

Green's function and generalized phase shift for surface and interface problems

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For electrons, phonons, etc., and regardless of symmetry, the Green's function in any mixed Wannier-Bloch representation is $G_0^+(z-z', \bar{k}n\omega) = -ia \sum_j e^{ik_j(z-z')/v(k_j\bar{k}n)} \text{sgn}(z-z') + G_{BC}$, where $\bar{k} = (k_x, k_y)$, n is the branch index, and the values of z correspond to lattice points. The k_j are those values of k_z for which the eigenvalue $\epsilon(k_z\bar{k}n)$ is equal to the parameter ω , and for which $v(k_j\bar{k}n)\text{sgn}(z-z') > 0$, if k_j is real, or $\text{Im} k_j \text{sgn}(z-z') > 0$, if k_j is complex. G_{BC} represents integrals around branch cuts, a is the height of a unit cell, and $v(k_z\bar{k}n) \equiv \partial \epsilon(k_z\bar{k}n)/\partial k_z$. The above expression can be regarded as a generalization of the usual one-dimensional Green's function of quantum mechanics. $G_0^+(\omega)$ diverges whenever ω is such that some $v(k_j\bar{k}n)$ goes to zero, and as a result the generalized phase shift $\eta(\omega\bar{k})$ has discontinuities of $-\pi/2$ at these values of ω . These discontinuities are present regardless of the strength of V , the perturbation associated with creating a pair of surfaces or interfaces. There is an exception: If $\det \bar{M} = 0$, where \bar{M} is a matrix defined in terms of the matrix elements of V , then the discontinuity is eliminated. This condition is analogous to that for a "zero-energy resonance" in s -wave potential scattering, and it will ordinarily occur only at particular transitional strengths of V . The condition is always satisfied for acoustic phonons at $\omega = \bar{k} = 0$, however, because of a restriction on the force constants. The significance of $\eta(\omega\bar{k})$ is that the surface or interface density of states $\Delta\rho(\omega\bar{k})$ is given by $\pi^{-1} \partial \eta(\omega\bar{k})/\partial \omega$. Each discontinuity of $-\pi/2$ in $\eta(\omega\bar{k})$ at an extremum ω_0 thus produces a contribution $-\delta(\omega-\omega_0)/2$ in $\Delta\rho(\omega\bar{k})$.

I. INTRODUCTION

The purposes of this paper are (i) to obtain a form for the Green's function G_0^+ which should be useful in treating surface and interface problems, and (ii) to prove that there are discontinuities of $-\frac{1}{2}\pi$ in the generalized phase shift^{1,2} $\eta(\omega)$ at certain values of ω . The significance of $\eta(\omega)$ is that it gives the change in the density of states when a pair of surfaces or interfaces is created, $\Delta\rho(\omega)$, through the relation²

$$\Delta\rho(\omega) = \frac{1}{\pi} \frac{\partial \eta(\omega)}{\partial \omega}. \quad (1.1)$$

Thus a discontinuity of $-\frac{1}{2}\pi$ in $\eta(\omega)$ at some ω_0 leads to a contribution $-\frac{1}{2}\delta(\omega-\omega_0)$ in $\Delta\rho(\omega)$.

The present treatment does not assume any symmetries (such as the existence of a reflection plane perpendicular to the z axis, or time-reversal symmetry) other than translational invariance, and it is valid for any eigenvalue equation involving an Hermitian operator or matrix, such as the Schrödinger equation for electrons and the matrix eigenvalue equation for phonons.

In the following it is assumed that the eigenvalue $\epsilon(k_z\bar{k}n)$ of Sec. II is an analytic function of the complex variable k_z for all k_z except branch points off the real axis. Kohn has shown that this is true for electrons³ and phonons⁴ in one dimension, and Blount⁵ and Krieger⁶ have extended the proof to three dimensions. There are some restrictions. For example, as Kohn points out,⁴ the behavior of the force constants in a metal implies that the

phonon frequencies are not analytic for some real values of k_z .

It is also assumed that the matrix elements of the perturbation V associated with creating a pair of surfaces or interfaces, the $V(k_x k_y n n' \bar{k})$ of Sec. V, are not infinite. This is analogous to the assumption in potential scattering theory that certain integrals involving the potential are not infinite. (See Sec. VI.) The potential must fall off sufficiently fast as $r \rightarrow \infty$ and must not diverge too fast as $r \rightarrow 0$ in order for, e.g., Levinson's theorem to hold.⁷

We evaluate the Green's function in a mixed Wannier-Bloch representation.⁸⁻¹⁰ Such a representation is appropriate for surface and interface problems because the basis functions are localized in the z direction, perpendicular to the surface or interface.

II. UNPERTURBED CRYSTAL

Consider a crystal with translational invariance in the x , y , and z directions, for which some eigenvalue equation

$$H_0 |\bar{k}n\rangle = \epsilon(\bar{k}n) |\bar{k}n\rangle \quad (2.1)$$

holds. The $|\bar{k}n\rangle$ are (generalized) Bloch functions, with k_x and k_y taken to be real but k_z possibly complex, and n is a branch index which distinguishes solutions with the same wave vector \bar{k} . It is assumed that the matrix or (possibly nonlocal) operator H_0 is Hermitian when the vectors or functions $|\bar{k}n\rangle$ are restricted to those with real k_z . This implies that $\epsilon(\bar{k}n)$ is real when k_z is real.

