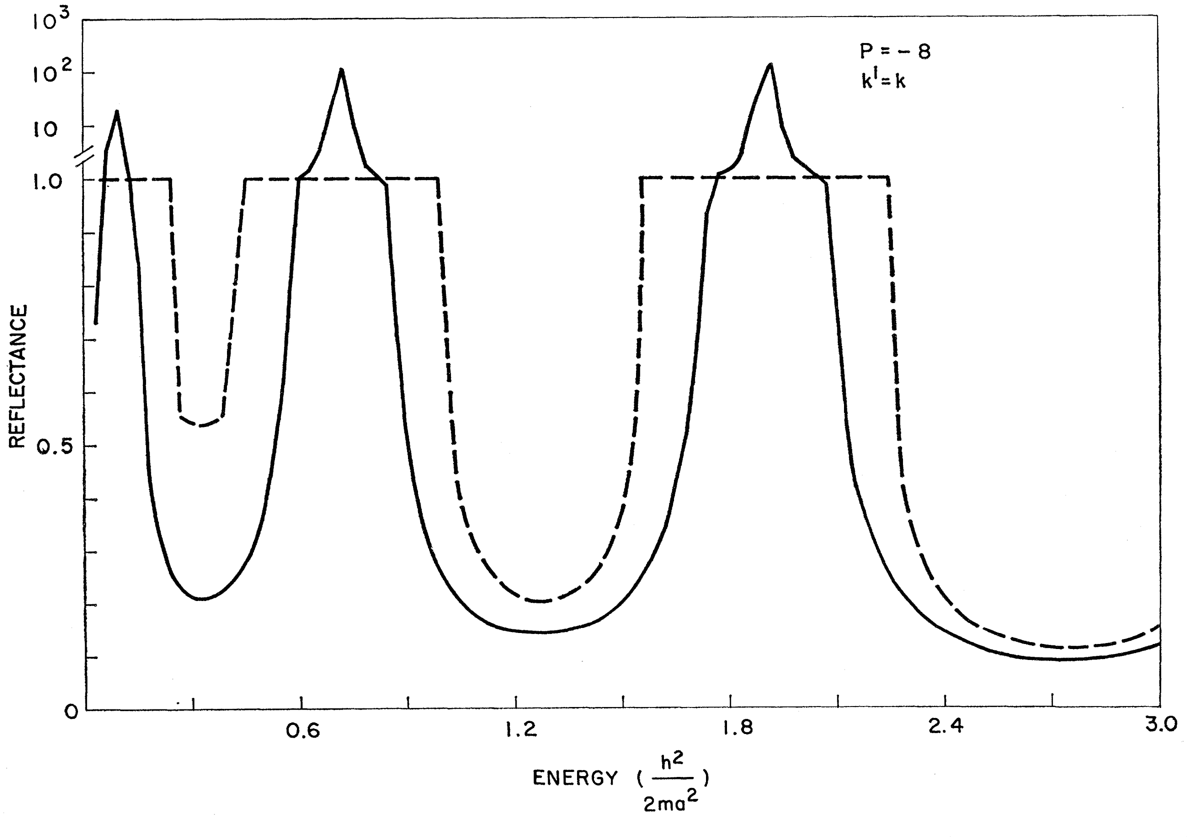

FIG. 2. Reflectance $|R|^2$ versus incident electron energy E for $P=-8$. The energy scale is in units of $h^2/2ma^2$. The dotted curve is the exact solution. The solid curve is obtained by putting e^{ikx} as the trial wave function.

