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Uniform Strains and Deformation Potentials

R. H. PARMENTER
RCA Laboratories, Radio Corporation of America, Princeton, New Jersey

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A perturbation method of calculating the energy levels of a crystal modified by an arbitrary uniform strain is studied. A modified form of first-order perturbation theory is used, a form particularly appropriate to cases where the unperturbed wave functions are expanded in terms of orthogonalized plane waves. Not only are the conventional uniform strains considered but also the special types of deformations whereby the relative positions of the atoms in a unit cell are changed without distorting the Bravais lattice of the crystal. Thus the results of this paper may be applied to the deformation-potential theory of mobility with regard to both acoustic and optical lattice vibrations.

I. INTRODUCTION

IN a previous paper the effect of a uniform dilation upon the one-electron energy bands of a monatomic crystal was determined.[1] In this paper we will generalize this to the case of an arbitrary uniform strain. We will use the same method of calculation used in the previous paper; namely, a modified form of first-order perturbation theory which will be discussed in detail in the following section. The quantities to be determined in the present study may be referred to as "deformation potentials," a deformation potential for a given energy level and for a given strain being defined as the difference in energy between the energy level in the strained and unstrained crystals. The deformation potential will, of course, be a linear function of the amount of strain. The concept of a deformation potential was first introduced by Bardeen and Shockley[2] in connection with the study of the scattering of electrons by lattice vibrations in crystals. They demonstrated the fact that a *long-wavelength* lattice vibration has the same effect locally upon an electron of the crystal as does the locally equivalent uniform strain. By assuming that this is also true to a good approximation in the case of short-wavelength lattice vibrations, these authors were able to compute the electron mobility from a knowledge of the deformation potentials. Associated with each sinusoidal lattice vibration, there may be considered to be a sinusoidally varying deformation potential which will scatter electrons in the crystal, the dependence upon position in the crystal of the deformation potential resulting from the dependence upon position of the local strain resulting from the lattice vibration. The long-wavelength *acoustic* lattice vibrations give rise to conventional strains in the crystal; the long-wavelength *optical* lattice vibrations do not give rise to any conventional strain, however, but rather to a special type of deformation whereby the relative positions of the atoms in a unit cell are changed without distorting the Bravais lattice of the crystal. (We restrict ourselves to long wavelengths in order to maintain the condition of local uniformity of strain in the crystal.) For obvious reasons we will refer to such a deformation as an *optical* strain. When we wish to distinguish between the two types, we will refer to the conventional strain as an *acoustic* strain. In Sec. II, we will work out the deformation potentials for acoustic strains, and in Sec. III we will do the same for optical strains. In Sec. IV, we will show how the modified first-order perturbation approach used in this paper is particularly appropriate for a crystal whose wave functions and energy levels have been determined by the orthogonalized plane wave method.[3] As an example we will consider in detail a crystal of the diamond structure. This is a particularly appropriate case, since OPW (orthogonalized plane wave) solutions have been obtained for the three most important crystals of this type, namely, diamond,[4] silicon,[5] and germanium.[6]

Since the crystal potential in Schrödinger's equation may be chosen arbitrarily to the extent of an additive constant, it follows that the one-electron energy levels are arbitrary to the same extent. From the definition of a deformation potential given in the preceding paragraph, it now follows that the deformation potential is also unspecified to the extent of an arbitrary constant (the same constant for all deformation potentials associated with a given strain). In the case of a *uniformly* strained crystal, this is of no consequence, since the only quantities of real physical significance are the *rates of change relative to each other* of the various deformation potentials with strain, these quantities being completely specified. On the other hand, in the case of a *nonuniformly* strained crystal (resulting from the presence of a lattice vibration), the additive constant in the deformation potential does have physical significance and is connected with an additional electrostatic potential (varying with position) which may be set up as a result of the *nonuniformity* of the strain. In their paper, Bardeen and Shockley[2] argue that this additional electrostatic potential is negligible. Although

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[1] R. H. Parmenter, preceding paper [Phys. Rev. **99**, 1759 (1955)].

[2] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[3] C. Herring, Phys. Rev. **57**, 1169 (1940).

[4] F. Herman, Phys. Rev. **88**, 1210 (1952); **93**, 1214 (1954).

[5] T. O. Woodruff, dissertation, California Institute of Technology, 1955 (unpublished); Phys. Rev. **98**, 1741 (1955).

[6] F. Herman and J. Calloway, Phys. Rev. **89**, 518 (1953); F. Herman, Physica **20**, 801 (1954).

this question is perhaps worthy of further study, we shall in this paper assume the correctness of their conclusions. The assumption that this additional electrostatic potential vanishes implies the specification that the crystal potential in the interior of an ion-core of the crystal is unaffected by straining the crystal. Such a specification serves to define uniquely the deformation potentials. This specification will be followed in the succeeding sections of this paper.

The primary purpose of this paper is to develop a method of studying deformation potentials suitable for detailed numerical computations on specific systems. As with the previous paper devoted to crystals modified by alloying or by pressure,[1] the present study arose as a part of a program of computation of various physical properties of the germanium crystal, a program making use of the availability of wave functions and energy levels for germanium.[6] No attempt will be made in this paper to consider further the application of deformation potentials to mobility theory.

II. ACOUSTIC STRAINS

Consider an unstrained monatomic crystal. The one-electron crystal potential may be written in the form

$$\textstyle\sum_n V(\mathbf{r}-\mathbf{R}_n)-\mathbf{V}(0), \tag{1}$$

where $V(\mathbf{r})$ is an atomic-like potential, the vectors $\mathbf{R}_n$ denote the positions of the atoms of the crystal, and $\mathbf{V}(0)$ is a constant which will be specified presently. The Schrödinger equation for this problem is

$$H\Psi_q(\mathbf{k},\mathbf{r})=E_q(\mathbf{k})\Psi_q(\mathbf{k},\mathbf{r}), \tag{2}$$

where the Hamiltonian is given by

$$H=-\nabla^2+\textstyle\sum_n V(\mathbf{r}-\mathbf{R}_n)-\mathbf{V}(0). \tag{3}$$

(We are using atomic units.) Here q denotes the particular energy band under consideration, and $\mathbf{k}$ determines the translational properties of the wave function, i.e.,

$$\Psi_q(\mathbf{k},\,\mathbf{r}+\mathbf{R}_n')=\exp(i\mathbf{k}\cdot\mathbf{R}_n')\Psi_q(\mathbf{k},\mathbf{r}), \tag{4}$$

where the $\mathbf{R}_n'$ denote the positions of the centers of the unit cells of the crystal. (The $\mathbf{R}_n'$ will not coincide with the $\mathbf{R}_n$ when there is more than one atom per unit cell.) We wish to consider the effects of a uniform (acoustic) strain[7] upon the crystal, whereupon the positions of the atoms become $\mathfrak{a}\cdot\mathbf{R}_n$ where[8]

$$\mathfrak{a}=\mathbf{1}+\mathfrak{e}. \tag{5}$$

$\mathbf{1}$ is the unit tensor (whose elements are δ_{ij}), and $\mathfrak{e}$ is the symmetric strain tensor. We shall assume that the crystal potential appropriate to the strained crystal is

$$\textstyle\sum_n V(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n)-\mathbf{V}(\mathfrak{e}), \tag{6}$$

where the constant $\mathbf{V}(\mathfrak{e})$ is given by

$$\mathbf{V}(\mathfrak{e})=\textstyle\sum_n{}' V(\mathfrak{a}\cdot[\mathbf{R}_n-\mathbf{R}_m]). \tag{7}$$

The prime over the summation sign denotes that the term for $\mathbf{R}_n=\mathbf{R}_m$ is omitted. We shall restrict ourselves to crystals having sufficient symmetry for $\mathbf{V}(\mathfrak{e})$ to be independent of the index m. The constant $\mathbf{V}(0)$ occurring in Eq. (1) is now defined as $\mathbf{V}(\mathfrak{e})$ for $\mathfrak{e}=0$. Because of these additive constants in Eqs. (1) and (6), it can be seen that, in the neighborhood of any ion-core of the crystal, the crystal potential can be approximated by the atomic-like potential centered on this ion core, both for the strained and the unstrained lattices. Thus the crystal potential in the neighborhood of an ion-core is unaffected by straining the crystal, as was specified in the previous section. Consistent with such a requirement, the only simple assumption concerning the variation of the crystal potential with strain seems to be that expressed by Eq. (6). The Schrödinger equation for the strained crystal is

$$H'\Psi_q'(\mathbf{k},\mathbf{r})=E_q'(\mathbf{k})\Psi_q'(\mathbf{k},\mathbf{r}), \tag{8}$$

where the Hamiltonian is given by

$$H'=-\nabla^2+\textstyle\sum_n V(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n)-\mathbf{V}(\mathfrak{e}). \tag{9}$$