Let a be the repeat distance for H_0 in the z direction (i.e., the height of a "surface-adapted unit cell"). Because of the translational invariance of H_0 , one can choose

$$\epsilon(k_z + 2\pi/a, \bar{k}n) = \epsilon(k_z \bar{k}n), \quad (2.2)$$

$$|k_z + 2\pi/a, \bar{k}n) = |k_z \bar{k}n), \quad (2.3)$$

where

$$\bar{k} \equiv (k_x, k_y), \quad (2.4)$$

so all the distinct solutions to (2.1) are given by

$$-\frac{\pi}{a} < \text{Re} k_z \leq \frac{\pi}{a}. \quad (2.5)$$

Two representations will be used in the following: In the "Bloch representation" (or "crystal momentum representation"), the basis functions are the $|k_z \bar{k}n)$ for real k_z which satisfy (2.5) and periodic boundary conditions, with L being the periodicity length in the z direction. In the "Wannier-Bloch representation," the basis functions are

$$|z \bar{k}n) \equiv N^{-1/2} \sum_{k_z} e^{-ik_z z} |k_z \bar{k}n), \quad (2.6)$$

where

$$N \equiv L/a \quad (2.7)$$

and the summation includes all the real k_z which satisfy (2.5) and the periodic boundary conditions. The values of z are discrete and correspond to the positions of (surface-adapted) lattice points: $z = z(l_3)$, with $\vec{l} = (l_1, l_2, l_3)$ labeling a lattice point.

The Green's function for the unperturbed crystal is, in the Wannier-Bloch representation,

$$G_0(zz', \bar{k}\bar{k}', nm', \omega) \equiv \langle z \bar{k}n | (\omega - H_0)^{-1} | z' \bar{k}'n' \rangle \quad (2.8)$$

$$= \delta_{\bar{k}\bar{k}'} \delta_{nm'} G_0(z - z', \bar{k}n\omega), \quad (2.9)$$

$$G_0(z - z', \bar{k}n\omega) \equiv N^{-1} \sum_{k_z} \frac{e^{ik_z(z-z')}}{\omega - \epsilon(k_z \bar{k}n)}. \quad (2.10)$$

For ω real, the "retarded" Green's function is

$$G_0^+(z - z', \bar{k}n\omega) \equiv G_0(z - z', \bar{k}n, \omega + i\delta), \quad (2.11)$$

with δ positive and $\delta \rightarrow 0$.

III. EVALUATION OF GREEN'S FUNCTION

After the recipe $\sum_{k_z} \rightarrow (L/2\pi) \int dk_z$ is used, (2.10) becomes

$$G_0^+(z - z', \bar{k}n\omega) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk_z \frac{e^{ik_z(z-z')}}{\omega - \epsilon(k_z \bar{k}n) + i\delta}. \quad (3.1)$$

We evaluate this integral by using the rectangular contour of Fig. 1, which is closed in the upper half-plane for $\text{sgn}(z - z') = +1$ and in the lower half-plane for $\text{sgn}(z - z') = -1$. The existence of branch points, and a possible choice of branch cuts, are indicated schematically in Fig. 1. In general, let C' represent curves around all the branch cuts (with each curve traversed in a positive direction, as illustrated in the figure), and let

$$G_{BC}(z - z', \bar{k}n\omega) \equiv -\text{sgn}(z - z') \frac{a}{2\pi} \times \int_{C'} dk_z \frac{e^{ik_z(z-z')}}{\omega - \epsilon(k_z \bar{k}n) + i\delta}, \quad \delta \rightarrow 0. \quad (3.2)$$

In the following, we assume that G_{BC} does not diverge as $\omega \rightarrow \omega_0$, where ω_0 is an extremal point defined by (4.1) and (4.7).

The contributions from the vertical-line segments of C cancel because of (2.2) and the fact that $z - z' = a \times \text{integer}$. The contribution at infinity clearly vanishes for $z \neq z'$. It also vanishes for $z = z'$ if we now assume that $|\epsilon(k_z \bar{k}n)| \rightarrow \infty$ as $|\text{Im} k_z| \rightarrow \infty$ with $\text{Re} k_z$ fixed ["almost everywhere" in the interval of (2.5)]. Then $G_0^+ = G_{BC} + 2\pi i \text{sgn}(z - z') \times (\text{sum of residues at poles})$, with the $\text{sgn}(z - z')$ factor coming from the fact that C follows the real axis in a negative direction for $\text{sgn}(z - z') = -1$, in Fig. 1(b). Whenever

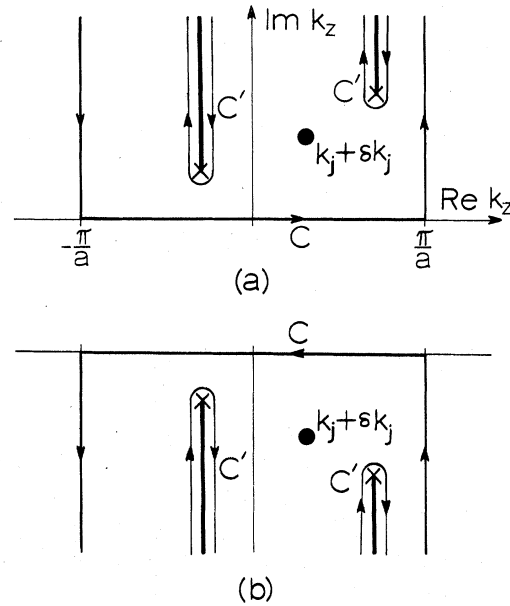


FIG. 1. (a) Contour C used in evaluating (3.1) when $\text{sgn}(z - z') = +1$. The vertical lines extend to infinity. The existence of branch points is indicated schematically. A representative pole $k_j + \delta k_j$ is shown. (b) Contour C for $\text{sgn}(z - z') = -1$.

