PHYSICAL REVIEW VOLUME 177, NUMBER 3 15 JANUARY 1969

Derivation of the Shell Model of Lattice Dynamics and its Relation to the Theory of the Dielectric Constant*

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(Received 9 November 1967; Revised manuscript received 16 August 1968)

A quantum-mechanical derivation of the dipolar models of lattice dynamics is presented, with particular reference to the shell model. The method is based on a systematic self-consistent Born-Oppenheimer perturbation expansion in powers of the lattice displacements, and utilizes a formalism previously developed by the author, whereby the perturbation in electronic charge density is obtained self-consistently in terms of a "bound" part moving rigidly with the cores and a "deformation part" representing the distortion effects. A certain approximation made in the relevant matrix elements is shown to lead to a self-consistent solution for the deformation part in terms of polarization waves, provided the dipole polarization vectors satisfy an equation which is exactly of the form of the shell equations of the shell model. The lattice equations of motion are then obtained and are exactly the same as the shell-model equations. The validity of the central assumption is discussed in terms of the band structure, and it is shown why the model should be reasonably good for insulators with large band gaps. It is shown how local-field corrections to the point-dipole approximation arise naturally out of the solution of the self-consistency conditions and may be incorporated into the theory. Explicit expressions are derived for the various bonding coefficients in terms of the general band structure of the solid. The close connection between the shell model and the pseudopotential theory for the lattice dynamics of metals is established, both being limiting cases of guessing at the nature of the solution for the self-consistent electron response to the lattice perturbation. Finally, the close relationship between the quantum-mechanical derivation of the shell model and the theory of the dielectric constant is pointed out. Rigorous relations are established between the dielectric constant obtained from the shell model and that calculated from the band structure in the random-phase approximation.

I. INTRODUCTION

In the last few years, the problem of performing a proper quantum-mechanical calculation of phonon-dispersion relations in the nearly-free-electron type metals has been successfully tackled by several authors.[1-6] For such metals it is possible to use perturbation theory, utilizing the fact that the ionic potential may be replaced by a pseudopotential[1-6] or model potential,[7] and many-electron effects may be taken into account by performing a self-consistent screening calculation. For ionic and covalent solids, however, the situation is not quite so satisfactory. The original model used to explain the lattice dynamics of ionic crystals was the "rigid-ion model"[8] in which the ions were supposed to move as rigid units interacting via electrostatic forces and short-range "overlap" forces. The reasonably good agreement which this model gave with experiment for such quantities as Debye temperatures was shown to be fortuitous, however, when account was taken of the electrostatic polarizability of the ions.[9,10] Subsequently, more sophisticated "dipolar" models were evolved, where the ions were assumed to interact directly with each other via electrostatic and overlap forces but were also assumed to suffer a distortion of their valence electron shells during the lattice motions due to both electrostatic and overlap or "mechanical" forces. This distortion was then represented as a dipole moment developing at the equilibrium lattice site, and these dipole moments were supposed to introduce further interaction both between themselves and with the ions. This is the basic idea behind the theories of Tolpygo and co-workers,[11-16] the "shell model" (SM) of lattice dynamics as developed by Cochran and others,[16-18] and the "deformation-dipole model" (DDM)

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* Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2150.

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developed by Hardy.[19] A recent review of these methods has been given by Dick.[20]

Although the SM and DDM were essentially phenomenological, their justification rested on the pioneering work of Tolpygo, Mashkevich, and others[11–16] who were the first to construct a microscopic quantum-mechanical theory. Their approach is reviewed by Kaplan,[15] who, however, also pointed out some of its shortcomings. Cowley[21] also established the formal equivalence between Mashkevich's formulation and the SM.

It is the purpose of this paper to take a slightly different approach to the microscopic theory, by deriving the equations of motion for such dipole models starting from the actual crystal wave functions of the unperturbed lattice (which are now available for a large number of solids, including ionic crystals,[22] with the advent of self-consistent band-structure calculations on high-speed computers), and using a self-consistent Born-Oppenheimer expansion to obtain the perturbed wave functions and energies in powers of the ionic displacements. In this way, one may relate the bonding coefficients of the model to quantities which are obtained in the course of a band-structure calculation. Also one may discuss the validity of the approximations made to derive the dipole model in terms of the band structure of the solid in question. Further, if one assumes that the adiabatic and harmonic approximations of lattice dynamics are valid, the Born-Oppenheimer expansion (where self-consistency for the perturbation in electronic wave functions is achieved at each stage of the expansion[23]) offers a systematic and rigorous way of working to the correct order of approximation, namely, energy perturbation need be considered only to second order in the nuclear displacements, and the self-consistent perturbations in the wave functions need be considered only to first order. Sham[1] has used this approach to derive the phonon-dispersion relation for sodium, where the existence of a weak pseudopotential makes the result essentially equivalent to using direct perturbation theory to second order, with the change in pseudopotential as a weak perturbation.[2] Thus the derivation of the equations of motion of a dipole model for tightly bound solids from such an approach would provide a very definite link with the theory of lattice dynamics of metals, showing that the equations of motion for these two types of solids arise in a sense as two limiting cases of the same formalism. The achievement of these objectives is the purpose of this paper.

There are essentially two main reasons why the above kind of approach has not hitherto been applied to solids such as ionic crystals. The first reason is that the rigorous solution to the self-consistency problem involves the inversion of a dielectric matrix[24] which is enormously difficult (though probably not impossible) to carry through for a crystal where the wave functions are far from free-electron-like. The second reason is the absence hitherto of anything like a pseudopotential for such solids, which in the case of the simple metals enormously simplifies the evaluation of the matrix elements and the convergence of the expansions in reciprocal space.

With regard to the first point, it should be noted that Cochran[25] noticed a formal similarity between the equations of motion of the SM (once the dipole moments were eliminated) and the equations of motion for the lattice dynamics of the simple metals, as obtained by Sham,[1] Toya,[4] and Harrison.[2] He also pointed out that both types of theory had the property that the electron-charge distribution was deformed by the lattice motion, and this deformation at the same time served to "screen out" the perturbation. He further suggested that the shell equations of the SM corresponded to the self-consistency conditions for electron screening used in the theory of metals. We shall see that the shell equations may indeed be derived as a limiting case of the self-consistency equations, provided a certain assumption (corresponding essentially to the dipolar approximation) is made about the nature of the solution to these equations. This will lead to a certain restriction on the band structure which will have to be satisfied for the model to be valid. Thus the dipole models for the lattice dynamics of such solids may be regarded as physically intuitive guesses as to what best approximates the true solution for the self-consistent electron response appropriate to these solids. The same remark may in fact be applied to all the other models proposed for the lattice dynamics of different types of solids such as the free-electron models, exchange-charge models, quadrupole models, and so on.

Very recently, in fact, Phillips[26] has developed a theory of covalent bonding in terms of "bonding charges" situated on the bonds, and Martin[27] has used this model to calculate the phonon-dispersion relations in silicon, with a fair degree of success. Such a model corresponds to yet another guess, in the sense mentioned above, about the self-consistent solution for the electron response, and an alternative approximation for the microscopic polarizability tensor to our basic approximation in Eq. (28). Such a model may be more appropriate for covalent solids, whereas it is likely that for ionic crystals the dipolar model is likely to be a better approximation.