In analogy with Eq. (4), we have

$$\Psi_q'(\mathbf{k},\,\mathbf{r}+\mathfrak{a}\cdot\mathbf{R}_n')=\exp[i\mathbf{k}\cdot(\mathfrak{a}\cdot\mathbf{R}_n')]\Psi_q'(\mathbf{k},\mathbf{r}). \tag{10}$$

We define $\mathfrak{a}^{-1}$ such that

$$\mathfrak{a}^{-1}\cdot\mathfrak{a}\equiv\mathbf{1}, \tag{11}$$

and define

$$\Upsilon_q'(\mathbf{k},\mathbf{r})\equiv\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathfrak{a}^{-1}\cdot\mathbf{r}). \tag{12}$$

Making use of Eq. (4) and the fact that

$$[\mathfrak{a}\cdot\mathbf{k}]\cdot[\mathfrak{a}^{-1}\cdot(\mathfrak{a}\cdot\mathbf{R}_n')]=\mathbf{k}\cdot(\mathfrak{a}\cdot\mathbf{R}_n'),$$

we have

$$\Upsilon_q'(\mathbf{k},\,\mathbf{r}+\mathfrak{a}\cdot\mathbf{R}_n')=\exp[i\mathbf{k}\cdot(\mathfrak{a}\cdot\mathbf{R}_n')]\Upsilon_q'(\mathbf{k},\mathbf{r}), \tag{13}$$

so that Υ' has the correct translational periodicity properties for the strained lattice. This suggests that we take the Υ''s as the unperturbed wave functions in a first-order degenerate perturbation calculation, a procedure which is quite straightforward once the wave functions Ψ appropriate to the unstrained crystal have been obtained. There is, however, one basic objection to the use of Υ''s as the unperturbed wave functions. We note that Eq. (12) represents a scaling

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[7] For brevity, the word *acoustic* will be dropped throughout the remainder of this section but is to be understood in all references to strain.

[8] We use the above symbolic tensor notation (boldface German script) in order to minimize the number of subscripts in this paper. $\mathfrak{a}$ may be considered to be the 3×3 matrix whose elements are a_{ij}. The dot product of two tensors, $\mathfrak{a}\cdot\mathfrak{e}$, is itself a tensor and may be considered to be the matrix whose elements are $\sum_p a_{ip}e_{pj}$ i.e., the product of the two matrices $\mathfrak{a}$ and $\mathfrak{e}$. The double dot product of two tensors, $\mathfrak{a}:\mathfrak{e}$ is the scalar defined as $\sum_{ij} a_{ij}e_{ji}$, which may be considered to be the trace of the matrix $\mathfrak{a}\cdot\mathfrak{e}$. The dot product of a tensor and a vector, $\mathfrak{a}\cdot\mathbf{c}$, is that vector whose components are $\sum_p a_{ip}c_p$. The dyadic tensor $\mathbf{cd}$ is the direct product of the two vectors $\mathbf{c}$ and $\mathbf{d}$ and may be considered to be a matrix whose elements are c_id_j. The transpose of $\mathbf{cd}$, namely that matrix obtained by interchanging rows and columns of the $\mathbf{cd}$ matrix, will sometimes be written as $\mathbf{cd}^\dagger$.

of the wave function appropriate to the unstrained crystal, this scaling to be done in both r- and k-space. In reality, however, when a crystal is strained, the change in the wave function cannot be represented by scaling alone (at least in r-space). In fact, in the immediate vicinity of a particular ion core of the crystal, the wave function, rather than being scaled, probably remains unchanged (aside from a phase factor) since as a first approximation the crystal potential remains unchanged.

The above objection can be largely overcome by replacing Υ' as our unperturbed wave function for the strained crystal by another wave function, the latter having been made orthogonal to the ion-core wave functions appropriate to the strained crystal. We now give the details of this procedure. First we consider the unstrained crystal. We designate by $\Phi_s(\mathbf{k},\mathbf{r})$ any ion-core Bloch wave function appropriate to this case and by $\Psi_q(\mathbf{k},\mathbf{r})$ any of the other Bloch wave functions appropriate to this case. Since the Ψ's and the Φ's are solutions to the same Schrödinger equation, the Ψ's must be orthogonal to the Φ's. In analogy with Herring's method of defining an orthogonalized plane wave,[3] we consider a function $\Gamma_q(\mathbf{k},\mathbf{r})$ such that

$$\Psi_q(\mathbf{k},\mathbf{r})=\Gamma_q(\mathbf{k},\mathbf{r}) -\sum_s \Phi_s(\mathbf{k},\mathbf{r})\int_\infty \Phi_s^*(\mathbf{k},\mathbf{r})\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \quad (14)$$

($\int d\tau$ denotes an integration over the entire volume of the crystal.) Assuming the orthogonality of the Φ's,

$$\int_\infty \Phi_s^*(\mathbf{k},\mathbf{r})\Phi_t(\mathbf{k},\mathbf{r})d\tau=\delta_{s,\,t}, \quad (15)$$

we see that Eq. (14) merely expresses the fact that the Ψ's are orthogonal to the Φ's, i.e.,

$$\int_\infty \Phi_s^*(\mathbf{k},\mathbf{r})\Psi_q(\mathbf{k},\mathbf{r})d\tau=0. \quad (16)$$

In the case of a monatomic host crystal where there is more than one atom per unit cell of the crystal, the index s appearing in the last three equations really stands for two indices, s and σ, where s denotes the type of atomic orbital from which the Bloch function is composed, while σ denotes with which atom in the unit cell the Bloch function is associated; i.e.,

$$\Phi_{s,\sigma}(\mathbf{k},\mathbf{r})=N^{-\frac{1}{2}}\textstyle\sum_n \exp[i\mathbf{k}\cdot(\mathbf{R}_n'+\mathfrak{R}_\sigma)] \times\varphi_s(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R}_\sigma). \quad (17)$$

The vector $\mathfrak{R}_\sigma$ denotes the position of the σth atom of the unit cell with respect to the center of the unit cell. As before, the Bravais lattice vectors $\mathbf{R}_n'$ denote the positions of the centers of the unit cells, while the atomic positions, previously denoted by $\mathbf{R}_n$, can be written as $\mathbf{R}_n'+\mathfrak{R}_\sigma$. N denotes the number of unit cells in the complete crystal. Let us take the ion-core orbitals on a given atomic site to be orthonormal, and assume that the atomic orbitals on neighboring atomic sites do not overlap, i.e.,

$$\int_\infty \varphi_s^*(\mathbf{r}-\mathbf{R}_m'-\mathfrak{R}_\sigma)\varphi_t(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R}_\tau)d\tau=\delta_{st}\delta_{mn}\delta_{\sigma\tau}. \quad (18)$$

We see that Eq. (15) is consistent with Eqs. (17) and (18). Using the fact that

$$\Gamma_q(\mathbf{k},\ \mathbf{r}+\mathbf{R}_n')=\exp(i\mathbf{k}\cdot\mathbf{R}_n')\Gamma_q(\mathbf{k},\mathbf{r}), \quad (19)$$

we see that Eq. (14) can be rewritten

$$\Psi_q(\mathbf{k},\mathbf{r})=\Gamma_q(\mathbf{k},\mathbf{r})-\sum_{s,n}\varphi_s(\mathbf{r}-\mathbf{R}_n) \times\int_\infty \varphi_s^*(\mathbf{r}-\mathbf{R}_n)\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \quad (20)$$

By means of Eq. (20), we have broken up the wave function $\Psi_q(\mathbf{k},\mathbf{r})$ into two parts, one part

$$-\sum_{s,n}\varphi_s(\mathbf{r}-\mathbf{R}_n)\int_\infty \varphi_s^*(\mathbf{r}-\mathbf{R}_n)\Gamma_q(\mathbf{k},\mathbf{r})d\tau \quad (21)$$

being appreciable only in the immediate vicinity of each ion core of the crystal and representing the rapid variations of the wave function in these regions, while the other part $\Gamma_q(\mathbf{k},\mathbf{r})$ is more smoothly varying and is of importance throughout all regions of the crystal.