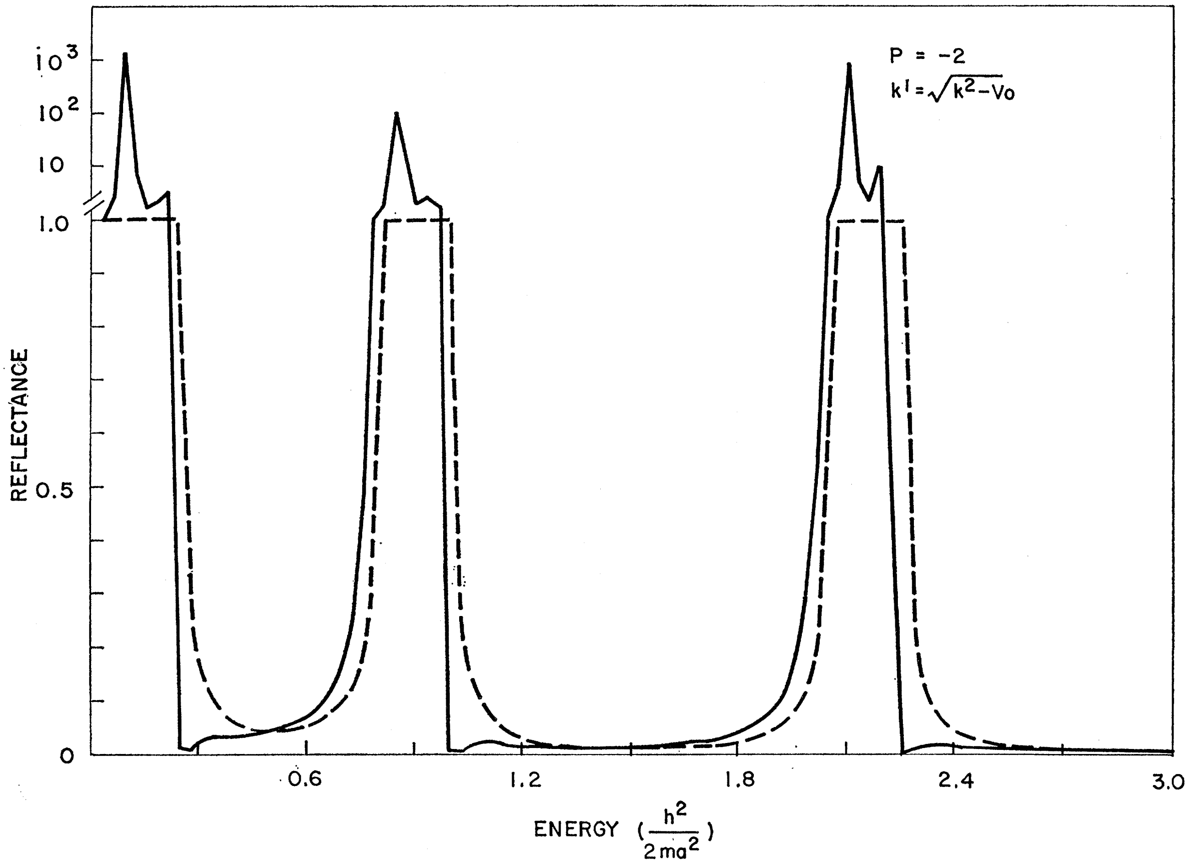

FIG. 3. Reflectance $|R|^2$ versus incident electron energy E for $P=-2$. The energy scale is in units of $h^2/2ma^2$. The dotted curve is the exact solution. The solid curve is obtained by putting $e^{i(k^2-V_0)^{1/2}x}$ as the trial wave function, where V_0 is the average inner potential.

solubility of the three-dimensional Hill's determinant for the corresponding values of k's is questionable, i.e., we show in Appendix B that Morse's solution for the three-dimensional case diverges. It is consequently of interest to consider an exactly soluble problem, such as scattering from the Kronig-Penney[14] potential, and to compare the exact results to those obtained by a direct use of the variational principle with certain approximate wave functions.

We thus consider a potential defined by an array of one-dimensional δ functions located at lattice sites

$$x_n = na + a/2 \quad n = 0, 1, 2, \ldots ,$$

corresponding to a one-dimensional semi-infinite crystal. Then,

$$V(x) = \sum_{n=0}^{\infty} \lambda \delta(x - x_n) , \tag{26}$$

where λ is a constant. The exact solution for the reflection amplitude R may be obtained directly from the variational principle by the following procedure. We take as the exact solution for the wave function inside the crystal the Bloch wave given by Eq. (22), where

$$U_{k'}(x) = U_{k'}(x+a) . \tag{27}$$

Substituting Eq. (22) into Eq. (8) yields

$$R = -\frac{i\lambda}{2k}\left(\frac{1}{1-e^{i(k+k')a}}\right)^2 e^{ika} \bigg/ \frac{1}{1-e^{i2k'a}} + \frac{\lambda i}{2k} \frac{1+e^{i(k+k')a}}{(1-e^{i(k+k')a})(1-e^{i2k'a})} , \tag{28}$$

for the potential given by Eq. (26), where we have assumed that k' has a small imaginary part, so that the term

$$\lim_{D\to\infty} e^{ik'D} \to 0 .$$

We note that $U_{k'}(x)$ drops out of the calculation in this case since it is evaluated only at the lattice points at which it always has the same value. Equation (28) is exact, provided the correct k' is inserted. The latter can be obtained by treating k' as a nonlinear variational parameter, i.e., using $\partial R/\partial k' = 0$. The resulting equa-