With regard to the pseudopotential problem, we note that in a previous paper by the author[28] (henceforth referred to as I) a formalism was developed whereby phonon-dispersion relations in a variety of solids could

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be derived in terms of the band structure using a self-consistent Born-Oppenheimer expansion. It was noted there that the use of the latter eliminated the objections to the use of perturbation theory, even in the case where the ionic potentials could not be replaced by weak pseudopotentials as in the simple metals, but that for tightly-bound solids, as well as for simple metals, one could nevertheless define a quantity in the lattice-dynamical problem, which was exactly analogous to the pseudopotential. The formalism showed that one could regard the deep potential well near the ion cores as essentially moving some part of the valence charge distribution rigidly with the core, and that the further distortion of this charge distribution could then be regarded as arising self-consistently in response to a weaker perturbation, described as the "residual potential," with the deep wells near the cores eliminated. The dynamical matrix was then shown to be made up of a part due to interactions between "rigid pseudoatoms" and a part due to the distortion of the valence charge distribution. The similarity with the physical ideas underlying the above dipole models is obvious, and the exact connection may be made by regarding the deformation part of the valence charge distribution in I as being in some sense a polarization wave propagating through the valence charge in the crystal. In fact we shall see how the point-dipole assumption may be relaxed slightly while still preserving the form of the SM equations which we shall derive from this approach. This is equivalent to allowing approximately for local-field corrections to the fields produced by the electronic distortion, and we shall see how we may define form factors for the shells as originally suggested by Cochran.[25] Finally, we shall discuss the relationship of our method to the quantum theory of the dielectric constant. Cochran and Phillips[29] have already gone far in establishing such a connection, by comparing the static wave-number-dependent dielectric function obtained from the SM to that obtained from band theory in the random-phase approximation (RPA), and have suggested reasons for the discrepancies between the two. By means of our method, we shall in fact be able to demonstrate rigorously the exact relationship between the two dielectric functions.

Since the SM contains all the essential features of the dipole models discussed earlier, it is sufficient to compare the equations we derive with those of the SM. It is worth re-emphasizing that our discussion will be most relevant to crystals containing atoms with tightly bound electronic configurations.

II. SHELL-MODEL EQUATIONS

Let us assume that there are r atoms per unit cell. With each atom we can associate a symmetric volume around it which has a fixed geometrical configuration with respect to the unit cell, and we may call this the "subcell" associated with the atom. (By "atom" we mean the core plus the total valence charge density inside the subcell in the unperturbed lattice. Thus we really mean an ion if each subcell carries a net ionic charge as in an ionic crystal.) We shall follow convention in referring to the nuclei together with their tightly bound electrons as the cores and to the loosely bound electrons which suffer distortion during the lattice motion as the valence electrons. These correspond to the shells of the SM. We now briefly discuss the SM equations of motion.

Let $u_{\kappa,\alpha}{}^l$ denote the α component of the displacement of the atom in the κth subcell of the lth unit cell. The SM assumes that there is also a dipole moment representing the distortion of the valence charge density in that subcell, whose α component is $w_{\kappa,\alpha}{}^l$ when the lattice is vibrating. It also assumes that both $u_{\kappa,\alpha}{}^l$ and $w_{\kappa,\alpha}{}^l$ may be written in the form

$$u_{\kappa,\alpha}{}^l=(N\Omega)^{-1/2}(Q_{\mathbf{q}}e_{\kappa,\alpha}e^{i\mathbf{q}\cdot(\mathbf{r}_l+\mathbf{r}_\kappa)}+Q_{\mathbf{q}}{}^*e_{\kappa,\alpha}{}^*e^{-i\mathbf{q}\cdot(\mathbf{r}_l+\mathbf{r}_\kappa)}), \quad (1a)$$

$$w_{\kappa,\alpha}{}^l=(N\Omega)^{-1/2}(Q_{\mathbf{q}}w_{\kappa,\alpha}e^{i\mathbf{q}\cdot(\mathbf{r}_l+\mathbf{r}_\kappa)}+Q_{q}{}^*w_{\kappa,\alpha}{}^*e^{-i\mathbf{q}\cdot(\mathbf{r}_l+\mathbf{r}_\kappa)}), \quad (1b)$$

where N is the number of unit cells per unit volume, Ω is the total crystal volume, $Q_{\mathbf{q}}$ is the normal coordinate operator, and $\mathbf{e}$ and $\mathbf{w}$ are $3r$-component unit polarization vectors associated with $e_{\kappa,\alpha}{}^*$ and $w_{\kappa,\alpha}{}^l$, respectively. $\mathbf{r}_l$ is the equilibrium position of the origin of the lth unit cell, and $\mathbf{r}_\kappa$ is the equilibrium position of the atom in the κth subcell relative to this origin. The SM associates with each atom an ionic charge Z_κ and with each shell a shell charge Y_κ. We may define a shell displacement $\mathbf{w}'$ defined by

$$\mathbf{w}=\mathbf{Y}\mathbf{w}'. \quad (2)$$

In matrix form, the SM equations of motion may then be written as

$$\omega^2\mathbf{Me}=(\mathbf{ZCZ}+\mathbf{R})\mathbf{e}+(\mathbf{ZCY}+\mathbf{T})\mathbf{w}', \quad (3a)$$

$$0=(\mathbf{YCZ}+\mathbf{T}^\dagger)\mathbf{e}+(\mathbf{YCY}+\mathbf{S})\mathbf{w}', \quad (3b)$$

where $\mathbf{Z}$ is the diagonal matrix $Z_\kappa\delta_{\kappa\kappa'}\delta_{\alpha\beta}$ (M_κ is the mass of the κth atom), $\mathbf{C}$ is the electrostatic bonding coefficient between unit charges, as defined by Kellerman,[8] and $\mathbf{R}$, $\mathbf{T}$, and $\mathbf{S}$ are $3r\times 3r$ matrices describing the overlap or nonelectrostatic short-range bonding coefficients between rigid atoms, between atoms and shells, and between shells, respectively. Elimination of $\mathbf{w}'$ from Eqs. (3) gives us the equation of motion of the atoms alone as

$$\omega^2\mathbf{Me}=[(\mathbf{ZCZ}+\mathbf{R})-(\mathbf{ZCY}+\mathbf{T})(\mathbf{YCY}+\mathbf{S})^{-1}\times(\mathbf{YCZ}+\mathbf{T}^\dagger)]\mathbf{e}, \quad (4)$$

from which we may obtain the phonon frequencies in the usual manner. We note that the shell-charges Y_κ are actually fictitious charges and so are the shell dis-

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[29] W. C. Cochran and C. J. Phillips, Phys. Rev. **134**, A1402 (1964).

placements, the physically meaningful quantities being of course the dipole moment polarization vectors $\mathbf{w}$. It is therefore convenient to eliminate these from Eqs. (3), by defining new short-range bonding coefficients $\mathbf{T}'$, $\mathbf{S}'$ related to the SM bonding coefficients by

$$\mathbf{T}=\mathbf{T}'\mathbf{Y}, \tag{5a}$$

$$\mathbf{S}=\mathbf{Y}\mathbf{S}'\mathbf{Y}. \tag{5b}$$

In terms of these, Eqs. (3) become

$$\omega^2\mathbf{M}\mathbf{e}=(\mathbf{ZCZ}+\mathbf{R})\mathbf{e}+(\mathbf{ZC}+\mathbf{T}')\mathbf{w}, \tag{6a}$$

$$0=(\mathbf{CZ}+\mathbf{T}'^{\dagger})\mathbf{e}+(\mathbf{C}+\mathbf{S}')\mathbf{w}. \tag{6b}$$