Turning to the strained crystal, we shall assume that the crystal potential is essentially unchanged by the strain over the region of a given ion core of the crystal, so that the ion-core Bloch wave functions are

$$\Phi_{s,\sigma}'(\mathbf{k},\mathbf{r})=N^{-\frac{1}{2}}\textstyle\sum_n \exp[i\mathbf{k}\cdot\boldsymbol{\mathfrak{a}}\cdot(\mathbf{R}_n'+\mathfrak{R}_\sigma)] \times\varphi_s(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R}_\sigma). \quad (22)$$

In analogy with Eq. (14), we construct an approximate wave function for the strained crystal by writing

$$\mathfrak{S}_q'(\mathbf{k},\mathbf{r})\equiv\mathfrak{G}_q'(\mathbf{k},\mathbf{r})-\sum_{s,\sigma}\Phi_{s,\sigma}'(\mathbf{k},\mathbf{r}) \times\int_\infty \Phi_{s,\sigma}'^*(\mathbf{k},\mathbf{r})\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau, \quad (23)$$

where

$$\mathfrak{G}_q'(\mathbf{k},\mathbf{r})\equiv\Gamma_q(\boldsymbol{\mathfrak{a}}\cdot\mathbf{k},\ \boldsymbol{\mathfrak{a}}^{-1}\cdot\mathbf{r}). \quad (24)$$

Similar to Eqs. (19) and (20), we have

$$\mathfrak{G}_q'(\mathbf{k},\ \mathbf{r}+\boldsymbol{\mathfrak{a}}\cdot\mathbf{R}_n')=\exp(i\mathbf{k}\cdot\boldsymbol{\mathfrak{a}}\cdot\mathbf{R}_n')\mathfrak{G}_q'(\mathbf{k},\mathbf{r}), \quad (25)$$

so that

$$\mathfrak{S}_q'(\mathbf{k},\mathbf{r})=\mathfrak{G}_q'(\mathbf{k},\mathbf{r})-\sum_{s,n}\varphi_s(\mathbf{r}-\boldsymbol{\mathfrak{a}}\cdot\mathbf{R}_n) \times\int_\infty \varphi_s^*(\mathbf{r}-\boldsymbol{\mathfrak{a}}\cdot\mathbf{R}_n)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau. \quad (26)$$

Like Ψ_q, the wave function $\mathfrak{S}_q'$ consists of two parts, the portion $\mathfrak{G}_q'$ having been scaled from the corresponding portion of Ψ_q appropriate to the unstrained crystal. The portion

$$-\sum_{s,n}\varphi_s(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n)\int_\infty \varphi_s^*(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau \quad (27)$$

has not been obtained by scaling (21), however, but by replacing (21) by linear combinations of the ion-core atomic orbitals centered on the atomic sites of the strained crystal, the linear combinations being chosen such that the $\mathfrak{S}_q'$'s so obtained are orthogonal to the $\Phi_{s,\sigma}'$'s, i.e.,

$$\int_\infty \Phi_{s,\sigma}'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau=0. \quad (28)$$

We see that $\mathfrak{S}_q'$ has the correct translational periodicity properties for the strained lattice, since

$$\mathfrak{S}_q'(\mathbf{k},\,\mathbf{r}+\mathfrak{a}\cdot\mathbf{R}_n')=\exp(i\mathbf{k}\cdot\mathfrak{a}\cdot\mathbf{R}_n')\mathfrak{S}_q'(\mathbf{k},\mathbf{r}). \quad (29)$$

The ion-core atomic orbitals used in specifying Φ and Φ' are chosen such that

$$[-\nabla^2+V(\mathbf{r})]\varphi_s(\mathbf{r})=E_s\varphi_s(\mathbf{r}), \quad (30)$$

$V(\mathbf{r})$ being the atomic potential occurring in Eq. (1). This can be done since in the immediate neighborhood of any atomic site of the crystal, the crystal potential may be closely approximated (aside from an additional constant) by the atomic-like potential V centered on that site. We shall assume that V may be approximated by the corresponding isolated-atom potential, so that the φ_s's and the E_s's are those for the isolated atom. Thus, to a good approximation,

$$\begin{aligned} H\varphi_s(\mathbf{r}-\mathbf{R}_n)&=E_s\varphi_s(\mathbf{r}-\mathbf{R}_n),\\ H'\varphi_s(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n)&=E_s\varphi_s(\mathbf{r}-\mathfrak{a}\cdot\mathbf{R}_n). \end{aligned} \quad (31)$$

For a given $\mathfrak{a}\cdot\mathbf{k}$, there will be various sets of degenerate wave functions $\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})$ associated with the unstrained crystal, the members of a given set all having different point symmetries with respect to their arguments in real space so that they are mutually orthogonal.[9] There will be corresponding sets of functions $\mathfrak{S}_q'(\mathbf{k},\mathbf{r})$, the members of these sets serving as our unperturbed wave functions, the previous objection to the use of the Υ''s as unperturbed wave functions not applying to the use of the $\mathfrak{S}'$'s. In other words, for a given $\mathfrak{a}\cdot\mathbf{k}$, we diagonalize $[H'-E'(\mathbf{k})]$ with respect to each set of functions $\mathfrak{S}_q'(\mathbf{k},\mathbf{r})$. Since the Γ_q's have the same point symmetries as do the corresponding Ψ_q's, it follows that the Γ_q's associated with a given set are likewise mutually orthogonal. Since uniform scaling in real space will not affect this orthogonality property, it follows that the corresponding $\mathfrak{G}_q'$'s are also mutually orthogonal. Note, however, that the $(\mathfrak{S}_q'-\mathfrak{G}_q')$'s, and thus the $\mathfrak{S}_q'$'s themselves, are not mutually orthogonal. It will be necessary to consider matrix elements of unity and of the respective Hamiltonians for both the unstrained and the strained crystals. We may write

$$\begin{aligned}\int_\infty \Psi_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau &=\delta_{pq}\int_\infty|\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})|^2d\tau-N\sum_{s,\sigma}\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\\ &\quad\times\Gamma_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau, \end{aligned} \quad (32)$$

$$\begin{aligned}\int_\infty \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau &=\delta_{pq}\int_\infty|\mathfrak{G}_q'(\mathbf{k},\mathbf{r})|^2d\tau-N\sum_{s,\sigma}\int_\infty\varphi_s(\mathbf{r}-\mathfrak{a}\cdot\mathfrak{R}_\sigma)\\ &\quad\times\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{a}\cdot\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau, \end{aligned} \quad (33)$$

$$\begin{aligned}\int_\infty \Psi_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})H\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau &=\int_\infty\Gamma_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})H\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\\ &\quad-N\sum_{s,\sigma}E_s\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\\ &\quad\times\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau, \end{aligned} \quad (34)$$

$$\begin{aligned}\int_\infty \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})H'\,\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau &=\int_\infty\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})H'\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau\\ &\quad-N\sum_{s,\sigma}E_s\int_\infty\varphi_s(\mathbf{r}-\mathfrak{a}\cdot\mathfrak{R}_\sigma)\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\\ &\quad\times\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{a}\cdot\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau. \end{aligned} \quad (35)$$

Consider a set of n degenerate wave functions $\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})$, q ranging over n values. The secular equation we must solve is given by

$$\det\left\{\int_\infty\mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})[H'-E'(\mathbf{k})]\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau\right\}=0. \quad (36)$$

There will, of course, be n roots $E'(\mathbf{k})$. We make use of

$$\int_\infty\Psi_p^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})[H-E(\mathfrak{a}\cdot\mathbf{k})]\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau=0. \quad (37)$$

(Here we have temporarily dropped the index q on $E(\mathfrak{a}\cdot\mathbf{k})$ since the energy is the same for all n wave functions.) We now divide each element of the secular determinant appearing in Eq. (36) by the constant

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[9] We are disregarding the possibility of *accidental* degeneracies.