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[14] C. Kittel, in *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed.

tion for k' is simply

$$\frac{P\sin(ka)}{ka}+\cos ka=\cos k'a\,, \tag{29}$$

where $P\equiv\frac{1}{2}\lambda a$, which is precisely the usual equation for the energy-band structure for the Kronig-Penney model. Finally, substituting Eq. (29) into Eq. (28) gives

$$|R|^2=\left|\left(1-\frac{\sin k'a}{\sin ka}-i\frac{P}{ka}\right)\Big/\left(1+\frac{\sin k'a}{\sin ka}-i\frac{P}{ka}\right)\right|^2, \quad \text{for } k' \text{ real} \tag{30}$$

$$|R|^2=1\,, \qquad \text{for } k' \text{ complex}$$

where k' is given by Eq. (29).

This result is equivalent to that obtained by Gerstner and Cutler,[15] who actually solved for the wave function inside the crystal and performed the matching on the surface to determine the reflection coefficient. However, we need not depend on a comparison with their results to conclude that our result is exact because our derivation involves no approximation once the Kronig-Penney model is assumed. Furthermore, our results suggest that if the potential is well localized but not a δ function, a trial wave function of the form $e^{ik'x}$ may yield a very good approximate value for R, provided k' is chosen to make R an extremum.

IV. USE OF VARIATIONAL EXPRESSION WITH APPROXIMATE SOLUTIONS

A main problem in the approximate calculation of LEED intensities is the failure of the Born approximation. The latter approximation is valid, provided the change in the incident wave function is small due to the perturbing potential. However, for energies in a band gap, the wave function inside the crystal is a Bloch wave with a complex value of k', and thus it exponentially decays away from the surface into the crystal, which in no way resembles the incident plane wave. Consequently, when the Born approximation is applied, certain unphysical results are obtained (i.e., the reflection coefficient diverges if the change in wave number is 2π times a reciprocal-lattice vector, which in one dimension is equivalent to $2k'=2\pi n/a$), and the reflection maxima occur only at these discrete energies,