It is important to note that in practice, the elimination of the quantities $\mathbf{w}$ leads to two types of nonuniqueness in the SM bonding coefficients if one wishes to work back from the dispersion relations to obtain the latter quantities. In the first place, we note that if $\mathbf{F}$ is any $3r\times 3r$ matrix which is a periodic function of $\mathbf{q}$ and satisfies the same symmetry requirements as the $\mathbf{R}$, $\mathbf{S}'$, and $\mathbf{T}'$ matrices, then the transformation

$$(\mathbf{ZC}+\mathbf{T}')\rightarrow(\mathbf{ZC}+\mathbf{T}')\mathbf{F}, \tag{7a}$$

$$(\mathbf{C}+\mathbf{S}')\rightarrow\mathbf{F}(\mathbf{C}+\mathbf{S}')\mathbf{F} \tag{7b}$$

will not affect the phonon frequencies or eigenvectors. Further, if $\mathbf{F}=1$ for $\mathbf{q}\rightarrow 0$, the transformations in Eqs. (7) will not affect the static polarizabilities of the atoms either. Hence, the SM which is fitted to these polarizabilities and the phonon frequencies will not be unique relative to such a transformation. The nonuniqueness of the shell charges Y_κ as exemplified by the transformation from Eqs. (3) to Eqs. (6) is just a trivial example of this where $\mathbf{F}$ is in fact the constant diagonal matrix $\mathbf{Y}$. In this case the physical quantity $\mathbf{w}$ is unchanged by such a transformation, but in the most general case [Eqs. (7)] it may not be unchanged. Also, in general, the transformations in Eqs. (7) may change the values of both the Coulomb and short-range parts of the "atom-shell" and "shell-shell" bonding coefficients. To eliminate this lack of uniqueness, the conventional SM fits to the experimental data usually assume $\mathbf{R}=\mathbf{S}=\mathbf{T}$ for all $\mathbf{q}$, where these are the short-range bonding coefficients in Eqs. (3). We shall presently derive quantum-mechanically based expressions for these coefficients which do indeed exhibit some similarity between them but do not justify making them equal.

Secondly, we note that the division of the valence charge density perturbation into a bound or rigid-atom part and a dipolar part may be made more generally than in the case of the conventional SM. In the latter, the restriction to the case where the bound part represents the rigid motion of *all* the valence charge within the whole subcell and the dipolar part represents the rest of the perturbation is made by imposing the particular form which the conditions of translational invariance take in this case, namely,

$$\lim_{\mathbf{q}\to 0}\sum_{\kappa'}(\mathbf{ZCY}+\mathbf{T})_{\alpha\beta}{}^{\kappa\kappa'}=0 \tag{8a}$$

and

$$\lim_{\mathbf{q}\to 0}\sum_{\kappa'}(\mathbf{ZCZ}+\mathbf{R})_{\alpha\beta}{}^{\kappa\kappa'}=0, \tag{8b}$$

implying that for $\mathbf{q}=0$ there is a solution to Eqs. (3) for which $u_{\kappa,\alpha}{}^{l}=$ a constant, $w_{\kappa,\alpha}{}^{l}=0$, and $\omega=0$.

On the other hand, it may be more convenient to split the perturbation in valence charge density more generally into a bound part corresponding to the rigid motion of the valence charge within a volume V_0 (not necessarily the whole subcell) surrounding the core, and a deformation part representing the rest of the perturbation. This was the approach from which the formalism in I was developed. If the deformation part now can be identified with a dipolar deformation, the SM equations of motion, as represented by Eqs. (3), would still be true but the quantities $\mathbf{w}'$, $\mathbf{Z}$, $\mathbf{R}$, $\mathbf{S}$, and $\mathbf{T}$ would obviously have different meanings. For instance, $\mathbf{Z}$ would now represent only the total valence charge inside V_0 and not the whole ionic charge. As we shall see later, it is quite possible that the dipolar approximation is better satisfied by not choosing V_0 to be the whole subcell volume, and there is experimental evidence[14,17,18] that SM fits for ionic crystals tend to favor ionic charges smaller than the actual ionic charges. The condition of translational invariance in the general case only requires that the over-all dynamical matrix for the atoms $D_{\alpha\beta}{}^{\kappa\kappa'}(q)$ [defined in Eq. (4)] satisfies

$$\lim_{\mathbf{q}\to 0}\sum_{\kappa'}D_{\alpha\beta}(\mathbf{q})_{\alpha\beta}{}^{\kappa\kappa'}=0. \tag{9}$$

In our treatment we shall therefore derive the SM equations as represented by Eqs. (3) in the above, more general, sense.

Finally, we discuss the relationship of the SM to the pseudopotential method. As stated in the Introduction, our formalism as developed in I is based on the fact that by explicitly building the rigid motion of the bound part into the perturbed valence charge density, the effect of the perturbation on the remainder may be expressed in terms of a weak residual potential not involving the deep potential well due to the cores. (This is very similar to the use of pseudopotentials in lattice-dynamics calculations for simple metals, but is more general in nature.) Since we intend to derive the SM from this formalism, the SM should also exhibit this elimination of the strongest part of the interaction between its cores and shells. The core-shell bonding coefficients depend on the matrices $\mathbf{C}$ and $\mathbf{T}$. It is interesting to note that $\mathbf{C}$ specifically eliminates the Coulomb interaction between a core and the shell in its own subcell. This is the familiar elimination of the "exciting field" in a unit cell in evaluating dipolar sums as discussed by Born and Huang.[30] $\mathbf{T}$ contains short-range interactions be-

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[30] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).

tween nearest neighbors, and the interaction between a core and its own shell is represented by an isotropic spring of force constant k, which merely contributes a constant to the bonding coefficient. Thus the strong short-range part of the ion-electron interaction has been effectively "transformed away" in the SM formalism and for the same general reasons as in our quantum-mechanical treatment.

III. SELF-CONSISTENT FIELD EQUATIONS AND THE DIPOLAR APPROXIMATION

We now briefly describe the results obtained in I for the self-consistent perturbed charge density for a crystal with one atom per unit cell. Strictly speaking, the SM has never been applied to monatomic crystals, but we shall continue to assume one atom per unit cell for the purpose of deriving the SM equations in order to keep the notation from becoming too complicated. However, we shall not assume a neutral unit cell as in a metal. The generalization to the case of crystals with basis is then straightforward and is made in Sec. IV.

In I, we split the first-order term in a Born-Oppenheimer expansion for the perturbed valence-electron charge density into two parts:

$$\Delta\rho(\mathbf{r})=\Delta\rho^{(0)}(\mathbf{r})+\Delta\rho_d(\mathbf{r}), \qquad (10)$$

where $\Delta\rho^{(0)}(\mathbf{r})$ describes the first-order change due to a rigid movement along with the core of the valence charge within some characteristic volume V_0 surrounding the core and is designated as the bound part, defined by

$$\Delta\rho^{(0)}(\mathbf{r})=-\sum_l \frac{\partial}{\partial x_\alpha}\rho(\mathbf{r}-\mathbf{r}_l)u_\alpha{}^l, \qquad (11)$$

where $\rho(\mathbf{r}-\mathbf{r}_l)$ describes that function which is equal to the unperturbed valence charge distribution inside the volume V_0 around the lth atom, and is zero outside.