$\det\mathfrak{a}$ and from the result subtract Eq. (37), so that Eq. (36) becomes

$$\det\left\{(\det\mathfrak{a})^{-1}\int_{\infty}\mathfrak{S}_p{}'^*(\mathbf{k},\mathbf{r})[H'-E'(\mathbf{k})]\mathfrak{S}_q{}'(\mathbf{k},\mathbf{r})d\tau\right.$$

$$\left.-\int_{\infty}\Psi_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})[H-E(\mathfrak{a}\cdot\mathbf{k})]\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\right\}=0. \quad (38)$$

($\det\mathfrak{a}$ designates the determinant whose elements equal those of the tensor $\mathfrak{a}$.) In the integrals pertaining to the strained crystal appearing in Eq. (38) we replace the variable of integration $\mathbf{r}$ by $\mathfrak{a}\cdot\mathbf{r}$ so that $\boldsymbol{\nabla}$ is replaced by $\mathfrak{a}^{-1}\cdot\boldsymbol{\nabla}$ and $d\tau$ by $(\det\mathfrak{a})d\tau$. Making use of Eqs. (3), (7), (9), (24), and (32) through (35), we obtain

$$\det\left\{\int_{\infty}\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})[-(\mathfrak{a}^{-1}\cdot\boldsymbol{\nabla})^2+\nabla^2\right.$$

$$+\sum_n\{V(\mathfrak{a}\cdot[\mathbf{r}-\mathbf{R}_n])-V(\mathbf{r}-\mathbf{R}_n)\}$$

$$-\sum_n{}'\{V(\mathfrak{a}\cdot[\mathbf{R}_n-\mathbf{R}_m])-V(\mathbf{R}_n-\mathbf{R}_m)\}]\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$-N\sum_{s,\sigma}E_s\left[(\det\mathfrak{a})\int_{\infty}\varphi_s(\mathfrak{a}\cdot[\mathbf{r}-\mathfrak{R}_\sigma])\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\right.$$

$$\times\int_{\infty}\varphi_s{}^*(\mathfrak{a}\cdot[\mathbf{r}-\mathfrak{R}_\sigma])\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$-\int_{\infty}\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$\left.\times\int_{\infty}\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\right]$$

$$-[E'(\mathbf{k})-E(\mathfrak{a}\cdot\mathbf{k})]\int_{\infty}\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$+N\sum_{s,\sigma}\left[(\det\mathfrak{a})E'(\mathbf{k})\int_{\infty}\varphi_s(\mathfrak{a}\cdot[\mathbf{r}-\mathfrak{R}_\sigma])\right.$$

$$\times\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\int_{\infty}\varphi_s{}^*(\mathfrak{a}\cdot[\mathbf{r}-\mathfrak{R}_\sigma])\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$-E(\mathfrak{a}\cdot\mathbf{k})\int_{\infty}\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau$$

$$\left.\left.\times\int_{\infty}\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau\right]\right\}=0. \quad (39)$$

Since we desire the eigenvalues $E'(\mathbf{k})$ only to the accuracy of terms linear in the strain tensor $\mathfrak{e}$, we may define the tensor $\mathfrak{D}(\mathbf{k})$, which is independent of $\mathfrak{e}$, such that

$$E'(\mathbf{k})=E(\mathbf{k})+\mathfrak{e}:\mathfrak{D}(\mathbf{k}). \quad (40)$$

We substitute (40) into (39) and expand everything as a power series in $\mathfrak{e}$, retaining only the lowest order nonvanishing terms. Thus we expand

$$E(\mathfrak{a}\cdot\mathbf{k})=E(\mathbf{k})+\mathfrak{e}:[\mathbf{k}\mathbf{v}(\mathbf{k})+\mathbf{v}(\mathbf{k})\mathbf{k}], \quad (41)$$

where the velocity $\mathbf{v}$ is given by

$$\mathbf{v}(\mathbf{k})=\tfrac{1}{2}\boldsymbol{\nabla}_kE(\mathbf{k}). \quad (42)$$

Similarly we expand

$$-(\mathfrak{a}^{-1}\cdot\boldsymbol{\nabla})^2=-\nabla^2+\mathfrak{e}:2\boldsymbol{\nabla}\boldsymbol{\nabla}, \quad (43)$$

and

$$V(\mathfrak{a}\cdot\mathbf{r})=V(\mathbf{r})+\mathfrak{e}:\mathfrak{U}'(\mathbf{r}), \quad (44)$$

where

$$\mathfrak{U}'(\mathbf{r})\equiv\mathbf{r}\boldsymbol{\nabla}V(\mathbf{r}). \quad (45)$$

We shall henceforth assume that $V(\mathbf{r})$ is a function of the *magnitude* of $\mathbf{r}$ alone, so that

$$\begin{aligned}\mathfrak{U}'(\mathbf{r})&=\mathbf{r}\mathbf{r}\left(\frac{1}{r}\frac{dV}{dr}\right)\\&=-\boldsymbol{\nabla}\boldsymbol{\nabla}\int_r^{\infty}rV(r)dr-\mathbf{1}V(\mathbf{r}).\end{aligned} \quad (46)$$

We also expand

$$\det\mathfrak{a}=1+\mathfrak{e}:\mathbf{1}, \quad (47)$$

and

$$\varphi_s(\mathfrak{a}\cdot\mathbf{r})=\varphi_s(\mathbf{r})+\mathfrak{e}:\tfrac{1}{2}[\mathbf{r}\boldsymbol{\nabla}\varphi_s(\mathbf{r})+\{\boldsymbol{\nabla}\varphi_s(\mathbf{r})\}\mathbf{r}]. \quad (48)$$

Substituting Eqs. (40), (41), (43), (44), (47), and (48) into Eq. (39), making use of the facts that

$$\int_{\infty}[\Psi_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})-\Gamma_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})][H-E(\mathfrak{a}\cdot\mathbf{k})]$$

$$\times[\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})-\Gamma_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})]d\tau=0, \quad (49)$$

and

$$\int_{\infty}\Psi_p{}^*(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})\Psi_q(\mathfrak{a}\cdot\mathbf{k},\,\mathbf{r})d\tau=0, \quad (50)$$

when $p\neq q$, and dividing the pqth element of the secular determinant by $[I_p{}^*(\mathbf{k})I_q(\mathbf{k})]^{\frac{1}{2}}$ where

$$I_q(\mathbf{k})=\int_{\infty}|\Gamma_q(\mathbf{k})|^2d\tau$$

$$-N\sum_{s,\sigma}\left|\int_{\infty}\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2, \quad (51)$$

we finally obtain

$$\det\,\mathfrak{e}:\{\mathfrak{A}_{pq}(\mathbf{k})+\mathfrak{B}_{pq}(\mathbf{k})+\mathfrak{C}_{pq}(\mathbf{k})$$

$$-[\mathfrak{D}(\mathbf{k})-\mathbf{k}\mathbf{v}_q(\mathbf{k})-\mathbf{v}_q(\mathbf{k})\mathbf{k}]\delta_{pq}\}=0, \quad (52)$$

where

$$\mathfrak{A}_{pq}(\mathbf{k})\equiv[I_p{}^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\int_{\infty}\Gamma_p{}^*(\mathbf{k},\mathbf{r})2\boldsymbol{\nabla}\boldsymbol{\nabla}\Gamma_q(\mathbf{k},\mathbf{r})d\tau, \quad (53)$$

$$\mathfrak{B}_{pq}(\mathbf{k})\equiv[I_p{}^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\int_\infty \Gamma_p{}^*(\mathbf{k},\mathbf{r})\Gamma_q(\mathbf{k},\mathbf{r})$$

$$\times[\sum_n \mathfrak{U}'(\mathbf{r}-\mathbf{R}_n)-\sum_n{}'\mathfrak{U}'(\mathbf{R}_n-\mathbf{R}_m)]d\tau, \quad (54)$$

$$\mathfrak{C}_{pq}(\mathbf{k})\equiv[I_p{}^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}N\sum_{s,\sigma}[E(\mathbf{k})-E_s]$$

$$\times\biggl[\delta_{pq}\mathbf{1}\left|\int_\infty \varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2$$

$$+\tfrac{1}{2}\int_\infty \Gamma_p{}^*(\mathbf{k},\mathbf{r})\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)d\tau$$

$$\times\int_\infty \Gamma_q(\mathbf{k},\mathbf{r})\{(\mathbf{r}-\mathfrak{R}_\sigma)\nabla\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)$$

$$+(\nabla\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma))(\mathbf{r}-\mathfrak{R}_\sigma)\}d\tau$$

$$+\tfrac{1}{2}\int_\infty \Gamma_q(\mathbf{k},\mathbf{r})\varphi_s{}^*(\mathbf{r}-\mathfrak{R}_\sigma)d\tau$$

$$\times\int_\infty \Gamma_p{}^*(\mathbf{k},\mathbf{r})\{(\mathbf{r}-\mathfrak{R}_\sigma)\nabla\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)$$

$$+(\nabla\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma))(\mathbf{r}-\mathfrak{R}_\sigma)\}d\tau\biggr]. \quad (55)$$