$$\epsilon(k_j + \delta k_j, \bar{k}n) = \omega + i\delta \quad (3.3)$$

with $\delta k_j \rightarrow 0$ as $\delta \rightarrow 0$, there is a pole with residue

$$\frac{a}{2\pi} \lim_{k_z \rightarrow k_j + \delta k_j} [k_z - (k_j + \delta k_j)] \frac{e^{ik_z(z-z')}}{\epsilon(k_j + \delta k_j, \bar{k}n) - \epsilon(k_z, \bar{k}n)} \\ = -\frac{a}{2\pi} \frac{e^{i(k_j + \delta k_j)(z-z')}}{v(k_j + \delta k_j, \bar{k}n)}, \quad (3.4)$$

where

$$v(k_z, \bar{k}n) \equiv \frac{\partial \epsilon(k_z, \bar{k}n)}{\partial k_z}. \quad (3.5)$$

We have assumed that $v \neq 0$ at the poles. The behavior of G_0^+ as $v \rightarrow 0$ will be considered in Sec. IV.

As shown in Fig. 1, $\text{Im}(k_j + \delta k_j) \text{sgn}(z - z') > 0$. If k_j is complex, no problems arise from just setting δ and δk_j equal to zero in (3.3), so the requirement is just $\text{Im}k_j \text{sgn}(z - z') > 0$. If k_j is real, the expansion

$$\epsilon(k_j + \delta k_j) = \epsilon(k_j) + v(k_j)\delta k_j + \dots, \quad (3.6)$$

in conjunction with (3.3), implies that $v(k_j)\text{Im}\delta k_j > 0$. [Notice that $v(k_j)$ is real for k_j real, since $\epsilon(k_z)$ is real for k_z real.] This requirement, plus the one in the first sentence of this paragraph, then implies that $v(k_j) \text{sgn}(z - z') > 0$.

Combining the above results, we get

$$G_0^+(z - z', \bar{k}n\omega) = -ia \sum_j \frac{e^{ik_j(z-z')}}{v(k_j, \bar{k}n)} \text{sgn}(z - z') \\ + G_{BC}(z - z', \bar{k}n\omega), \quad (3.7)$$

where the k_j are those values of k_z satisfying

$$\epsilon(k_j, \bar{k}n) = \omega, \quad (3.8)$$

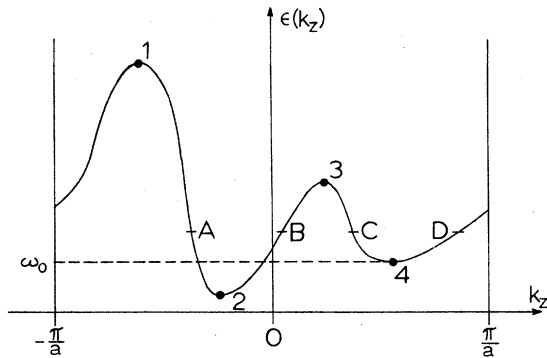


FIG. 2. Representative graph of eigenvalue $\epsilon(k_z, \bar{k}n)$ vs real wave vector k_z , for a fixed planar wave vector \bar{k} and a given branch labeled by n . The four numbered points are extrema where $v(k_z) = 0$. As ω increases from just below an extremum ω_0 to just above, $\eta(\omega)$ usually changes discontinuously by $\frac{1}{2}\pi$. The four lettered points illustrate that, at fixed ϵ , there are as many solutions with $v(k_z)$ negative (A and C) as with $v(k_z)$ positive (B and D).

and for which

$$v(k_j, \bar{k}n) \text{sgn}(z - z') > 0, \quad k_j \text{ real}, \quad (3.9a)$$

$$\text{Im}k_j \text{sgn}(z - z') > 0, \quad k_j \text{ complex}. \quad (3.9b)$$

Exactly half the solutions to (3.8) also satisfy (3.9), regardless of symmetry: If k_z is complex, then Schwarz's reflection principle¹¹ requires that $\epsilon(k_z^* \bar{k}n) = \epsilon^*(k_z \bar{k}n)$. For every k_z corresponding to a real eigenvalue $\epsilon(k_z)$, therefore, there is a k_z^* corresponding to the same eigenvalue. I.e., for every evanescent wave decaying toward the right and satisfying (3.8), there is another decaying toward the left. If k_z is real, (2.2) implies that there is some k_z' such that $\epsilon(k_z') = \epsilon(k_z)$ and $v(k_z')$ is opposite in sign to $v(k_z)$, as illustrated in Fig. 2. I.e., for every wave propagating to the right, and satisfying (3.8), there is another propagating to the left.

IV. BEHAVIOR OF GREEN'S FUNCTION AT EXTREMA

Let k_0 represent an extremum in $\epsilon(k_z, \bar{k}n_0)$ for some branch n_0 at a fixed \bar{k} ,

$$v(k_0, \bar{k}n_0) = 0, \quad \epsilon(k_0, \bar{k}n_0) \text{ real}. \quad (4.1)$$

For nearby k_z ,

$$\epsilon(k_z, \bar{k}n_0) - \epsilon(k_0, \bar{k}n_0) \simeq (k_z - k_0)^2 / 2m^*, \quad (4.2)$$

$$v(k_z, \bar{k}n_0) \simeq (k_z - k_0) / m^*, \quad (4.3)$$

$$\frac{1}{m^*} \equiv \left(\frac{\partial^2 \epsilon(k_z, \bar{k}n_0)}{\partial k_z^2} \right)_{k_z=k_0}. \quad (4.4)$$

We assume that k_0 must be real, since, according to Heine,¹² it is "vanishingly probable" for (4.1) to hold if k_0 is not real. We also assume that m^* is finite—i.e., that the second derivative $\partial^2 \epsilon / \partial k_z^2$ is nonzero at those points where the first derivative vanishes.