$\Delta\rho_d(\mathbf{r})$ represents the rest of the perturbation and is designated as the deformation part.

By using the Schrödinger equation to transform the total self-consistent electron-ion matrix element, and applying self-consistent Born-Oppenheimer perturbation theory, we obtained $\Delta\rho(\mathbf{r})$ back in the assumed form of Eq. (10). Thus we had effectively a self-consistency equation for $\Delta\rho_d(\mathbf{r})$ which was written as

$$\begin{aligned}\Delta\rho_d(\mathbf{q}+\mathbf{H})=\sum_{\mathbf{H}'}\big[&\Omega v(\mathbf{q}+\mathbf{H}')\Delta\rho_d(\mathbf{q}+\mathbf{H}')\\ &-i(N\Omega)^{1/2}Q_\mathbf{q}\sum_\alpha(\mathbf{q}+\mathbf{H}')_\alpha e_\alpha W'(\mathbf{q}+\mathbf{H}')\big]\\ &\times\chi(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')+\sum_{kk'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\\ &\times M_{k'k}\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle, \qquad (12)\end{aligned}$$

where ψ_k represents the valence wave function with energy E_k and occupation number $n(k)$, $\Delta\rho_d(\mathbf{K})$ represents the Fourier transform of $\Delta\rho_d(\mathbf{r})$, $\mathbf{H}$ and $\mathbf{H}'$ represent reciprocal lattice vectors, and $\chi(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')$ is defined by

$$\begin{aligned}\chi(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')=&\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\\ &\times\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H}')\cdot\mathbf{r}}|\psi_k\rangle. \qquad (13)\end{aligned}$$

(The prime over the summation means the terms for which $k=k'$ are to be excluded from the sum.) $W'(\mathbf{K})$ is the Fourier transform of the potential $W'(\mathbf{r}-\mathbf{r}_l)$ defined as

$$W'(\mathbf{r}-\mathbf{r}_l)=\phi_t(\mathbf{r}-\mathbf{r}_l)-[V(\mathbf{r})-V(r_s)] \qquad (14\text{a})$$

for $\mathbf{r}$ inside $V_0(l)$, and

$$W'(\mathbf{r}-\mathbf{r}_l)=\phi_t(\mathbf{r}-\mathbf{r}_l) \qquad (14\text{b})$$

for $\mathbf{r}$ outside $V_0(l)$, where $\phi_t(\mathbf{r}-\mathbf{r}_l)$ represents the potential which a valence electron sees due to the whole pseudoatom inside the volume V_0, i.e., the core plus the unperturbed valence charge density inside V_0; $V(r_s)$ is the value of the crystal potential $V(\mathbf{r})$ (assumed spherically symmetric) on the surface of the volume V_0, and $v(\mathbf{r}-\mathbf{r}')$ is the unscreened electron-electron interaction including exchange and correlation effects in the local approximation.[1] Finally, $M_{k'k}$ is defined by

$$\begin{aligned}M_{k'k}=\frac{\hbar^2}{2m}\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}&d\mathbf{r}\\ &\times\left(\nabla^2\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k-\psi_{k'}{}^*\nabla^2\frac{\partial}{\partial x_\alpha}\psi_k\right) \qquad (15)\end{aligned}$$

or

$$\begin{aligned}M_{k'k}=\frac{\hbar^2}{2m}\sum_{l,\alpha}u_\alpha{}^l\int_{S_0(l)}&dS\\ &\times\left(\frac{\partial}{\partial n}\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k-\psi_{k'}{}^*\frac{\partial^2}{\partial n\partial x_\alpha}\psi_k\right), \qquad (16)\end{aligned}$$

where $\partial/\partial n$ denotes differentiation normal to the surface $S_0(l)$. Using the formula for the $u_\alpha{}^l$, $M_{k'k}$ was shown in I to be of the form

$$\begin{aligned}M_{k'k}=&\,i(N/\Omega)^{1/2}\\ &\times[Q_\mathbf{q}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+Q_\mathbf{q}{}^*\Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}}]\sum_\alpha e_\alpha I_\alpha{}^{k'k}, \qquad (17)\end{aligned}$$

where the symbol $\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}$ denotes unity if $\mathbf{k}'-\mathbf{k}=\mathbf{q}$ modulo a reciprocal lattice vector and zero otherwise, and $\mathbf{k},\mathbf{k}'$ denote the Bloch wave vectors of states k,k', respectively, in the reduced-zone scheme. Explicit expressions for $I_\alpha{}^{k'k}$ in the case where the wave functions were calculated by means of the augmented-plane-wave (APW) formalism, and the volumes V_0 were taken to be muffin tins surrounding the cores, were derived in Appendix A of I.

Note that $W'(\mathbf{r}-\mathbf{r}_l)$ is a weak potential which has the deep potential well near the core subtracted out; it is continuous at the surface $|\mathbf{r}-\mathbf{r}_l|=r_s$ of V_0, and for a metal, for instance, tends to become very small if V_0 is taken large enough so that the pseudoatom inside is almost neutral. Thus, in general, $W'(\mathbf{K})$ will be smoothly damped for large $\mathbf{K}$, and the sum over $\mathbf{H}'$ is expected to be fairly well convergent. Note that Eq. (12) has the form of a general self-consistency equation for $\Delta\rho_d$, where the driving perturbation is the direct interaction between the valence electrons and the pseudoatoms through the potential $W'(\mathbf{r}-\mathbf{r}_l)$ as well as an overlap or mechanical interaction with them through the term involving $M_{k'k}$. The latter give rise to the deformation dipoles of Hardy's model.[19]

Let us define a polarization wave $P(\mathbf{r})$ associated with the deformation part $\Delta\rho_d(\mathbf{r})$ of the perturbed charge density by means of the relation

$$-\nabla\cdot P(\mathbf{r})=\Delta\rho_d(\mathbf{r}). \qquad (18)$$

As is well known, such an equation does not define $P(\mathbf{r})$ uniquely. This point is discussed further in the last section. The Fourier transform of Eq. (18) is

$$-i\sum_{\alpha} K_\alpha P_\alpha(\mathbf{K})=\Delta\rho_d(\mathbf{K}), \qquad (19)$$

where we have defined $P(\mathbf{K})$ by

$$\mathbf{P}(\mathbf{r})=\sum_{\mathbf{K}} \mathbf{P}(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}. \qquad (20)$$

The simplest procedure is to make the literal point-dipole assumption for $\mathbf{P}(\mathbf{r})$ as in the conventional SM, i.e., to assume that we may write

$$P_\alpha(\mathbf{r})=(N\Omega)^{-1/2}\sum_{l,\alpha}\left[Q_{\mathbf{q}}w_\alpha e^{i\mathbf{q}\cdot\mathbf{r}_l}+Q_{\mathbf{q}}^*w_\alpha^*e^{-i\mathbf{q}\cdot\mathbf{r}_l}\right]\delta(\mathbf{r}-\mathbf{r}_l). \qquad (21)$$

Note that we cannot, as we shall see later, assume that the w_α are real, even though for a Bravais lattice we can take the e_α as real.