Equation (52) immediately may be rewritten in the form

$$\det\{\mathfrak{A}_{pq}(\mathbf{k})+\mathfrak{B}_{pq}(\mathbf{k})+\mathfrak{C}_{pq}(\mathbf{k})$$
$$-[\mathfrak{D}(\mathbf{k})-\mathbf{k}\mathbf{v}_q(\mathbf{k})-\mathbf{v}_q(\mathbf{k})\mathbf{k}]\delta_{pq}\}=0. \quad (56)$$

Equation (56) symbolically represents six sets of secular equations, each set individually determining one of the six components of the desired symmetric tensor $\mathfrak{D}(\mathbf{k})$ for all values of $\mathbf{k}$ allowed by the periodic boundary conditions. The fact that $\mathfrak{D}$ is symmetric follows from the fact that each of the four tensors $\mathfrak{A}$, $\mathfrak{B}$, $\mathfrak{C}$ and $(\mathbf{kv}+\mathbf{vk})$ are obviously symmetric.

Equation (56) is the general solution to the problem of uniform (acoustic) strains. Note that for cubic crystals the four above-mentioned tensors, and thus also $\mathfrak{D}$, all have cubic symmetry in k-space. Thus for a given tensor any diagonal element may be obtained from any other diagonal element by an appropriate rotation in k-space about one of the cube axes. The nondiagonal elements are similarly related. Physically this means that for cubic crystals it is sufficient to study (for all values of $\mathbf{k}$) the effects of a pure tensile strain along one of cube axes and the effects of a pure shear strain in one of the cube planes.

An interesting special case concerning the cubic crystal occurs when we examine a *nondegenerate* band for $\mathbf{k}$ lying along a symmetry axis. By a proper orientation of our coordinate axes (such that one of them lies parallel to the symmetry axis), we can make $\mathfrak{D}$ a diagonal tensor having only three (diagonal) components. In general, each of these three components will be different, but in the case of a three-fold or a four-fold symmetry axis, two of these components will be identical (those two associated with the two coordinate directions perpendicular to the symmetry axis). In this latter case the effect of an arbitrary strain may be determined from a knowledge of the effects of (*a*) a pure dilation and (*b*) a uniaxial shear along the symmetry direction (the latter being defined as a tensile strain of a given value along the axis and tensile strains of minus one-half this value along each of the other two coordinate directions). Such a case is of practical importance since it includes the bottom of the conduction band in both silicon and germanium, the bottom lying along the fourfold (100) axes in silicon and along the threefold (111) axes in germanium. It should be emphasized that the above conclusions, which follow from symmetry considerations, hold only for $\mathbf{k}$ along a symmetry axis and only for a nondegenerate band along this axis.

III. OPTICAL STRAINS

In this section, we wish to consider the effects of a uniform optical strain[10] upon a crystal. As much as possible, the notation developed in the previous section will be used here. Thus the Hamiltonian for the unstrained crystal is given by Eq. (3), while the Hamiltonian for the strained crystal is

$$H''=-\nabla^2+\sum_n V(\mathbf{r}-\mathbf{R}_n'')-\mathbf{V}(\mathbf{e}_\sigma). \quad (57)$$

Here $\mathbf{V}(\mathbf{e}_\sigma)$ is a constant which will be defined presently, and the $\mathbf{R}_n''$ represent the positions of the atoms in the strained crystal. The positions of the unit cells of the crystal, denoted by the $\mathbf{R}_n'$, are unaffected by the strain, but the positions of the various atoms of a unit cell relative to the center of that cell are changed by the strain from $\mathfrak{R}_\sigma$ to

$$\mathfrak{R}_\sigma''=\mathfrak{R}_\sigma+\mathbf{e}_\sigma. \quad (58)$$

The $\mathbf{e}_\sigma$ are infinitesimal vectors which specify the strain. It can be seen that

$$\mathbf{R}_n''=\mathbf{R}_n'+\mathbf{R}_\sigma''=\mathbf{R}_n+\mathbf{e}_{\sigma(n)}. \quad (59)$$

We shall restrict ourselves to crystals having sufficient symmetry for $\mathbf{V}(\mathbf{e}_\sigma)$, defined as

$$\mathbf{V}(\mathbf{e}_\sigma)\equiv\sum_n{}' V(\mathbf{R}_n''-\mathbf{R}_m''), \quad (60)$$

to be independent of the index m, at least in the limit of small $\mathbf{e}_\sigma$. (The prime over the summation indicates that the term $n=m$ is omitted.) This is necessary in order for the crystal potential in the neighborhood of any ion core of the crystal to be unaffected by the strain. Noting that, for the case $\mathbf{e}_\sigma=0$, Eq. (60) becomes the $\mathbf{V}(0)$ appearing in Eq. (3), we see that, in the neighborhood of any ion core of the crystal, the crystal

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[10] For brevity, the word *optical* will be dropped throughout the remainder of this section but is to be understood in all references to strain.

potential can be approximated by the atomic-like potential V centered on this ion core, both for the strained and the unstrained crystals. Since the $\mathbf{R}_n'$ are unaffected by the strain, it follows that the translational periodicity properties of the wave functions for both the strained and the unstrained crystals are identical. This fact, plus the fact that here we are dealing with the vectors $\mathbf{e}_\sigma$ rather than the tensor $\mathfrak{e}$, makes the treatment of optical strains somewhat simpler than that of acoustic strains.

We shall use the analog of the method used in the previous section in order to construct an approximate wave function for the strained crystal. Thus, in analogy with Eqs. (20) and (26), we take our approximate wave function to be

$$\mathfrak{S}_q''(\mathbf{k},\mathbf{r})=\Gamma_q(\mathbf{k},\mathbf{r})-\sum_{s,n}\varphi_s(\mathbf{r}-\mathbf{R}_n'')\times\int_\infty\varphi_s^*(\mathbf{r}-\mathbf{R}_n'')\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \quad (61)$$

Note that here it is not necessary to scale Γ since the translational periodicities are unaffected by the strain. For a given $\mathbf{k}$ there will be various sets of degenerate wave functions Ψ_q associated with the unstrained crystal, the members of a given set all having different point symmetries with respect to their arguments in real space so that they are mutually orthogonal.[9] Since the Γ_q have the same point symmetries as do the corresponding Ψ_q, it follows that the Γ_q associated with a given set are likewise mutually orthogonal. There will be corresponding sets of functions $\mathfrak{S}_q''$, the members of these sets serving as our unperturbed wave functions. In other words, for a given $\mathbf{k}$, we diagonalize $[H''-E''(\mathbf{k})]$ with respect to each set of functions $\mathfrak{S}_q''$. Note that the $(\mathfrak{S}_q''-\Gamma_q)$, and thus the $\mathfrak{S}_q''$ themselves, are not mutually orthogonal. It will be necessary to consider matrix elements of unity and of the respective Hamiltonians for both the unstrained and the strained crystals. We may write

$$\int_\infty\Psi_p^*(\mathbf{k},\mathbf{r})\Psi_q(\mathbf{k},\mathbf{r})d\tau=\delta_{pq}\int_\infty|\Gamma_q(\mathbf{k},\mathbf{r})|^2d\tau-N\sum_{s,\sigma}\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\times\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau, \quad (62)$$

$$\int_\infty\mathfrak{S}_p''^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q''(\mathbf{k},\mathbf{r})d\tau=\delta_{pq}\int_\infty|\Gamma_q(\mathbf{k},\mathbf{r})|^2d\tau-N\sum_{s,\sigma}\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma'')\times\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma'')\Gamma_q(\mathbf{k},\mathbf{r})d\tau, \quad (63)$$

$$\int_\infty\Psi_p^*(\mathbf{k},\mathbf{r})H\Psi_q(\mathbf{k},\mathbf{r})d\tau=\int_\infty\Gamma_p^*(\mathbf{k},\mathbf{r})H\Gamma_q(\mathbf{k},\mathbf{r})d\tau-N\sum_{s,\sigma}E_s\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\times\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau, \quad (64)$$

$$\int_\infty\mathfrak{S}_p''^*(\mathbf{k},\mathbf{r})H''\mathfrak{S}_q''(\mathbf{k},\mathbf{r})d\tau=\int_\infty\Gamma_p^*(\mathbf{k},\mathbf{r})H''\Gamma_q(\mathbf{k},\mathbf{r})d\tau-N\sum_{s,\sigma}E_s\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma'')\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\times\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma'')\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \quad (65)$$