Since k_0 is real, we can choose k_z , and thus $\epsilon(k_z)$, to be real in evaluating m^* according to (4.4), so m^* is real. As $\omega - \epsilon(k_0, \bar{k}n_0)$, the dominant k_j in (3.7) is

$$\bar{k} \simeq k_0 + \Delta k \text{sgn}(z - z'), \quad (4.5)$$

where

$$(\Delta k)^2 \equiv 2m^*(\omega - \omega_0), \quad (4.6)$$

$$\omega_0 \equiv \epsilon(k_0, \bar{k}n_0), \quad (4.7)$$

according to (3.8) and (4.2). The sign of Δk is determined by (3.9) and (4.3): At a minimum (along the real axis), m^* is positive and

$$\Delta k = \begin{cases} i [2m^*(\omega_0 - \omega)]^{1/2}, & \omega < \omega_0, \end{cases} \quad (4.8a)$$

$$\Delta k = \begin{cases} [2m^*(\omega - \omega_0)]^{1/2}, & \omega > \omega_0. \end{cases} \quad (4.8b)$$

At a maximum, m^* is negative and

$$\Delta k = \begin{cases} -[2m^*(\omega - \omega_0)]^{1/2}, & \omega < \omega_0 \\ i[2m^*(\omega_0 - \omega)]^{1/2}, & \omega > \omega_0. \end{cases} \quad (4.9a)$$

$$(4.9b)$$

The positive root is to be taken in (4.8) and (4.9). Thus,

$$\text{disc Arg} \Delta k = -\frac{1}{2}\pi, \quad (4.10)$$

regardless of whether this point is a minimum or a maximum along the real axis, where $\text{disc}A(\omega)$ is defined to be the discontinuous change in a quantity $A(\omega)$ as ω increases through ω_0 .

There is a point worth mentioning: From (4.8) and (4.9) alone, it is not clear whether we should take the change in $\text{Arg} \Delta k$ to be $-\frac{1}{2}\pi$ or $-\frac{1}{2}\pi + 2\pi \times \text{integer}$. This ambiguity is resolved by recalling that a $+i\delta$ should really be added to ω to obtain $G_0^*(\omega)$, which implies, according to the first sentence of the paragraph containing (3.6), that a $+i|\delta k|$ should really be added to Δk . We should really let δ and $\delta k \rightarrow 0$ only after determining the phase shift. This point is made by de Witt¹ for the case of bound states on his p. 1567: As ω increases from $-\infty$, the addition of a $+i\delta$ to ω requires that we pass around the bound state energy ω_b in the upper half-plane, so that a $-\pi$ is added to the phase of $\det[\bar{1} - \bar{G}_0^*(\omega) \cdot \bar{V}]$, and a $+\pi$ to $\eta(\omega)$. In the present case, suppose first that $m^* < 0$, so that (4.9) applies. Then, as ω increases to ω_0 , $\Delta k + i|\delta k|$ moves along just above the negative real axis until it reaches the imaginary axis, and $\text{Arg}(\Delta k + i|\delta k|)$ changes continuously by $-\frac{1}{2}\pi$. If $m^* > 0$, (4.8) applies, and as ω increases past ω_0 , $\Delta k + i|\delta k|$ moves away from the imaginary axis just above the positive real axis, so that $\text{Arg}(\Delta k + i|\delta k|)$ again changes continuously by $-\frac{1}{2}\pi$. In the limit $\delta \rightarrow 0$, $\eta(\omega)$ changes discontinuously by $+\pi$ when ω increases through some ω_b . In the limit $\delta k \rightarrow 0$, $\text{Arg} \Delta k$ changes discontinuously by $-\frac{1}{2}\pi$ when ω increases through some ω_0 . But for $\delta \neq 0$, the phase of $\det[\bar{1} - \bar{G}_0^*(\omega + i\delta) \cdot \bar{V}]$ changes continuously in the first case, and for $\delta k \neq 0$, the phase of $\Delta k + i|\delta k|$ changes continuously in the second case.

According to (4.3) and (4.5),

$$v(\bar{k} \bar{n}_0) \approx \Delta k \text{sgn}(z - z')/m^*, \quad (4.11)$$

so (3.7) implies that

$$G_0^*(z - z', \bar{k} n_0) = -iam^* e^{ik_0(z-z')} \frac{e^{i\Delta k|z-z'|}}{\Delta k} - ia \sum_j' \frac{e^{ik_j(z-z')}}{v(k_j \bar{k} n_0)} \text{sgn}(z - z') + G_{BC}(z - z', \bar{k} n_0), \quad (4.12)$$

where the primed summation excludes the value $k_j = \bar{k}$.

Eq. (4.12) [or, more generally, (3.7)] is a generalization of the usual one-dimensional Green's

function for particles of mass m in quantum mechanics, which can be obtained as a special case by suppressing the branch index n_0 , the planar wave vector \bar{k} , the primed summation over j , the contribution G_{BC} from branch cuts, and a , and letting $m^* \rightarrow m$, $k_0 \rightarrow 0$, and $\Delta k \rightarrow k$.