In this case,

$$P_\alpha(\mathbf{K})=(N/\Omega)^{1/2}\left[Q_{\mathbf{q}}w_\alpha\delta_{\mathbf{K},\mathbf{q}+\mathbf{H}}+Q_{\mathbf{q}}^*w_\alpha^*\delta_{-\mathbf{K},\mathbf{q}+\mathbf{H}}\right]. \qquad (22)$$

Substituting this into Eq. (19) and then into Eq. (12), we may show by means of certain transformations that Eq. (12) leads to the shell equations of the SM provided $\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')$ satisfies a certain relation. However, this relation is unnecessarily restrictive because of the rather unrealistic nature of the point-dipole approximation which completely neglects local-field corrections.[25,31] It was pointed out by Cochran and Phillips[29] that such corrections could be incorporated into the SM without changing the general form of the SM equations by postulating a form factor for the shells. Accordingly, we assume $P_\alpha(\mathbf{K})$ to be of the much more general form

$$P_\alpha(\mathbf{K})=(N/\Omega)^{1/2}\left[Q_{\mathbf{q}}w_\alpha\delta_{\mathbf{K},\mathbf{q}+\mathbf{H}}f(\mathbf{K})+Q_{\mathbf{q}}^*w_\alpha^*\delta_{-\mathbf{K},\mathbf{q}+\mathbf{H}}f^*(\mathbf{K})\right], \qquad (23)$$

where the function $f(\mathbf{K})$ is left undefined at present.

Substituting this form in Eq. (19), we get

$$\Delta\rho_d[\mathbf{q}+\mathbf{H}]=-iQ_{\mathbf{q}}(N/\Omega)^{1/2}\times\sum_{\alpha}(\mathbf{q}+\mathbf{H})_\alpha w_\alpha f(\mathbf{q}+\mathbf{H}) \qquad (24\text{a})$$

and

$$\Delta\rho_d[-(\mathbf{q}+\mathbf{H})]=iQ_{\mathbf{q}}^*(N/\Omega)^{1/2}\times\sum_{\alpha}(\mathbf{q}+\mathbf{H})_\alpha w_\alpha^* f^*(\mathbf{q}+\mathbf{H}). \qquad (24\text{b})$$

We now use a result derived by Pines,[32]

$$\langle\psi_k|e^{i\mathbf{K}\cdot\mathbf{r}}|\psi_{k'}\rangle=\frac{\hbar}{m}\sum_{\alpha} K_\alpha\frac{\langle\psi_k|p_\alpha e^{i\mathbf{K}\cdot\mathbf{r}}|\psi_{k'}\rangle}{E_k-E_{k'}+\hbar^2K^2/2m}, \qquad (25)$$

where p_α is the operator for electron momentum, and m is the electron mass. Equation (25) is an identity valid for any eigenfunctions of a crystal Hamiltonian. Using Eq. (25) we may write $\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')$ as defined in Eq. (13) in the form

$$\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')=-\sum_{\alpha\beta}(\mathbf{q}+\mathbf{H})_\alpha a'_{\alpha\beta}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')(\mathbf{q}+\mathbf{H}')_\beta, \qquad (26)$$

where we define the microscopic polarizability tensor per unit volume of crystal by

$$a'_{\alpha\beta}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')=\frac{\hbar^2}{m^2}\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\times\left\{\left(E_k-E_{k'}+\frac{\hbar^2(\mathbf{q}+\mathbf{H})^2}{2m}\right)\left(E_{k'}-E_k+\frac{\hbar^2(\mathbf{q}+\mathbf{H}')^2}{2m}\right)\right\}^{-1}\times\langle\psi_k|p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle\langle\psi_{k'}|p_\beta e^{i(\mathbf{q}+\mathbf{H}')\cdot\mathbf{r}}|\psi_k\rangle. \qquad (27)$$

For the case $\mathbf{H}=\mathbf{H}'=0$, and $\mathbf{q}\rightarrow 0$. we see that this reduces to the ordinary static polarizability tensor $a_{\alpha\beta}(0)$ for the crystal. We note here that Eq. (27) is completely general and applies also to the case of crystals with more than one atom per unit cell. We shall use it later to discuss what is meant by polarizabilities which we can ascribe to particular ions in the cell.

We now make the central approximation which leads to the SM equations and from which Eq. (12) may be solved without the enormous difficulty of inverting a dielectric matrix as required by the rigorous solution discussed in I. This consists of assuming that the

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[31] M. Lax, *Lattice Dynamics* (Pergamon Press, Inc., New York, 1965), p. 184.

[32] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 171, Eq. (4-12).

polarizability tensor may be factorized as

$$a_{\alpha\beta}(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')=f(\mathbf{q}+\mathbf{H})a'_{\alpha\beta}(\mathbf{q})f^*(\mathbf{q}+\mathbf{H}')\,. \quad (28)$$

It is this factorization which makes a solution of Eq. (12) possible. The approximation (28) is equivalent to putting

$$\chi(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')=-\sum_{\alpha\beta}\,(\mathbf{q}+\mathbf{H})_\alpha f(\mathbf{q}+\mathbf{H}) \times a'_{\alpha\beta}(\mathbf{q})f^*(\mathbf{q}+\mathbf{H}')(\mathbf{q}+\mathbf{H}')_\beta\,. \quad (29)$$

Note that the approximation in Eq. (29) represents the other extreme limit from the case of nearly-free electrons, where the off-diagonal terms in $\chi(\mathbf{q}+\mathbf{H},\,\mathbf{q}+\mathbf{H}')$ are neglected altogether. For most solids, the latter underestimates the local field corrections, while Eq. (29) probably overestimates these corrections.

The validity of the approximation in Eqs. (28) and (29) is discussed in detail in the Appendix, and depends on the detailed band structure of the solid in question. For instance, it is shown that it is rigorously true in the tight-binding limit of two flat bands of importance. Very recently, Pick, Cohen, and Martin[33] have arrived at a more general formulation of the approximation embodied above, and also discussed its application to the lattice dynamics of insulators.

Let us define a polarizability tensor per unit cell

$$\mathbf{a}=(1/N)\mathbf{a}'\,, \quad (30)$$

where $\mathbf{a}'$ is the matrix defined by Eq. (A8) and appears on the right in Eq. (28). Note that $\mathbf{a}$ is a Hermitian matrix. Let us also define matrices **V**, **W**, and **J** by the equations

$$V_{\alpha\beta}(\mathbf{q})=N\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\alpha(\mathbf{q}+\mathbf{H})_\beta f(\mathbf{q}+\mathbf{H}) \times f^*(\mathbf{q}+\mathbf{H})\Omega v(\mathbf{q}+\mathbf{H})\,, \quad (31)$$

$$W_{\alpha\beta}(\mathbf{q})=N\sum_{H}(\mathbf{q}+\mathbf{H})_\alpha(\mathbf{q}+\mathbf{H})_\beta \times f(\mathbf{q}+\mathbf{H})\Omega W'(\mathbf{q}+\mathbf{H})\,, \quad (32)$$

and

$$J_{\alpha\beta}(\mathbf{q})=\frac{\hbar}{m}N\sum_{k,k'}{}'\,\frac{1}{\Omega}\,\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^* \times\left[\int_0 dr\;\phi_{k'}{}^*(\mathbf{r})p_\beta\phi_k(\mathbf{r})/(E_k-E_{k'})\right]\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}\,, \quad (33)$$

where the integration is over the origin unit cell. If we now substitute Eq. (24a) as a trial solution in Eq. (12) and use Eqs. (17), (A5), and (29), we find that the resulting equation is satisfied if

$$\mathbf{w}+\mathbf{a}(\mathbf{V}\mathbf{w}+\mathbf{W}^\dagger\mathbf{e})+\mathbf{J}^\dagger\mathbf{e}=0\,, \quad (34)$$