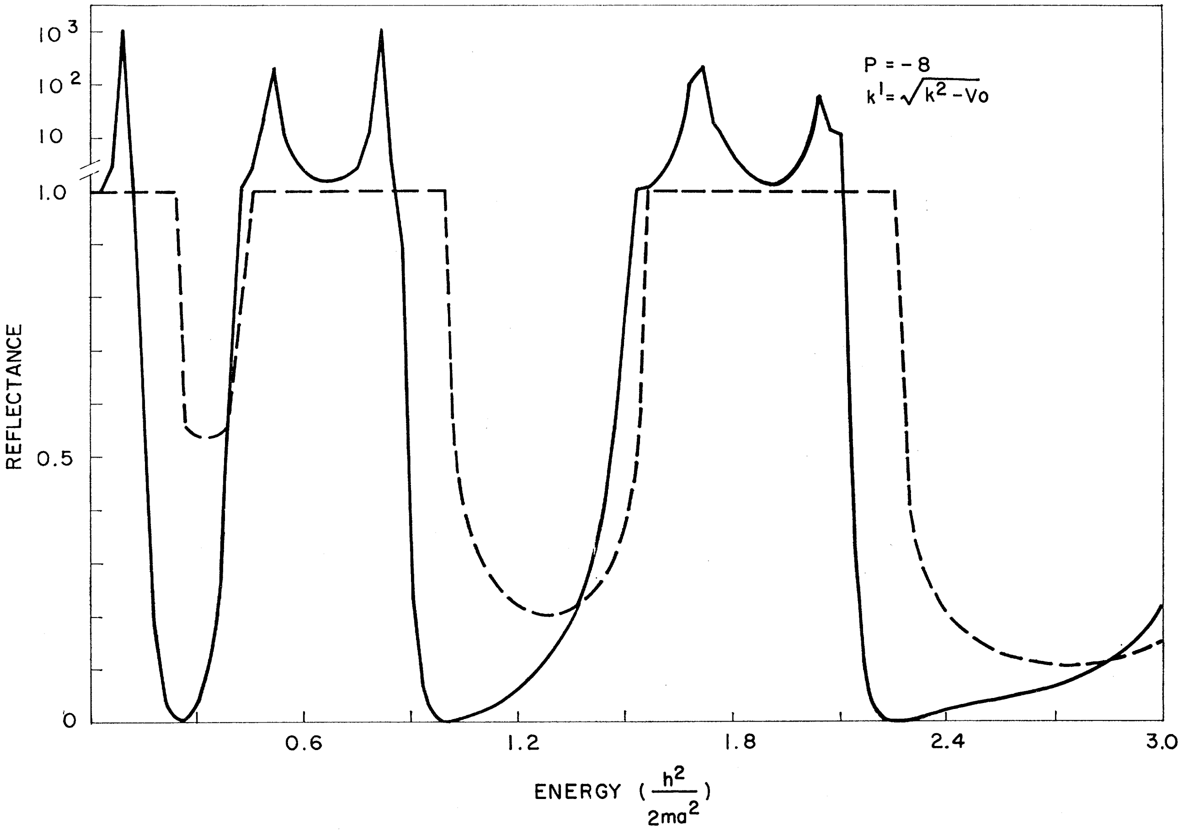

FIG. 4. Reflectance $|R|^2$ versus incident electron energy E for $P=-8$. The energy scale is in units of $h^2/2ma^2$. The dotted curve is the exact solution. The solid curve is obtained by putting $e^{i(k^2-V_0)^{1/2}x}$ as the trial wave function, where V_0 is the average inner potential.

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[15] J. Gerstner and P. H. Cutler, Surface Sci. 9, 198 (1968).