V. DISCONTINUITIES IN THE GENERALIZED PHASE SHIFT

Starting with the unperturbed crystal of the preceding sections, we break the translational invariance in the z direction by creating a pair of surfaces or interfaces, and we represent the new matrix or operator in the perturbed crystal by

$$H = H_0 + V. \quad (5.1)$$

The new eigenvalue equation is

$$H|i\bar{k}\rangle = \epsilon(i\bar{k})|i\bar{k}\rangle, \quad (5.2)$$

where i distinguishes solutions with the same \bar{k} .

We assume that V can be represented in terms of the Bloch functions which satisfy the periodic boundary conditions of Sec. II. This requires (as a mathematical device) that V satisfy these same boundary conditions, i.e., that

$$V(z + L, \bar{r}) = V(z, \bar{r}) \quad (5.3)$$

if V is local, or

$$V(z + L, \bar{r}; z' + L, \bar{r}') = V(z, \bar{r}; z', \bar{r}') \quad (5.4)$$

if V is nonlocal, where

$$\bar{r} = (x, y). \quad (5.5)$$

V corresponds to creating interfaces between two materials A and B at two planes $z = 0$ and $z = z_0$, starting with only material A . The perturbed crystal has material A between $z = 0$ and $z = z_0$, material B between $z = z_0$ and $z = L$, material A between $z = L$ and $z = L + z_0$, etc. If free surfaces are created, then material B is vacuum. It is, of course, impossible to create a single interface, and V always corresponds to complementary interfaces at $z = 0$ and $z = z_0$. If we do not want the interfaces to interfere, we choose $z_0 \rightarrow \infty$ and $L - z_0 \rightarrow \infty$, as well as $L \rightarrow \infty$.

The generalized phase shift resulting from the perturbation V is^{1,2}

$$\eta(\omega \bar{k}) = -\text{Arg} \det[\bar{1} - \bar{G}_0^*(\bar{k}\omega) \cdot \bar{V}(\bar{k})]. \quad (5.6)$$

In the Wannier-Bloch representation, the elements of \bar{G}_0^* and \bar{V} are labeled by z, n and z', n' . In the Bloch representation, the elements are labeled by k_z, n and k_z', n' .

As $\omega \rightarrow \omega_0$, all the elements $G_0^*(z - z', \bar{k} n_0 \omega)$ in the Wannier-Bloch representation diverge as $1/\Delta k$, according to (4.12). Since there are N values of z it may then appear that a $(1/\Delta k)^N$ can be factored out

of the determinant of (5.6). However, cancellations within a determinant can cause it to diverge more slowly than may first seem the case. For example,

$$\begin{vmatrix} \frac{1}{x} & \frac{1}{x} - 1 \\ \frac{1}{x} - 1 & \frac{1}{x} \end{vmatrix} \quad (5.7)$$

diverges as $1/x$, instead of $1/x^2$, as $x \rightarrow 0$. By switching to the Bloch representation, we now show that the determinant of (5.6) diverges as $1/\Delta k$, instead of $(1/\Delta k)^N$.

In the Bloch representation,

$$G_0^+(k_z k'_z, \bar{k} \bar{k}', n n', \omega) = G_0^+(k_z k'_z, \bar{k} n \omega) \times \delta_{\bar{k} \bar{k}'} \delta_{n n'}, \quad (5.8)$$

$$G_0^+(k_z k'_z, \bar{k} n \omega) \equiv N^{-1} \sum_{z''} e^{-i k_z z''} G_0^+(z - z'', \bar{k} n \omega) e^{i k_z z''} \quad (5.9)$$

after (2.6) and (2.9) are used. The periodic boundary conditions require that

$$\sum_z e^{i(k_z - k'_z)z} = N \delta_{k_z k'_z}, \quad (5.10)$$

so

$$G_0^+(k_z k'_z, \bar{k} n \omega) = N^{-1} \sum_{z'} e^{i(k'_z - k_z)z'} \quad (5.11)$$

$$\times \sum_{z''} G_0^+(z - z'', \bar{k} n \omega) e^{-i k_z (z - z'')} \\ = \delta_{k_z k'_z} G_0^+(k_z \bar{k} n \omega), \quad (5.12)$$

$$G_0^+(k_z \bar{k} n \omega) \equiv \sum_{z''} e^{-i k_z (z - z'')} G_0^+(z - z'', \bar{k} n \omega). \quad (5.13)$$

Let $G'(z - z', \bar{k} n \omega)$ represent that part of $G_0^+(z - z', \bar{k} n \omega)$ that remains finite as $\omega \rightarrow \omega_0$. According to (4.12),

$$G_0^+(z - z', \bar{k} n \omega) = -iam^* e^{i k_0 (z - z')} \frac{e^{i \Delta k |z - z'|}}{\Delta k} \delta_{n n_0} \\ + G'(z - z', \bar{k} n \omega). \quad (5.14)$$

Beyond this point the argument becomes awkward unless k_0 is one of the values of k_z allowed by the periodic boundary conditions. Since this has zero probability for a given dispersion relation, we resort to the artifice of perturbing H_0 (once \bar{k} , n_0 , and L have been specified) in such a way that the extremum in the dispersion relation is shifted from k_0 to k'_0 , the value of k_z that is closest to k_0 of the N values allowed by the periodic boundary conditions. Since $|k'_0 - k_0| < 2\pi/L$, the new H_0 , G_0^+ , and $\eta(\omega \bar{k})$ are indistinguishable from the old as $L \rightarrow \infty$. In the following, we rename k'_0 and call it k_0 .