Equations (62) and (64) can, of course, be obtained directly from Eqs. (32) and (34), respectively, simply by replacing $\mathfrak{a}\cdot\mathbf{k}$ by $\mathbf{k}$. In obtaining Eq. (65) we made use of the fact that

$$H''\varphi_s(\mathbf{r}-\mathbf{R}_n'')=E_s\varphi_s(\mathbf{r}-\mathbf{R}_n'') \quad (66)$$

to a good approximation, in analogy with Eq. (31). Consider a set of n degenerate wave functions $\Psi_q(\mathbf{k},\mathbf{r})$, q ranging over n values. The secular equation we must solve is given by

$$\det\left\{\int_\infty\mathfrak{S}_p''^*(\mathbf{k},\mathbf{r})[H''-E''(\mathbf{k})]\mathfrak{S}_q''(\mathbf{k},\mathbf{r})d\tau\right\}=0. \quad (67)$$

There will, of course, be n roots $E''(\mathbf{k})$. In Eq. (37) we replace $\mathfrak{a}\cdot\mathbf{k}$ by $\mathbf{k}$ and subtract this from Eq. (67), obtaining

$$\det\left\{\int_\infty\mathfrak{S}_p''^*(\mathbf{k},\mathbf{r})[H''-E''(\mathbf{k})]\mathfrak{S}_q''(\mathbf{k},\mathbf{r})d\tau-\int_\infty\Psi_p^*(\mathbf{k},\mathbf{r})[H-E(\mathbf{k})]\Psi_q(\mathbf{k},\mathbf{r})d\tau\right\}=0. \quad (68)$$

Making use of Eqs. (3), (57), (60), and (62) through (65), we find that Eq. (68) becomes

$$\det\left\{\int_\infty\Gamma_p^*(\mathbf{k},\mathbf{r})\Big[\sum_n\{V(\mathbf{r}-\mathbf{R}_n'')-V(\mathbf{r}-\mathbf{R}_n)\}-\textstyle\sum_n\{V(\mathbf{R}_n''-\mathbf{R}_m'')-V(\mathbf{R}_n-\mathbf{R}_m)\}-\delta_{pq}\{E''(\mathbf{k})-E(\mathbf{k})\}\Big]\Gamma_q(\mathbf{k},\mathbf{r})d\tau+N\sum_{s,\sigma}\bigg[\{E''(\mathbf{k})-E_s\}\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma'')\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\times\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma'')\Gamma_q(\mathbf{k},\mathbf{r})d\tau-\{E(\mathbf{k})-E_s\}\times\int_\infty\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_p^*(\mathbf{k},\mathbf{r})d\tau\times\int_\infty\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\bigg]\right\}=0. \quad (69)$$

Since we desire the eigenvalues $E''(\mathbf{k})$ only to the accuracy of terms linear in the strain vectors $\mathbf{e}_\sigma$, we can expand everything as a power series in the $\mathbf{e}_\sigma$, retaining only the lowest order nonvanishing terms. Thus we define the vector $\mathbf{F}_\sigma$ such that

$$E''(\mathbf{k})-E(\mathbf{k})=\sum_\sigma \mathbf{e}_\sigma\cdot\mathbf{F}_\sigma(\mathbf{k}). \tag{70}$$

We shall at this point assume that the crystal symmetry is such that

$$\boldsymbol{\nabla}\sum_n V(\mathbf{R}_n'+\mathfrak{R}_\sigma-\mathfrak{R}_\tau)=0, \tag{71}$$

for any two distinct position vectors $\mathfrak{R}_\sigma$ and $\mathfrak{R}_\tau$. Thus it follows that

$$\begin{aligned}\sum_n\{V(\mathbf{R}_n''-\mathbf{R}_m'')-V(\mathbf{R}_n-\mathbf{R}_m)\}&\\ =\sum_\sigma(\mathbf{e}_\sigma-\mathbf{e}_\tau)\cdot\boldsymbol{\nabla}\sum_n V(\mathbf{R}_n'+\mathfrak{R}_\sigma-\mathfrak{R}_\tau)&=0,\end{aligned} \tag{72}$$

$\mathfrak{R}_\tau$ being associated with $\mathbf{R}_m$. Similarly expanding the other terms in Eq. (69), and making use of Eqs. (49) and (50) with $\mathfrak{a}\cdot\mathbf{k}$ replaced by $\mathbf{k}$, we finally obtain

$$\det\sum_\sigma \mathbf{e}_\sigma\cdot[{}_\sigma\mathbf{X}_{pq}(\mathbf{k})+{}_\sigma\mathbf{Y}_{pq}(\mathbf{k})-\delta_{pq}\mathbf{F}_\sigma(\mathbf{k})]=0, \tag{73}$$

where

$$\begin{aligned}{}_\sigma\mathbf{X}_{pq}(\mathbf{k})=[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\int_\infty \Gamma_p^*(\mathbf{k},\mathbf{r})\Gamma_q(\mathbf{k},\mathbf{r})&\\ \times\sum_n \boldsymbol{\nabla}V(\mathbf{r}-\mathbf{R}_n'-\mathbf{R}_\sigma)d\tau,&\end{aligned} \tag{74}$$

$$\begin{aligned}{}_\sigma\mathbf{Y}_{pq}(\mathbf{k})=&[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}N\sum_s[E(\mathbf{k})-E_s]\\ &\times\biggl[\int_\infty \Gamma_p^*(\mathbf{k},\mathbf{r})\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)d\tau\\ &\times\int_\infty \Gamma_q\boldsymbol{\nabla}\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)d\tau\\ &+\int_\infty \Gamma_q(\mathbf{k},\mathbf{r})\varphi_s^*(\mathbf{r}-\mathfrak{R}_\sigma)d\tau\\ &\times\int_\infty \Gamma_p^*(\mathbf{k},\mathbf{r})\boldsymbol{\nabla}\varphi_s(\mathbf{r}-\mathfrak{R}_\sigma)d\tau\biggr],\end{aligned} \tag{75}$$

and $I_q(\mathbf{k})$ is given by Eq. (51). Equation (73) may be rewritten in the form

$$\det[{}_\sigma\mathbf{X}_{pq}(\mathbf{k})+{}_\sigma\mathbf{Y}_{pq}(\mathbf{k})-\delta_{pq}\mathbf{F}_\sigma(\mathbf{k})]=0. \tag{76}$$

Equation (76) symbolically represents 3ν sets of equations, ν being the number of atoms per unit cell of the crystal, each set individually determining one of 3ν components $F_{\sigma(x,y,z)}(\mathbf{k})$ for all values of $\mathbf{k}$ allowed by the periodic boundary conditions.