where $\mathbf{w}$ and $\mathbf{e}$ denote the polarization vectors w_α and e_α, respectively. The dagger symbol denotes the Hermitian conjugate of a matrix. We may rewrite this equation as

$$0=(\mathbf{W}+\mathbf{J}\mathbf{a}^{-1})^\dagger\mathbf{e}+(\mathbf{V}+\mathbf{a}^{-1})\mathbf{w}\,, \quad (35)$$

where we see that it has the familiar form of the shell equation [compare Eq. (6b)]. Note that the matrix **V** is Hermitian but that the matrices **W** and **J** are not. However, all the matrices have the correct property that the transformation $\mathbf{q}\to-\mathbf{q}$ converts them into their complex conjugates. This ensures that $\Delta\rho(\mathbf{r})$ is real. Because $W'(\mathbf{r}-\mathbf{r}_l)$ is Coulomb-like at large distances with a charge $=Z$, the total charge on the pseudoatom in the volume V_0, and because $v(\mathbf{r}-\mathbf{r}')$ is also Coulomb-like at large distances (with unit charge), it follows that we may write

$$\mathbf{W}^\dagger=\mathbf{C}\mathbf{Z}+\mathbf{U}'^\dagger \quad (36)$$

and

$$\mathbf{V}=\mathbf{C}+\mathbf{V}'\,, \quad (37)$$

where $\mathbf{U}'$ and $\mathbf{V}'$ are the short-range parts of **W** and **V** resulting from the effect of the form factors $f(\mathbf{q}+\mathbf{H})$ and departures of the potentials $\mathbf{W}'$ and $\mathbf{v}$ from Coulomb potentials at short distances due to exchange and correlation effects. The matrices **C** and **Z** were defined in Sec. II. Therefore, we finally obtain

$$O=[\mathbf{C}\mathbf{Z}+(\mathbf{U}'+\mathbf{J}\mathbf{a}^{-1})^\dagger]\mathbf{e}+[\mathbf{C}+(\mathbf{V}'+\mathbf{a}^{-1})]\mathbf{w}\,. \quad (38)$$

Thus the short-range or mechanical coupling between the dipole moments and the ions is through $\mathbf{U}'$ and the overlap matrix $\mathbf{J}\mathbf{a}^{-1}$. Note that if the wave functions were well localized so that there was no overlap, the $I_\beta{}^{k'k}$ would vanish and hence this term as well. This point is similar to that discussed in more detail in I. The "first-principles" calculation of the overlap interaction involves calculating the $I_\beta{}^{k'k}$ (as discussed in Appendix A of I), the dipole oscillator strengths, and the $\mathbf{q}$-dependent polarizability from Eq. (A8). The short-range shell-shell or dipole-dipole coupling is through $\mathbf{V}'$ and the possible $\mathbf{q}$ dependence of $a'_{\alpha\beta}(\mathbf{q})$. For the case described previously, namely, only two flat bands with tightly bound atomiclike orbitals, the $\mathbf{q}$ dependence of $a_{\alpha\beta}'$ disappears, as assumed in the conventional SM, although the form factors $f(\mathbf{q}+\mathbf{H})$ still give a possible $\mathbf{q}$ dependence to $\mathbf{V}'$. It is interesting to note that for many ionic crystals, the mechanical dipole-dipole interactions are not important in getting a good fit to the experimental data,[34] but in other cases shell-shell force constants have to be assumed, presumably to take the above $\mathbf{q}$ dependence into account.

IV. EQUATIONS OF MOTION FOR CORES

In I, we obtained by means of a self-consistent Born-Oppenheimer expansion the potential function for the vibrating lattice up to second order in the nuclear dis-

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[33] R. Pick, M. H. Cohen, and R. M. Martin, in *Proceedings of IAEA Symposium on Inelastic Neutron Scattering, Copenhagen, Denmark* (International Atomic Energy Agency, Vienna, 1968).

[34] J. R. Hardy (private communication).

placements. This was written as

$$\Phi^{(2)}=\tfrac{1}{2}\sum_{\substack{l,l'\\ \alpha\beta}}\varphi_{\alpha\beta}{}^{ll'}u_\alpha{}^l u_\beta{}^{l'}+Q_{\mathbf{q}}Q_q{}^*\sum_{\alpha\beta}e_\alpha e_\beta R_{\alpha\beta}{}^{(0)}(\mathbf{q})$$
$$+\Bigg[\tfrac{1}{2}i(N\Omega)^{1/2}Q_{\mathbf{q}}{}^*\sum_{\mathbf{H},\alpha}e_\alpha[\Delta\rho_d(\mathbf{q}+\mathbf{H})]$$
$$\times\Bigg((\mathbf{q}+\mathbf{H})_\alpha\Omega W'(\mathbf{q}+\mathbf{H})+\sum_{k;k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}$$
$$\times(I_\alpha{}^{k'k})^*\Omega v(\mathbf{q}+\mathbf{H})\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\Bigg)+\text{c.c.}\Bigg], \quad (39)$$

where we have chosen to write the deformation part explicitly in terms of $\Delta\rho_d(\mathbf{q}+\mathbf{H})$ rather than in terms of the related functions $F_\alpha(\mathbf{q}+\mathbf{H})$ as in Eq. (66) of I. In Eq. (39), $\phi_{\alpha\beta}{}^{ll'}$ are force constants representing direct interactions between the pseudoatoms in the volumes V_0 in the lth and l'th unit cells, respectively. They may be split up into an electrostatic force constant and a short-range force constant due to the exchange and correlation corrections to the direct interaction $\mathbf{v}(\mathbf{r}-\mathbf{r}')$ between valence electrons. Thus,

$$\phi_{\alpha\beta}{}^{ll'}(l\neq l')=-\left[\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\left(\frac{Z^2e^2}{r}\right)\right]_{\mathbf{r}=\mathbf{r}_l-\mathbf{r}_{l'}}-\int_{V_0(l)}d\mathbf{r}$$
$$\times\int_{V_0(l')}d\mathbf{r}'\rho(\mathbf{r}-\mathbf{r}_l)\rho(\mathbf{r}'-\mathbf{r}'_{l'})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v_{xc}(\mathbf{r}-\mathbf{r}'), \quad (40)$$

where Z is the total charge on the pseudoatom inside V_0. For $l=l'$, $\phi_{\alpha\beta}{}^{ll'}$ contributes merely a constant to the dynamical matrix which may be fixed by the translational invariance condition as discussed in I. $R_{\alpha\beta}{}^{(0)}(\mathbf{q})$ corresponds to the overlap interaction as discussed in I and is given by

$$R_{\alpha\beta}{}^{(0)}(\mathbf{q})=\Bigg(\tfrac{1}{2}N\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*$$
$$\times\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\beta\Omega W'(\mathbf{q}+\mathbf{H})\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle$$
$$-\tfrac{1}{2}N\sum_{k,k'}\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*I_\beta{}^{k'k}$$
$$\times\tfrac{1}{2}(\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+\Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}})\Bigg)+\text{c.c.}+C, \quad (41)$$

where C is a constant which may be incorporated formally in the term involving $\phi_{\alpha\beta}{}^{ll}$ and hence need not be evaluated explicitly. It is to be noted that the overlap interaction $R_{\alpha\beta}{}^{(0)}(\mathbf{q})$ actually contains a long-range part in the term involving $W'(\mathbf{q}+\mathbf{H})$ since the potential $W'(\mathbf{r}-\mathbf{r}_l)$ is Coulomb-like at large distances. The physical reasons for this term are as follows. This term represents the overlap interaction between the core and the charge distortion in its own cell caused by interaction with the motion of cores in other cells through the potential $W'(\mathbf{r}-\mathbf{r}_l)$. (See the discussion in I.) This causes an effective coupling between the cores through the charge distortion. Unfortunately the form of the overlap interaction does not lend itself to expressing it in terms of dipole moments of the perturbed charge distribution, so for the present we shall have to keep this term as a long-range, core-core interaction. Later on we shall see how it nevertheless fits into the SM formalism and may be interpreted as part of the core-shell-core interaction.