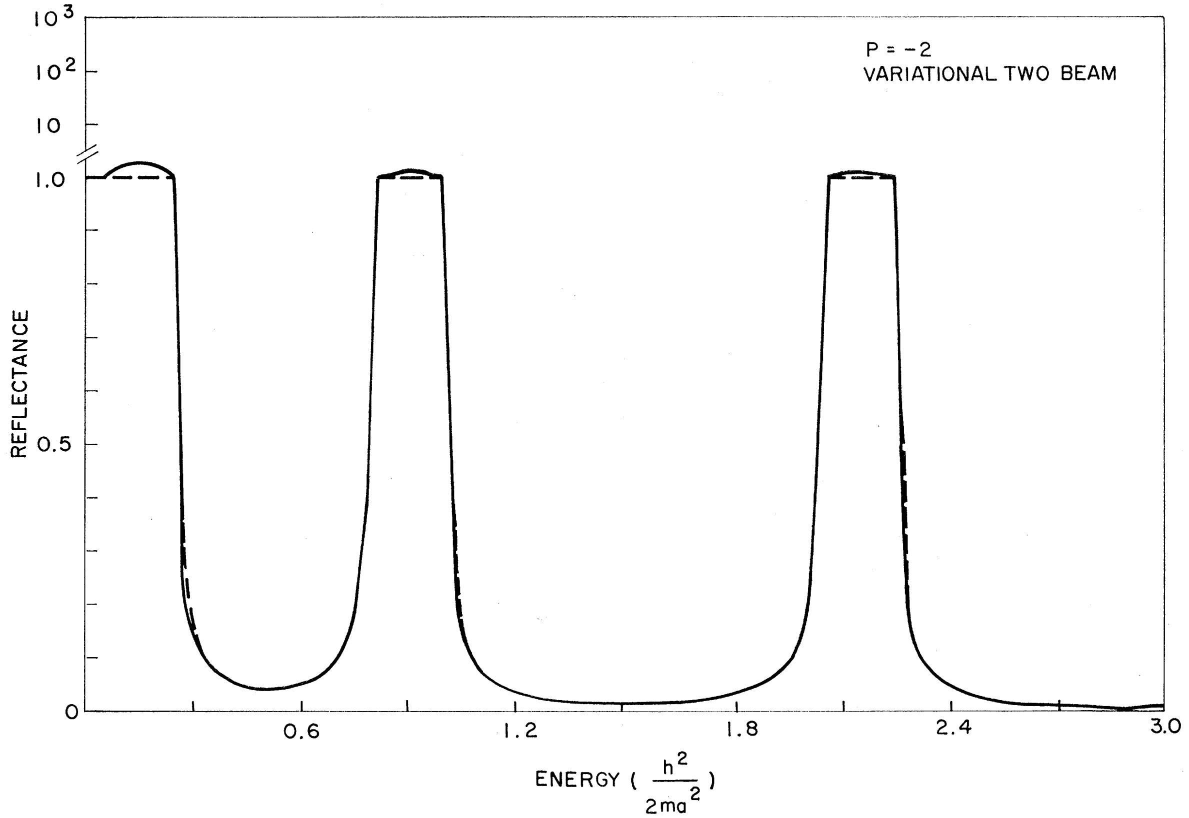

FIG. 5. Reflectance $|R|^2$ versus incident electron energy E for $P=-2$. The energy scale is in units of $h^2/2ma^2$. The dotted curve is the exact solution. The solid curve is obtained by taking $e^{ik'x}$ as the trial wave function, where k' is obtained by the two-beam approximation-energy secular equation.

with no width in energy. It is possible to include the effect of the average crystal potential by assuming that the incident wave number is changed when the electron crosses the crystal boundary, so that energy is conserved. This inner-potential correction, however, merely shifts the maxima but continues to give rise to divergent reflection coefficients with no width in energy.

In Sec. IV A, we consider the use of the variational expression given by Eq. (8) together with some approximate wave functions and compare our results to the exact solution of the Kronig-Penney model [Eq. (30)].

A. Modified Born Approximation

If we substitute the original plane wave $\psi(x)=e^{ikx}$ into Eq. (8), we obtain the modified Born approximation

$$R=-\frac{i}{2k}\left(\int V(x)e^{i2kx}dx\right)^2 \Big/ \int e^{ikx}V(x) \times\left(e^{ikx}-\int G(x,x')V(x')e^{ikx'}dx'\right). \quad (31)$$

We note that, as in the case of the transmission coefficient[10] in the thin crystal limit, the first Born approximation is obtained by omitting the second term in the denominator. The second-order Born approximation may be obtained by expanding the denominator, assuming the second term is small compared to the first. Higher-order terms may be obtained by using iterated solutions of Eq. (3) as trial wave functions in Eq. (8). However, for a semi-infinite crystal, all these terms diverge, and the approximation breaks down. Nevertheless, Eq. (31) has a finite limit as the size of the crystal approaches infinity, and, thus, it can serve as an approximate solution for the reflection coefficient.

We have compared this result for the Kronig-Penney model to the exact solution. The result obtained from Eq. (31) is given simply by $k'=k$ in Eq. (28). Figures 1 and 2 are plots of the reflection coefficient $|R|^2$ versus energy for two different potential strengths. The dotted curves are the exact results given by Eq. (30). In these and all subsequent curves, the unshifted Bragg position is at the extreme right edge of each band gap, i.e., at the highest energy for which the exact reflection coefficient is 1.

We see that, unlike the Born approximation, the reflection coefficient has been shifted and has a finite energy width. Furthermore, the maxima of the reflectance is almost precisely in the center of the band gap,