IV. APPLICATION TO THE DIAMOND STRUCTURE

The procedure developed in the preceding sections is particularly suited to an unmodified crystal for which wave functions and energy levels have been calculated by the orthogonalized plane wave method.[3] In this method the wave function is expanded in terms of orthogonalized plane waves $X(\mathbf{k}_i,\mathbf{r})$, $\mathbf{k}_i$ being defined as

$$\mathbf{k}_i\equiv\mathbf{k}+\mathbf{K}_i. \tag{77}$$

$\mathbf{K}_i$ being a vector of the reciprocal lattice such that

$$\exp(i\mathbf{K}_i\cdot\mathbf{R}_n')=1, \tag{78}$$

for all i and n. $X(\mathbf{k}_i,\mathbf{r})$ is defined as

$$\begin{aligned}X(\mathbf{k}_i,\mathbf{r})=(N\Omega)^{-\frac{1}{2}}e^{i\mathbf{k}_i\cdot\mathbf{r}}-\Omega^{-\frac{1}{2}}\sum_{s,\sigma}\exp(i\mathbf{K}_i\cdot\mathfrak{R}_\sigma)&\\ \times\mu_s(\mathbf{k}_i)\Phi_{s,\sigma}(\mathbf{k},\mathbf{r}),&\end{aligned} \tag{79}$$

where

$$\begin{aligned}\mu_s(\mathbf{k}_i)&=N^{-\frac{1}{2}}\exp(-i\mathbf{K}_i\cdot\mathfrak{R}_\sigma)\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\Phi_{s,\sigma}^*(\mathbf{k},\mathbf{r})d\tau\\ &=\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_s^*(\mathbf{r})d\tau,\end{aligned} \tag{80}$$

and where Ω is the volume of the unit cell of the unstrained crystal. We see now that

$$\int_\infty \Phi_{s,\sigma}^*(\mathbf{k},\mathbf{r})X(\mathbf{k}_i,\mathbf{r})d\tau=0. \tag{81}$$

Expanding $\Psi_q(\mathbf{k},\mathbf{r})$ in terms of the X's, we have

$$\Psi_q(\mathbf{k},\mathbf{r})=\sum_i \mathcal{A}_q(\mathbf{k}_i)X(\mathbf{k}_i,\mathbf{r}). \tag{82}$$

Hence it follows that $\Gamma_q(\mathbf{k},\mathbf{r})$, as defined by Eq. (14), can be written as

$$\Gamma_q(\mathbf{k},\mathbf{r})=(N\Omega)^{-\frac{1}{2}}\sum_i \mathcal{A}_q(\mathbf{k}_i)e^{i\mathbf{k}_i\cdot\mathbf{r}}. \tag{83}$$

It is because of the simplicity of Eq. (83) that the OPW method is particularly adapted to the results of Secs. II and III.

We shall now specialize to the case where the unstrained crystal has the diamond structure, this being a case of great practical importance. There are now two atoms per unit cell such that $\mathfrak{R}_\sigma=\pm\mathfrak{R}$ where $\mathfrak{R}$ points along the (111) direction, and $2\mathfrak{R}$ is the nearest neighbor distance. The optical strain vectors are thus given by $\mathbf{e}_\sigma=\pm\mathbf{e}$ in order that there be no displacement of the center of mass of the crystal during an optical strain. It follows that Eqs. (73) and (76) may be written in the form

$$\det[\mathbf{X}_{pq}(\mathbf{k})+\mathbf{Y}_{pq}(\mathbf{k})-\delta_{pq}\mathbf{F}(\mathbf{k})]=0, \tag{84}$$

where $\mathbf{X}_{pq}$ is the difference of the two ${}_\sigma\mathbf{X}_{pq}$, and similarly for $\mathbf{Y}_{pq}$ and $\mathbf{F}$. Thus, Eq. (70) becomes

$$E''(\mathbf{k})-E(\mathbf{k})=\mathbf{e}\cdot\mathbf{F}(\mathbf{k}). \tag{85}$$

We define

$$\mathcal{B}_{ij}{}^{pq}(\mathbf{k})\equiv\mathcal{A}_p^*(\mathbf{k}_i)\mathcal{A}_q(\mathbf{k}_j)\cos(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathfrak{R}, \tag{86}$$

$$\boldsymbol{\mathfrak{C}}_{ij}{}^{pq}(\mathbf{k})\equiv\mathcal{A}_p^*(\mathbf{k}_i)\mathcal{A}_q(\mathbf{k}_j)(\mathbf{K}_j-\mathbf{K}_i)\sin(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathfrak{R}. \tag{87}$$

Since we now have

$$\int_\infty X^*(\mathbf{k}_i,\mathbf{r})X(\mathbf{k}_j,\mathbf{r})d\tau$$
$$=\cos(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathfrak{R}\,[\delta_{ij}-(2/\Omega)\textstyle\sum_s \mu_s^*(\mathbf{k}_i)\mu_s(\mathbf{k}_j)], \quad (88)$$

it follows that

$$I_q(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}{}^{qq}(\mathbf{k})[\delta_{ij}-(2/\Omega)\sum_s \mu_s^*(\mathbf{k}_i)\mu_s(\mathbf{k}_j)]. \quad (89)$$

Since for the diamond structure

$$\boldsymbol{\nabla\nabla}\sum_n{}'\int_{|\mathbf{R}_n-\mathbf{R}_m|}^\infty rV(r)dr=0, \quad (90)$$

by symmetry, we have from Eqs. (7) and (46)

$$\textstyle\sum_n{}'\,\mathfrak{U}'(\mathbf{R}_n-\mathbf{R}_m)=-\mathbf{1}V(0), \quad (91)$$

so that we may write

$$\textstyle\sum_n \mathfrak{U}'(\mathbf{r}-\mathbf{R}_n)-\sum_n{}'\,\mathfrak{U}'(\mathbf{R}_n-\mathbf{R}_m)$$
$$=\textstyle\sum_i \cos\mathbf{K}_i\cdot\mathfrak{R}\;\mathfrak{W}'(\mathbf{K}_i)e^{-i\mathbf{K}_i\cdot\mathbf{r}}, \quad (92)$$

where

$$\mathfrak{W}'(\mathbf{K}_i)\equiv(2/\Omega)\int_\infty e^{i\mathbf{K}_i\cdot\mathbf{r}}\mathfrak{U}'(\mathbf{r})d\tau+\delta_{i0}\mathbf{1}V(0). \quad (93)$$

With the aid of Eq. (46), we may write

$$\mathfrak{W}'(\mathbf{K}_i)=-\mathbf{K}_i\mathbf{K}_i\mathcal{M}(\mathbf{K}_i)+\mathbf{1}\mathcal{N}(\mathbf{K}_i), \quad (94)$$

$\mathcal{M}$ and $\mathcal{N}$ being defined as

$$\mathcal{M}(\mathbf{K}_i)=-(8\pi/\Omega)\int_0^\infty drr^2\left(\frac{\sin K_ir}{K_ir}\right)\int_r^\infty r'V(r')dr', \quad (95)$$

$$\mathcal{N}(\mathbf{K}_i)=-(8\pi/\Omega)\int_0^\infty\left(\frac{\sin K_ir}{K_ir}\right)r^2V(r)dr+\delta_{i0}V(0). \quad (96)$$

Similarly, we have

$$\textstyle\sum_n \boldsymbol{\nabla}\{V(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R})-V(\mathbf{r}-\mathbf{R}_n'+\mathfrak{R})\}$$
$$=\textstyle\sum_i \sin\mathbf{K}_i\cdot\mathfrak{R}\;\mathbf{K}_i\,\mathcal{N}(\mathbf{K}_i)e^{i\mathbf{K}_i\cdot\mathbf{r}}, \quad (97)$$

since

$$-(2i/\Omega)\int_\infty e^{i\mathbf{K}_i\cdot\mathbf{r}}\boldsymbol{\nabla}V(\mathbf{r})d\tau=\mathbf{K}_i\mathcal{N}(\mathbf{K}_i).$$

It now follows that

$$\mathfrak{A}_{pq}(\mathbf{k})=[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\textstyle\sum_i \mathcal{B}_{ii}{}^{pq}(\mathbf{k})\mathbf{k}_i\mathbf{k}_i, \quad (98)$$

$$\mathfrak{B}_{pq}(\mathbf{k})=[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathcal{B}_{ij}{}^{pq}(\mathbf{k})\mathfrak{W}'(\mathbf{K}_j-\mathbf{K}_i), \quad (99)$$

$$\mathbf{X}_{pq}(\mathbf{k})=[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathfrak{C}_{ij}{}^{pq}(\mathbf{k})\mathcal{N}(\mathbf{K}_j-\mathbf{K}_i). \quad (100)$$

The divergence theorem of vector analysis tells us that

$$\int_\infty \boldsymbol{\nabla}[\mathbf{r}e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_s^*(\mathbf{r})]d\tau=0$$
$$=\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\mathbf{r}\boldsymbol{\nabla}^\dagger\varphi_s^*(\mathbf{r})d\tau$$
$$+[\mathbf{k}_i\boldsymbol{\nabla}_{k_i}+\mathbf{1}]\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_s^*(\mathbf{r})d\tau,$$

so that

$$\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\mathbf{r}\boldsymbol{\nabla}^\dagger\varphi_s^*(\mathbf{r})d\tau=-[\mathbf{1}+\mathbf{k}_i\boldsymbol{\nabla}_{k_i}]\mu_s(\mathbf{k}_i). \quad (101)$$