Equation (39) shows that the contributions to the dynamical matrix falls into two parts—one associated with the bound part and involving the direct interaction between the pseudoatoms, and another involving the part $\Delta\rho_d(\mathbf{r})$ of the perturbed charge density.

The expression for $\Phi^{(2)}$ given in Eq. (39) is quite rigorous. To obtain the SM equations of motion for the cores, we merely substitute the approximate form of the solution given in Eqs. (24) for $\Delta\rho_d(\mathbf{q}+\mathbf{H})$, namely, the solution obtained on the dipolar assumption. To be consistent we must also replace the matrix elements of the form $\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle$ by the expressions given in Eqs. (A5) and (A6) as required by the dipolar assumption.

Let us define a matrix $\mathbf{R}'$ by the relation

$$R_{\alpha\beta}{}'(\mathbf{q})=-N\sum_{k,k'}\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*I_\beta{}^{k'k}$$
$$\times\tfrac{1}{2}(\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+\Delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}}). \quad (42)$$

We note that according to Eq. (A6),

$$N\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\beta\Omega W'(\mathbf{q}+\mathbf{H})$$
$$\times\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle=-\sum_\gamma\Bigg(\frac{\hbar}{m}N\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}$$
$$\times(I_\alpha{}^{k'k})^*\int_0 d\mathbf{r}\frac{\phi_{k'}{}^*(\mathbf{r})p_\gamma\phi_k(\mathbf{r})}{E_k-E_{k'}}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}\Bigg)N\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\gamma$$
$$\times(\mathbf{q}+\mathbf{H})_\beta f^*(\mathbf{q}+\mathbf{H})\Omega W'(\mathbf{q}+\mathbf{H})=-(\mathbf{J}\mathbf{W}^*)_{\alpha\beta}, \quad (43)$$

where the matrix $\mathbf{J}$ was defined in Eq. (33), and $\mathbf{W}^*$ denotes the complex conjugate of the matrix $\mathbf{W}$ defined in Eq. (32). Similar results hold for the term involving $\Delta\rho_d(\mathbf{q}+\mathbf{H})$ in Eq. (39).

Using all these results, we finally obtain

$$\Phi^{(2)}=Q_{\mathbf{q}}Q_{\mathbf{q}}{}^*[\mathbf{e}\cdot(\mathbf{D}^{(0)}+\mathbf{R}')\cdot\mathbf{e}-\tfrac{1}{2}\mathbf{e}\cdot(\mathbf{J}^*\mathbf{W}+\mathbf{J}\mathbf{W}^*)\cdot\mathbf{e}$$
$$+\tfrac{1}{2}\mathbf{e}\cdot(\mathbf{W}^*-\mathbf{J}^*\mathbf{V})\cdot\mathbf{w}^*+\tfrac{1}{2}\mathbf{e}\cdot(\mathbf{W}-\mathbf{J}\mathbf{V})\cdot\mathbf{w}], \quad (44)$$

where

$$D_{\alpha\beta}{}^{(0)}(\mathbf{q})=\sum_{l'}\phi_{\alpha\beta}{}^{ll'}e^{i\mathbf{q}\cdot(\mathbf{r}_{l'}-\mathbf{r}_l)}. \quad (45)$$

(Note that the matrix $\mathbf{V}$ is real.) Now substituting the solution of Eq. (35) for $\mathbf{w}$, we obtain

$$\begin{aligned}\Phi^{(2)}=Q_{\mathbf{q}}Q_{\mathbf{q}}{}^{*}\mathbf{e}\cdot[\mathbf{D}^{(0)}+\mathbf{R}'-\tfrac{1}{2}\mathbf{J}^{*}\mathbf{W}-\tfrac{1}{2}\mathbf{J}\mathbf{W}^{*}\\ -\tfrac{1}{2}(\mathbf{W}^{*}-\mathbf{J}^{*}\mathbf{V})(\mathbf{V}+\mathbf{a}^{-1})^{-1}(\mathbf{W}^{*}+\mathbf{J}^{*}\mathbf{a}^{-1})^{\dagger}\\ -\tfrac{1}{2}(\mathbf{W}-\mathbf{J}\mathbf{V})(\mathbf{V}+\mathbf{a}^{-1})^{-1}(\mathbf{W}+\mathbf{J}\mathbf{a}^{-1})^{\dagger}]\cdot\mathbf{e}.\end{aligned}\tag{46}$$

We note that

$$\begin{aligned}&-\tfrac{1}{2}[\mathbf{W}-\mathbf{J}\mathbf{V}][\mathbf{V}+\mathbf{a}^{-1}]^{-1}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}\\ &=-\tfrac{1}{2}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}][\mathbf{V}+\mathbf{a}^{-1}]^{-1}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}\\ &\qquad+\tfrac{1}{2}\mathbf{J}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}\\ &=-\tfrac{1}{2}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}][\mathbf{V}+\mathbf{a}^{-1}]^{-1}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}\\ &\qquad+\tfrac{1}{2}\mathbf{J}\mathbf{W}^{*}+\tfrac{1}{2}\mathbf{J}\mathbf{a}^{-1}\mathbf{J}^{\dagger},\end{aligned}\tag{47}$$

since $\mathbf{W}^{\dagger}=\mathbf{W}^{*}$ [see Eq. (32)]. Using Eq. (47), we obtain for Eq. (46)

$$\begin{aligned}\Phi^{(2)}=Q_{\mathbf{q}}Q_{\mathbf{q}}{}^{*}\mathbf{e}\cdot(\mathbf{D}^{(0)}+\mathbf{R}'+\tfrac{1}{2}[\mathbf{J}\mathbf{a}^{-1}\mathbf{J}^{\dagger}+\mathbf{J}^{*}\mathbf{a}^{-1}(\mathbf{J}^{*})^{\dagger}]\\ -\tfrac{1}{2}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}][\mathbf{V}+\mathbf{a}^{-1}][\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}\\ -\tfrac{1}{2}[\mathbf{W}^{*}+\mathbf{J}^{*}\mathbf{a}^{-1}][\mathbf{V}+\mathbf{a}^{-1}][\mathbf{W}^{*}+\mathbf{J}^{*}\mathbf{a}^{-1}]^{\dagger})\cdot\mathbf{e}.\end{aligned}\tag{48}$$

For the case where the wave functions are such that the $\phi_k(\mathbf{r}-\mathbf{r}_l)$ in Eq. (A1) may be chosen to be real, it may also be shown that the matrices $\mathbf{J}$ and $\mathbf{W}$ are also real. Although it is difficult to prove this in the general case, we shall assume this to be true.