As $\Delta k \rightarrow 0$, $e^{i \Delta k |z - z'|} \rightarrow 1$ and (5.13) gives

$$G_0^+(k_z \bar{k} n \omega) = -\frac{iam^*}{\Delta k} \sum_z e^{i(k_0 - k_z)z} \delta_{n n_0} \\ + \sum_z e^{-i k_z z} G'(z \bar{k} n \omega) \quad (5.15)$$

$$= -\frac{im^* L}{\Delta k} \delta_{k_z k_0} \delta_{n n_0} + G'(k_z \bar{k} n \omega), \quad (5.16)$$

in view of (5.10). Thus, in the Bloch representation, \bar{G}_0^+ is diagonal and only the one element labeled by k_0 and n_0 diverges.

Consider the expression (5.6) for $\eta(\omega \bar{k})$: Since \bar{G}_0^+ is diagonal,

$$[\bar{I} - \bar{G}_0^+(\bar{k} \omega) \cdot \bar{V}(\bar{k})]_{k_z n, k'_z n'} \\ = \delta_{k_z k'_z} \delta_{n n'} - G_0^+(k_z \bar{k} n \omega) V(k_z k'_z n n' \bar{k}). \quad (5.17)$$

Then, according to (5.16),

$$\det[\bar{I} - \bar{G}_0^+(\bar{k} \omega) \cdot \bar{V}(\bar{k})] = \frac{1}{\Delta k} \det \bar{M}(\omega \bar{k}) \\ \text{as } \omega \rightarrow \omega_0, \quad (5.18)$$

where

$$M(k_z n k'_z n'; \omega \bar{k}) \equiv \delta_{k_z k'_z} \delta_{n n'} - G_0^+(k_z \bar{k} n \omega) V(k_z k'_z n n' \bar{k}), \\ k_z \neq k_0 \text{ or } n \neq n_0 \quad (5.19a)$$

$$\equiv im^* L V(k_0 k'_z n_0 n' \bar{k}), \\ k_z = k_0 \text{ and } n = n_0. \quad (5.19b)$$

We are temporarily assuming that at least one of the $V(k_0 k'_z n_0 n' \bar{k})$ is nonzero. Then

$$\eta(\omega \bar{k}) = -\text{Arg}(1/\Delta k) \det \bar{M}(\omega \bar{k}) \quad (5.20)$$

$$= \text{Arg} \Delta k - \text{Arg} \det \bar{M}(\omega \bar{k}) \quad (5.21)$$

in the limit $\omega \rightarrow \omega_0$. If $\det \bar{M}(\omega_0 \bar{k}) \neq 0$, (4.10) then implies that

$$\text{disc} \eta(\omega \bar{k}) = -\frac{1}{2} \pi \quad (5.22)$$

as ω increases through any ω_0 defined by (4.7) and (4.1).

VI. GENERALIZATIONS: MORE THAN ONE EXTREMUM

AT ω_0 OR $\det \bar{M}(\omega_0) = 0$

In the foregoing, it was tacitly assumed that at ω_0 there is an extremum for only one band n_0 at only one wave vector k_0 . We now generalize to the case that there are N_0 extrema at ω_0 , so that (4.1), (4.7), and (4.4) become

$$v(k_{0i} \bar{k} n_{0i}) = 0, \quad i = 1, 2, \dots, N_0, \quad (6.1a)$$

$$\epsilon(k_{0i} \bar{k} n_{0i}) = \omega_0, \quad \omega_0 \text{ real}, \quad (6.1b)$$

$$\frac{1}{m_i^*} \equiv \left(\frac{\partial^2 \epsilon(k_z \bar{k} n_{0i})}{\partial k_z^2} \right)_{k_z = k_{0i}}. \quad (6.1c)$$

After generalization of the various steps, (5.16) becomes

$$G_0^*(k_z \bar{k} n \omega) = -iL \sum_{i=1}^{N_0} \frac{m_i^*}{\Delta k_i} \delta_{k_z k_{0i}} \delta_{n m_{0i}} + G'(k_z \bar{k} n \omega), \quad (6.2)$$

where Δk_i is defined by (4.8) or (4.9) with $m^* - m_i^*$. Then (5.18) and (5.19) are changed to

$$\det[\bar{I} - \bar{G}_0^*(\bar{k} \omega) \cdot \bar{V}(\bar{k})] - \left(\prod_{i=1}^{N_0} \frac{1}{\Delta k_i} \right) \det \bar{M}(\omega \bar{k}) \quad \text{as } \omega \rightarrow \omega_0 \quad (6.3)$$

$$\begin{aligned} M(k_z n k'_z n'; \omega \bar{k}) &\equiv i m_i^* L V(k_{0i} k'_z n_{0i} n' \bar{k}), \\ &n = n_{0i} \text{ and } k_z = k_{0i} \quad (6.4a) \\ &= \delta_{k_z k'_z} \delta_{n n'} - G_0^*(k_z \bar{k} n \omega) \\ &\times V(k_z k'_z n n' \bar{k}) \text{ otherwise.} \quad (6.4b) \end{aligned}$$

I.e., N_0 rows of \bar{M} are different from those of $\bar{I} - \bar{G}_0^* \cdot \bar{V}$. Finally, (5.21) becomes

$$\eta(\omega \bar{k}) = \sum_{i=1}^{N_0} \text{Arg} \Delta k_i - \text{Arg} \det \bar{M}(\omega \bar{k}) \quad (6.5)$$

in the limit $\omega \rightarrow \omega_0$, and (4.10) implies that

$$\text{disc} \eta(\omega \bar{k}) = -N_0 \frac{1}{2} \pi \quad (6.6)$$

as ω increases through ω_0 .