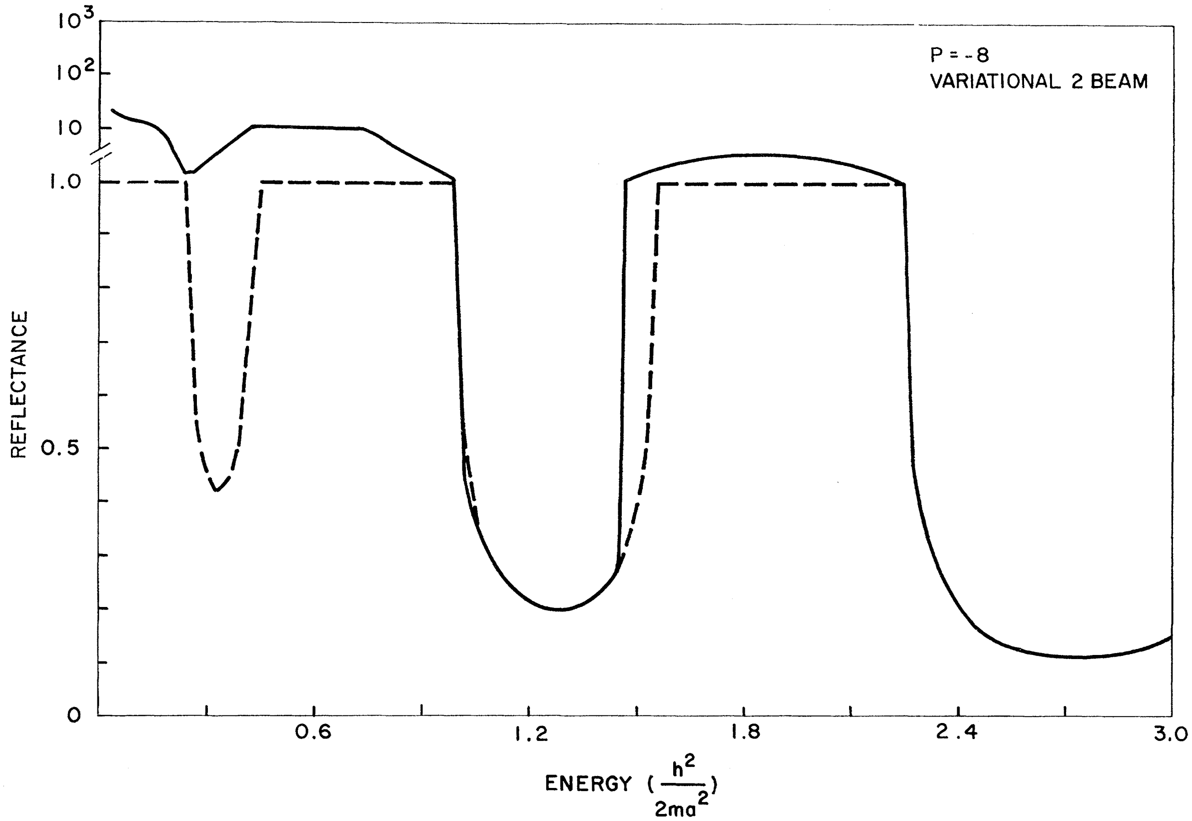

FIG. 6. Reflectance $|R|^2$ versus incident electron energy E for $P=-8$. The energy scale is in units of $h^2/2ma$. The dotted curve is the exact solution. The solid curve is obtained by taking $e^{ik'x}$ as the trial wave function, where k' is obtained by the two-beam approximation-energy secular equation.

even for potentials that are so strong that the band gaps are as wide as the bands. Similarly, the position of the reflection minima is accurately given by the approximate expression. However, the widths of the reflection maxima are narrower than those given by the exact solution, and the reflectance in energies inside the band gaps is sometimes greater than 1.

B. Correction for Inner Potential

Instead of taking the incident plane wave as the approximate solution, we can take account of the average crystal potential by taking

$$\psi(x)=\exp[i(k^2-V_0)^{1/2}x],$$

as the approximate wave function in Eq. (8), where V_0 is the average potential in the crystal. Figures 3 and 4 show some improvement for the sizes of widths of the reflection maxima, but the positions of the maxima have been slightly shifted from the more accurate results obtained with no inner-potential correction. This is due to the band structure for the Kronig-Penney model. We see from Eq. (29) that at the Bragg condition $k'=k$ (and, hence, electrons having a wave number near the Bragg value) nearly have their free-electron k value and thus have no inner-potential correction.

C. Use of Two-Beam Approximation for $k(\varepsilon)$

In both Secs. IV A and IV B, the magnitude of the reflectance for incident energies corresponding to band gaps inside the crystal was found to be many orders of magnitude too large. This result arises from the fact that, at these energies, the wave number in the crystal cannot be approximated by its free-electron value because the Bloch wave corresponds to an exponentially decaying function with complex k'. It is thus necessary to employ a better approximation for k' that includes the possibility of complex behavior such as the two-beam approximation originally used by Bethe.