(See footnote 8 for the meaning of $\mathbf{ab}^\dagger$.) Similarly

$$\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\mathbf{r}\boldsymbol{\nabla}\varphi_s^*(\mathbf{r})d\tau=-[\mathbf{1}+\mathbf{k}_i\boldsymbol{\nabla}_{k_i}{}^\dagger]\mu_s(\mathbf{k}_i). \quad (102)$$

We now find that

$$\mathfrak{G}_{pq}(\mathbf{k})=-(2/\Omega)[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathcal{B}_{ij}{}^{pq}(\mathbf{k})$$
$$\times\sum_s[E(\mathbf{k})-E_s]\{\mathbf{1}(2-\delta_{pq})$$
$$+\tfrac{1}{2}(\mathbf{k}_i\boldsymbol{\nabla}_{k_i}+\mathbf{k}_i\boldsymbol{\nabla}_{k_i}{}^\dagger+\mathbf{k}_j\boldsymbol{\nabla}_{k_j}+\mathbf{k}_j\boldsymbol{\nabla}_{k_j}{}^\dagger)\}$$
$$\times\mu_s^*(\mathbf{k}_i)\mu_s(\mathbf{k}_j). \quad (103)$$

In an analogous fashion, we find that

$$\mathbf{Y}_{pq}(\mathbf{k})=(2/\Omega)[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathfrak{C}_{ij}{}^{pq}(\mathbf{k})$$
$$\times\sum_s[E(\mathbf{k})-E_s]\mu_s^*(\mathbf{k}_i)\mu_s(\mathbf{k}_j). \quad (104)$$

Consistent with Eq. (18), we may define the *real* quantity $Q_{nl}(r)$ such that

$$\varphi_{nlm}(\mathbf{r})=i^lr^{-1}Q_{nl}(r)\mathcal{Y}_l{}^m(\theta,\varphi), \quad (105)$$

where

$$\int_0^\infty Q_{nl}(r)Q_{n'l}(r)dr=\delta_{nn'}, \quad (106)$$

and

$$\int\mathcal{Y}_l{}^m(\theta,\varphi)^*\mathcal{Y}_{l'}{}^{m'}(\theta,\varphi)d\omega=\delta_{ll'}\delta_{mm'}. \quad (107)$$

(Here $\int d\omega$ denotes a surface integral over the unit sphere.) $\mathcal{Y}_l{}^m$ is defined as

$$\mathcal{Y}_l{}^m(\theta,\varphi)=\left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l{}^{|m|}(\cos\theta)e^{im\varphi}. \quad (108)$$

Since

$$e^{i\mathbf{k}_i\cdot\mathbf{r}}=4\pi\sum_{l=0}^\infty\sum_{m=-l}^{+l}i^lj_l(k_ir)\mathcal{Y}_l{}^m(\theta,\varphi)\mathcal{Y}_l{}^m(\theta_i,\varphi_i)^*, \quad (109)$$

(where θ_i and φ_i give the orientation of $\mathbf{k}_i$), we have

$$\mu_{nlm}(\mathbf{k}_i)=4\pi g_{nl}(k_i)\mathcal{Y}_l^m(\theta_i,\varphi_i)^*, \tag{110}$$

where

$$g_{nl}(k_i)\equiv\int_0^\infty rQ_{nl}(r)j_l(k_ir)dr. \tag{111}$$

(j_l is the spherical Bessel function of order l.) Let θ_{ij} be the angle between $\mathbf{k}_i$ and $\mathbf{k}_j$. Unsöld's addition theorem states that

$$\sum_{m=-l}^{+l}\mathcal{Y}_l^m(\theta_i,\varphi_i)\mathcal{Y}_l^m(\theta_j,\varphi_j)^*=\left(\frac{2l+1}{4\pi}\right)P_l(\cos\theta_{ij}). \tag{112}$$

Equations (89) and (104) can now be written as

$$\begin{aligned}I_q(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}^{qq}(\mathbf{k})\Big[\delta_{ij}-(8\pi/\Omega)\sum_l(2l+1)\\ \times P_l(\cos\theta_{ij})\sum_n g_{nl}(k_i)g_{nl}(k_j)\Big],\end{aligned} \tag{113}$$

$$\begin{aligned}\mathbf{Y}_{pq}(\mathbf{k})=(8\pi/\Omega)[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathfrak{C}_{ij}^{pq}(\mathbf{k})\\ \times\sum_l(2l+1)P_l(\cos\theta_{ij})\sum_n[E(\mathbf{k})-E_{nl}]\\ \times g_{nl}(k_i)g_{nl}(k_j).\end{aligned} \tag{114}$$

If we define

$$\mathbf{u}=\mathbf{k}_i+\mathbf{k}_j,\quad \mathbf{v}=\mathbf{k}_i-\mathbf{k}_j,$$

then we have

$$k_ik_j\cos\theta_{ij}=\tfrac{1}{4}(u^2-v^2),$$

and

$$(\mathbf{k}_i\nabla_{k_i}+\mathbf{k}_j\nabla_{k_j})=(\mathbf{u}\nabla_u+\mathbf{v}\nabla_v).$$

Thus it follows that

$$(\mathbf{k}_i\nabla_{k_i}+\mathbf{k}_j\nabla_{k_j})k_ik_j\cos\theta_{ij}=\mathbf{k}_i\mathbf{k}_j+\mathbf{k}_j\mathbf{k}_i, \tag{115}$$

so that

$$\begin{aligned}\tfrac{1}{2}(\mathbf{k}_i\nabla_{k_i}+\mathbf{k}_i\nabla_{k_i}{}^\dagger+\mathbf{k}_j\nabla_{k_j}+\mathbf{k}_j\nabla_{k_j}{}^\dagger)P_l(\cos\theta_{ij})g(k_i)g(k_j)\\ =(\mathbf{k}_i\mathbf{k}_i/k_i^2)[k_ig'(k_i)P_l(\cos\theta_{ij})\\ -\cos\theta_{ij}P_l'(\cos\theta_{ij})g(k_i)]g(k_j)\\ +(\mathbf{k}_j\mathbf{k}_j/k_j^2)[k_jg'(k_j)P_l(\cos\theta_{ij})\\ -\cos\theta_{ij}P_l'(\cos\theta_{ij})g(k_j)]g(k_i)+(k_ik_j)^{-1}\\ \times[\mathbf{k}_i\mathbf{k}_j+\mathbf{k}_j\mathbf{k}_i]P_l'(\cos\theta_{ij})g(k_i)g(k_j).\end{aligned} \tag{116}$$

Analogously to Eqs. (113) and (114), we may now write Eq. (103) in the form

$$\begin{aligned}\mathfrak{G}_{pq}(\mathbf{k})=-(8\pi/\Omega)[I_p^*(\mathbf{k})I_q(\mathbf{k})]^{-\frac{1}{2}}\sum_{ij}\mathcal{B}_{ij}^{pq}(\mathbf{k})\\ \times\sum_{nl}(2l+1)[E(\mathbf{k})-E_{nl}]\{\mathbf{1}(2-\delta_{pq})\\ \times P_l(\cos\theta_{ij})g_{nl}(k_i)g_{nl}(k_j)\\ +(\mathbf{k}_i\mathbf{k}_i/k_i^2)[k_ig_{nl}'(k_i)P_l(\cos\theta_{ij})\\ -\cos\theta_{ij}P_l'(\cos\theta_{ij})g_{nl}(k_i)]g_{nl}(k_j)\\ +(\mathbf{k}_j\mathbf{k}_j/k_j^2)[k_jg_{nl'}(k_j)P_l(\cos\theta_{ij})\\ -\cos\theta_{ij}P_l'(\cos\theta_{ij})g_{nl}(k_j)]g_{nl}(k_i)\\ +(k_ik_j)^{-1}[\mathbf{k}_i\mathbf{k}_j+\mathbf{k}_j\mathbf{k}_i]\\ \times P_l'(\cos\theta_{ij})g_{nl}(k_i)g_{nl}(k_j)\}.\end{aligned} \tag{117}$$

[The primes in Eqs. (116) and (117) denote differentiation with respect to the argument.] In a specific application, Eqs. (98), (99), (100), (114), and (117) are what need to be evaluated numerically. The statements made at the conclusion of reference 1 also apply to these equations.

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