It was also assumed that $\det \bar{M}(\omega_0 \bar{k}) \neq 0$. Suppose that

$$\det \bar{M}(\omega \bar{k}) \propto (\Delta k)^{M_0} \text{ as } \omega \rightarrow \omega_0, \quad (6.7)$$

where Δk is any one of the Δk_i in the general case discussed just above. [According to (4.8) and (4.9), the Δk_i differ only by multiplicative constants.] Then (6.5) implies that

$$\text{disc} \eta(\omega \bar{k}) = (M_0 - N_0) \frac{1}{2} \pi \quad (6.8)$$

as ω increases through ω_0 . For example, if there were a simple pole in $\det \bar{M}$, $M_0 = -1$, we would have a discontinuous change in η of $-\pi$ (for $N_0 = 1$), i.e., the usual $-\frac{1}{2}\pi$ plus an extra $-\frac{1}{2}\pi$ from the pole in $\det \bar{M}$. However, our assumption that the matrix elements of V are not infinite implies that the same is true of $\det \bar{M}$. There is an analogy in s -wave potential scattering: For potentials $V(r)$ satisfying⁷

$$\int_0^\infty dr r |V(r)| < \infty, \quad \int_0^\infty dr r^2 |V(r)| < \infty, \quad (6.9)$$

the Jost function $f(k)$ is well behaved at $k=0$; but for model potentials violating these restrictions, $f(k)$ can have a pole at $k=0$, and a simple pole leads to a discontinuity of $-\frac{1}{2}\pi$ in the phase shift at $k=0$.¹³

Instead of $\det \bar{M}(\omega \bar{k}) \rightarrow 0$ as $\omega \rightarrow \omega_0$, we can have $\det \bar{M}(\omega \bar{k}) = 0$ for all ω if M_0 of the rows defined in (6.4a) are identically zero, with $M_0 \leq N_0$. Then, as can be seen from (5.17), M_0 factors of $1/\Delta k_i$ are removed from (6.3), and only $N_0 - M_0$ factors remain. It follows that (6.8) also holds in this case, although for a different reason. In either case, if $M_0 = N_0$, then (6.8) implies that

$$\text{disc} \eta(\omega \bar{k}) = 0 \quad (6.10)$$

i.e., the discontinuity is eliminated. This exceptional case (or any case when $M_0 \neq 0$) is analogous to a "zero-energy resonance" in s -wave potential scattering, for which the Jost function $f(0)$ equals zero and an exceptional version of Levinson's theorem holds.¹⁴ In s -wave potential scattering, a discontinuity of $+\frac{1}{2}\pi$ is added to the usual discontinuity of 0 when $f(0) = 0$. In the present case (for $M_0 = N_0 = 1$), a discontinuity of $+\frac{1}{2}\pi$ is added to the usual discontinuity of $-\frac{1}{2}\pi$ when $\det \bar{M}(\omega_0) = 0$.

A trivial example of (6.10) holds when the perturbation V is identically zero, so that all of the N_0 rows defined in (6.4a) contain zeros. In this case, of course, the phase shift can be taken to be identically zero, according to (5.6), and a discontinuity is impossible.

Whenever V produces a discrete "bound" state at an energy ω_b , there is a discontinuity of $+\pi$ in $\eta(\omega \bar{k})$ at $\omega = \omega_b$, according to (1.1). When (6.10) holds (for $N_0 = 1$), therefore, it is as if V is just strong enough to produce "half a bound state" at $\omega = \omega_0$, which gives a discontinuity of $+\frac{1}{2}\pi$ and thus cancels the usual discontinuity of $-\frac{1}{2}\pi$. The usual discontinuity, on the other hand, implies that a general perturbation V , no matter how weak, ordinarily "destroys half a state" at every eigenvalue ω_0 where there is an extremum in the dispersion relation $\epsilon(k_z \bar{k} n)$ versus k_z .

VII. ABSENCE OF DISCONTINUITY FOR ACOUSTIC PHONONS AT $\omega = \bar{k} = 0$

We expect that (6.10) will ordinarily have "zero probability," and will hold only when the perturbation has exactly the right transitional strength. This is the case for a zero-energy resonance in s -wave potential scattering, which occurs only when the parameters in a model potential have exactly the right values. However, as we show below, (6.10) always holds for acoustic phonons at $\omega = \bar{k} = 0$, because of a condition on the force constants. This corresponds to the fact that the three "uniform translation modes," at zero frequency, are present in both the perturbed and unperturbed crystals. If there were a discontinuity of $-3\pi/2$ in $\eta(\omega \bar{k})$ at $\omega = \bar{k} = 0$, then (1.1) implies that each of the uniform translation modes would be "half

destroyed" by the creation of a pair of surfaces or interfaces.