By combining the two-beam approximation of the energy-band structure with the variational principle, the reflectance is considerably improved. We take $\psi(x)=e^{ik'x}$ as the approximate wave function, where k' is the solution of the two-beam approximation secular equation for the energy given by

$$[k'^2-k^2+V_0]\left[\left(k'+\frac{2\pi n}{a}\right)-k^2+V_0\right]-|V_n|^2=0,$$

where, in turn, V_n is the Fourier coefficient of the potential. Figures 5 and 6 show that, not only are the widths of the reflection maxima and the reflectance for energies outside the band gaps accurately given, but also the reflectance for energies inside the band gaps has been reduced by orders of magnitude and is now much closer to the exact results. The use of a larger secular equation relating ϵ to k' would undoubtedly improve these results even further.

APPENDIX A: PROOF THAT $\delta R=0$ WHEN ψ IS VARIED ABOUT THE EXACT SOLUTION

From Eq. (8), we have

$$-(2k/i)\delta R=\frac{1}{D^2}\biggl\{\biggl(\int dx\psi(x)V(x)\psi(x)\biggr)-\biggl(\int G(x,x')V(x')\psi(x')dx'\biggr)2\biggl(\int e^{ikx}V(x)\delta\psi(x)dx\int e^{ikx}V(x)\psi(x)dx\biggr)$$
$$-\biggl(\int e^{ikx}V(x)\psi(x)dx\biggr)^2\biggl[\int dx\delta\psi(x)V(x)\biggl(\psi(x)-\int G(x,x')V(x')\psi(x)dx'\biggr)$$
$$+\int dx\psi(x)V(x)\biggl(\delta\psi(x)-\int G(x,x')V(x')\delta\psi(x')dx'\biggr)\biggr]\biggr\}\,, \tag{A1}$$

where D is the denominator of the right-hand side of Eq. (8).

Equation (A1) may be rewritten as

$$-(2k/i)\delta R=\frac{2}{D^2}\biggl(\int e^{ikx}V(x)\psi(x)dx\biggr)\biggl\{\int dx\psi(x)V(x)\biggl(\psi(x)-\int G(x,x')V(x')\psi(x')dx'\biggr)$$
$$-\int e^{ikx}V(x)\psi(x)dx\biggl[\int dxV(x)\psi(x)\biggl(\delta\psi(x)-\int G(x,x')V(x')\delta\psi(x')dx'\biggr)\biggr]\biggr\}\,,$$

where we have used $G(x,x')=G(x',x)$. But

$$\psi(x)-\int G(x,x')V(x')\psi(x')dx'=e^{ikx}.$$

Therefore,

$$\int\psi(x)V(x)\biggl(\psi(x)-\int G(x,x')V(x')\psi(x')dx'\biggr)dx=\int e^{ikx}V(x)\psi(x)dx\,,$$

and from this,

$$-(2k/i)\delta R=\frac{2}{D^2}\biggl(\int e^{ikx}V(x)\psi(x)dx\biggr)\biggl[\int e^{ikx}V(x)\psi(x)dx\int e^{ikx}V(x)\delta\psi(x)dx-\int e^{ikx}V(x)\psi(x)dx$$
$$\times\biggl(\int dx\psi(x)V(x)\delta\psi(x)-\int\int\delta\psi(x)V(x)G(x,x')V(x')\psi(x')dxdx'\biggr)\biggr].$$

Collecting terms, we obtain

$$-(2k/i)\delta R=\frac{2}{D^2}\biggl(\int e^{ikx}V(x)\psi(x)dx\biggr)^2\biggl[\int\biggl(e^{ikx}-\psi(x)+\int G(x,x')V(x')\psi(x')dx'\biggr)V(x)\delta\psi(x)dx\biggr].$$

Thus, if $\psi(x)$ satisfies the integral form of Schrödinger's equation given by Eq. (3), then $\delta R=0$.