For phonons, we introduce a third set of basis functions $|\vec{r}\kappa\rangle$, each of which is localized entirely on an atom labeled by κ in a unit cell whose lattice point is at $\vec{r}=(\vec{r}, z)$. We remark that $|\vec{r}\kappa\rangle$, $|k_z\bar{k}n\rangle$, and $|z\bar{k}n\rangle$ are all three-dimensional vectors (with x , y , and z components). In the $|\vec{r}\kappa\rangle$ representation, (2.1) becomes

$$\sum_{\vec{r}\kappa'} \langle \vec{r}\kappa | H_0 | \vec{r}'\kappa' \rangle \langle \vec{r}'\kappa' | k_z\bar{k}n \rangle = \epsilon(k_z\bar{k}n) \langle \vec{r}\kappa | k_z\bar{k}n \rangle. \quad (7.1)$$

Comparison with the usual eigenvalue equation for the normal modes of vibration¹⁵ shows that

$$\epsilon(k_z\bar{k}n) = \omega^2(k_z\bar{k}n), \quad (7.2a)$$

$$\langle \vec{r}\kappa | k_z\bar{k}n \rangle = M_\kappa^{-1/2} u(\vec{r}\kappa, k_z\bar{k}n), \quad (7.2b)$$

$$\langle \vec{r}\kappa | H_0 | \vec{r}'\kappa' \rangle = M_\kappa^{-1/2} \Phi_0(\vec{r}\kappa, \vec{r}'\kappa') M_{\kappa'}^{-1/2}. \quad (7.2c)$$

Here $\omega(k_z\bar{k}n)$ is the frequency for the mode labeled by $k_z\bar{k}n$, $u(\vec{r}\kappa, k_z\bar{k}n)$ is the properly normalized amplitude of displacement for the atom labeled by $\vec{r}\kappa$ when the crystal is vibrating in this mode, M_κ is the mass of this atom, and $\Phi_0(\vec{r}\kappa, \vec{r}'\kappa')$ is a

3×3 matrix whose elements are the force constants coupling the two atoms labeled by $\vec{r}\kappa$ and $\vec{r}'\kappa'$ in the unperturbed crystal. We label the three acoustic modes by $n=1, 2$, and 3 . Since all the atoms in the crystal have the same displacement as $\vec{k} \rightarrow 0$ for the acoustic modes, as indicated in (2.1.63) of Ref. 15,

$$u(\vec{r}\kappa, 00n) = A(n), \quad n=1, 2, \text{ or } 3, \quad (7.3)$$

where $A(n)$ is independent of \vec{r} and κ . Also, $\omega(k_z\bar{k}n) \propto |\vec{k}|$ for the acoustic modes as $\vec{k} \rightarrow 0$ along a fixed direction, so for small k_z

$$\epsilon(k_z 0n) \simeq k_z^2 / 2m_n^*, \quad n=1, 2, \text{ or } 3, \quad (7.4)$$

where m_n^* is a constant. This is of the form (4.2). We thus have three extrema of the kind indicated in (6.1)— $N_0=3$ —with $\omega_0 = \bar{k} = k_{0i} = 0$.

Let

$$\Delta\Phi(\vec{r}\kappa, \vec{r}'\kappa') \equiv \Phi(\vec{r}\kappa, \vec{r}'\kappa') - \Phi_0(\vec{r}\kappa, \vec{r}'\kappa') \quad (7.5)$$

where Φ represents the force constants for the perturbed crystal. According to (7.2c),

$$\langle \vec{r}\kappa | V | \vec{r}'\kappa' \rangle = M_\kappa^{-1/2} \Delta\Phi(\vec{r}\kappa, \vec{r}'\kappa') M_{\kappa'}^{-1/2}. \quad (7.6)$$

Consider

$$V(k_z k'_z n n' \bar{k}) = \langle k_z\bar{k}n | \sum_{\vec{r}\kappa} \sum_{\vec{r}'\kappa'} |\vec{r}\kappa\rangle \langle \vec{r}\kappa | V | \vec{r}'\kappa' \rangle \langle \vec{r}'\kappa' | | k'_z\bar{k}n' \rangle \quad (7.7)$$

$$= \sum_{\vec{r}\kappa} \sum_{\vec{r}'\kappa'} u^*(\vec{r}\kappa, k_z\bar{k}n) \Delta\Phi(\vec{r}\kappa, \vec{r}'\kappa') u(\vec{r}'\kappa', k'_z\bar{k}n'). \quad (7.8)$$

For $n=1, 2$, or 3 , (7.3) implies that

$$V(0k'_z n n' 0) = A^*(n) \sum_{\vec{r}\kappa'} u(\vec{r}'\kappa', k'_z\bar{k}n') \sum_{\vec{r}\kappa} \Delta\Phi(\vec{r}\kappa, \vec{r}'\kappa'). \quad (7.9)$$

According to (2.1.10) and (2.1.15) of Ref. 15,

$$\sum_{\vec{r}\kappa} \Phi_0(\vec{r}\kappa, \vec{r}'\kappa') = 0, \quad (7.10)$$

and the same is true of Φ , so

$$\sum_{\vec{r}\kappa} \Delta\Phi(\vec{r}\kappa, \vec{r}'\kappa') = 0. \quad (7.11)$$

This restriction on the change in the force constants makes (7.9) vanish, so

$$V(0k'_z n n' 0) = 0 \text{ for } n=1, 2, \text{ or } 3. \quad (7.12)$$

Thus three rows of $\tilde{V}(0)$ are equal to zero, or $M_0 = 3$. Then (6.8) implies that

$$\text{disc}\eta(\omega\bar{k}) = (3-3)^{1/2} \pi = 0 \quad (7.13)$$

at $\bar{k}=0$, as ω increases through $\omega_0=0$. I.e., there is no discontinuity in the phase shift at $\omega=\bar{k}=0$ for the acoustic modes, even though they have extrema there.

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