APPENDIX B: DIVERGENCE OF MORSE'S SOLUTION FOR THREE DIMENSIONS

For three dimensions, Morse[13] claims that the generalization of Eqs. (24) and (25) for the determination of the band structure is

$$S(k_x',k_y',k_z';\alpha,\beta,\lambda)=S(k_x,k_y,k_z;\alpha,\beta,\lambda)\Delta(0,0,0)\,, \tag{B1}$$

where $\Delta(0,0,0)$ is a determinant similar to the Hill's determinant $\Delta(0)$ for the one-dimensional case. Here, $\mathbf{k}'$ is the wave vector for the three-dimensional Bloch wave, and $\mathbf{k}$ is the wave vector if the potential were zero. The constants α, β, γ are the magnitudes of the reciprocal-lattice vectors in the x, y, and z direction for a system having orthogonal lattice vectors.

The function

$$S(x,y,z;\alpha,\beta,\gamma)=(x^2+y^2+z^2)\times\prod_{l,m,n=-\infty}^{\infty}\left(1-\frac{2l\alpha x+2m\beta y+2n\gamma z-x^2-y^2-z^2}{l^2\alpha^2+m^2\beta^2+n^2\gamma^2}\right),\tag{B2}$$

where the infinite product does not include the term for which $l=m=n=0$. We show below, however, that the right-hand side of Eq. (B2) diverges, and hence, Eq. (B1) cannot represent the correct band-structure equation with this S.

For simplicity we consider the case $\alpha=\beta=\gamma$. Then,

$$\ln S(x,y,z;\alpha)=\ln(x^2+y^2+z^2)+\sum_{l,m,n=-\infty}^{+\infty}{}'\ln\left(1-\frac{\alpha(2lx+2my+2nz)}{\alpha^2(l^2+m^2+n^2)}\right).\tag{B3}$$

For sufficiently large $l^2+m^2+n^2\equiv N^2$, the term

$$\left|\frac{\alpha(2lx+2my+2nz)-x^2-y^2-z^2}{\alpha^2(l^2+m^2+n^2)}\right|\ll 1.$$

So, using the expansion $\ln(1+x)=x-\frac{1}{2}x^2+\ldots$, we obtain

$$\begin{aligned}\sum_{l^2+m^2+n^2>N^2}^{\infty}&\ln\left(1-\frac{\alpha(2lx+2my+2nz-x^2-y^2-z^2)}{\alpha^2(l^2+m^2+n^2)}\right)\\&=\sum_{l^2+m^2+n^2>N^2}^{\infty}\left(\frac{-\alpha(2lx+2my+2nz-x^2-y^2-z^2)}{\alpha^2(l^2+m^2+n^2)}\right)-\frac{1}{2}\left(\frac{\alpha^2(2lx+2my+2nz-x^2-y^2-z^2)^2}{(\alpha^2(l^2+m^2+n^2))^2}\right)+O((l^2+m^2+n^2)^{-2})\\&=\sum_{l^2+m^2+n^2>N^2}\frac{x^2+y^2+z^2}{3\alpha^2(l^2+m^2+n^2)}+O((l^2+m^2+n^2)^{-2}),\end{aligned}\tag{B4}$$

where we have used both the fact that all terms in the expression that are odd in either l, m, or n must vanish because, when summed, they occur in pairs with opposite signs and the fact that

$$\sum\frac{l^2}{(l^2+m^2+n^2)^2}=\sum\frac{m^2}{(l^2+m^2+n^2)^2}=\sum\frac{n^2}{(l^2+m^2+n^2)^2}=\tfrac{1}{3}\sum\frac{1}{l^2+m^2+n^2}.$$

The sum

$$\sum_{l^2+m^2+n^2>N^2}^{\infty}\frac{1}{l^2+m^2+n^2}$$

is divergent, as can easily be seen by noting that it is larger than the divergent integral

$$\int\frac{1}{r^2}\,d\mathbf{r},$$

where the volume of integration is the region outside a sphere of radius $N+1$. It is easy to show that the terms of $O((l^2+m^2+n^2)^{-2})$ in Eq. (B4) lead to a correction of only $O(1/N)$; and since the terms in Eq. (B3) for which $l^2+m^2+n^2\leq N^2$ are finite, we conclude that S is divergent. We also note that the two-dimensional generalization also diverges since then we are left with the sum

$$\sum_{l^2+m^2>N^2}^{\infty}\frac{1}{l^2+m^2}$$

which is larger than the logarithmically divergent integral

$$\int\frac{1}{\rho^2}d\boldsymbol{\rho},$$

where the domain of integration is the region outside a circle of radius $N+1$.