Then Eq. (48) gives us the equations of motion,[35]

$$\begin{aligned}M\omega^2\mathbf{e}=\mathbf{D}^{(0)}+\mathbf{R}'+\mathbf{J}\mathbf{a}^{-1}\mathbf{J}^{\dagger}\\ -[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}][\mathbf{V}+\mathbf{a}^{-1}]^{-1}[\mathbf{W}+\mathbf{J}\mathbf{a}^{-1}]^{\dagger}.\end{aligned}\tag{49}$$

Note that by Eqs. (45) and (40) we may write

$$\mathbf{D}^{(0)}=\mathbf{ZCZ}+\mathbf{X},\tag{50}$$

where $\mathbf{X}$ is the bonding coefficient between the pseudoatoms due to the short-range exchange and correlation correction to the bare interaction between the valence charge distributions. We thus see that Eq. (49) represents the exact form of the SM equations of motion once the $\mathbf{w}'$ have been eliminated from Eqs. (6a) and (6b). Equations (49) and (38) thus show that the assumption represented by Eq. (A4) is sufficient to obtain faithfully the exact form of the SM equations from the very general formalism developed in I, based on a self-consistent Born-Oppenheimer expansion. In the Appendix, it is also shown that the validity of the central assumption may be evaluated in terms of the band structure of the solid in question, and is likely to be reasonable for simple kinds of insulators with fairly large band gaps. This shows that the form of the SM equations is probably valid for such substances more generally than one might suppose from the way that the SM equations were originally set up,[16,17] namely, in terms of simple spring interactions between cores and fictitious massless shells. Indeed, the bonding coefficients that we have derived are more general than those one might obtain from the simple SM with the short-range core-core, core-shell, and shell-shell interactions represented by central interactions between nearest neighbors, and so on. This might explain some of the complicated sets of force constants needed to fit experimentally measured dispersion curves according to the SM. In fact, the explicit values for the matrices $\mathbf{R}$, $\mathbf{T}'$, and $\mathbf{S}'$ introduced in Eqs. (3), (5), and (6), are given by Eqs. (36)–(38), (49), and (50).

$$\mathbf{R}=\mathbf{X}+\mathbf{R}'+\mathbf{J}\mathbf{a}^{-1}\mathbf{J}^{\dagger},\tag{51}$$

$$\mathbf{T}'=\mathbf{U}'+\mathbf{J}\mathbf{a}^{-1},\tag{52}$$

$$\mathbf{S}'=\mathbf{V}'+\mathbf{a}^{-1},\tag{53}$$

where $\mathbf{X}$ was defined in Eq. (50), $\mathbf{R}'$ in Eq. (42), $\mathbf{J}$ in Eq. (33), $\mathbf{a}$ in Eq. (30), and $\mathbf{V}'$ and $\mathbf{U}'$ are, respectively, the short-range or non-Coulombic parts of the bonding coefficients $\mathbf{V}$ and $\mathbf{W}$ defined in Eqs. (31) and (32). We note that the matrices $\mathbf{R}$ and $\mathbf{S}'$ are Hermitian, but that $\mathbf{T}'$ is not, since the matrix $\mathbf{J}$ is not symmetric. Indeed there is no reason for it to be Hermitian since the form of Eq. (49) ensures that the dynamical matrix as a whole is Hermitian even if $\mathbf{J}$ is not. In the conventional SM, however, because $\mathbf{T}'$ is obtained in terms of force constants, it always comes out Hermitian (or, in the case of a monatomic lattice such as considered here, symmetric). Note that although $\mathbf{R}$, $\mathbf{T}'$, and $\mathbf{S}'$ exhibit some similarities, they are, in general, not equal. Further, as mentioned before, we have described the model in terms of pseudoatoms sitting inside a certain volume V_0 surrounding each core. If this volume V_0 is taken as the unit cell itself, we have the conventional SM division into a pure rigid atom and a pure dipole part of the perturbed charge density, and in this case it may be verified that the translational invariance conditions in Eq. (8) are satisfied. However, for calculational purposes it will be most convenient to take V_0 to be, for instance, the APW sphere centered on each lattice site, in which case Z is now not to be taken as the whole ionic charge. It should be noted that $\mathbf{R}$ contains a constant term in this case which ensures that over-all translational invariance is satisfied.

From what has been said it is clear that our quantum-mechanical SM, if parametrized, allows in principle a large number of parameters. The theoretical expressions derived above may, however, be of considerable use as a guide to the reasonableness of such parameters. Of course, the ideal test of the theory would be to calculate the bonding coefficients from the given theoretical expressions in terms of a band-structure calculation. Such a calculation is presently being attempted for a number of ionic crystals.

Before closing this section, we discuss the generalization of the above theory to the case of a crystal with more than one atom per unit cell. The results, which we state here without detailed proof, may be verified by going through the derivation given in these last two sections in the same way for the general case.

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[35] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1963).

Let us assume the lattice displacements are given by Eq. (1a). The ionic charge matrix **Z** now becomes a $3r\times 3r$ diagonal matrix $Z_\kappa\delta_{\kappa\kappa'}\delta_{\alpha\beta}$, where Z_κ is the charge inside the volume $V_0{}^\kappa$ in the κth subcell. The $3r\times 3r$ matrix **C** is now the standard electrostatic bonding coefficient for a lattice with basis. The matrix **X** is now calculated in terms of short-range force constants.

$$[\phi_{\alpha\beta}{}^{\kappa\kappa',ll'}]^x=-\int_{V_0(l,\kappa)}d\mathbf{r}\int_{V_0(l',\kappa')}d\mathbf{r}'\,\rho_\kappa(\mathbf{r}-\mathbf{r}_l-\mathbf{r}_\kappa)\times\rho_{\kappa'}(\mathbf{r}'-\mathbf{r}_{l'}-\mathbf{r}_{\kappa'})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v_{xc}(\mathbf{r}-\mathbf{r}'),\quad(54)$$

where $V_0(l,\kappa)$ denotes the volume $V_0{}^\kappa$ in the κth subcell of the lth unit cell, having an origin at $(\mathbf{r}_l+\mathbf{r}_\kappa)$, and $\rho_\kappa(\mathbf{r}-\mathbf{r}_l-\mathbf{r}_\kappa)$ denotes the valence charge distribution inside $V_0(l,\kappa)$. The generalizations of the matrices **V** and **W** are

$$V_{\alpha\beta}{}^{\kappa\kappa'}(\mathbf{q})=N\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\alpha(\mathbf{q}+\mathbf{H})_\beta e^{i\mathbf{H}\cdot(\mathbf{r}_\kappa-\mathbf{r}_{\kappa'})}f^\kappa(\mathbf{q}+\mathbf{H})\times[f^{\kappa'}(\mathbf{q}+\mathbf{H})]^*\Omega v(\mathbf{q}+\mathbf{H}),\quad(55)$$

$$W_{\alpha\beta}{}^{\kappa\kappa'}(\mathbf{q})=N\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\alpha(\mathbf{q}+\mathbf{H})_\beta e^{i\mathbf{H}\cdot(\mathbf{r}_\kappa-\mathbf{r}_{\kappa'})}f^\kappa(\mathbf{q}+\mathbf{H})\times\Omega W_{\kappa'}{}'(\mathbf{q}+\mathbf{H}),\quad(56)$$

where $f^\kappa(\mathbf{q}+\mathbf{H})$ is the form factor for the "shell" in the κth subcell, and may be evaluated from Eq. (A4) by replacing the integrals over the unit cell on the left-hand side by integrals over the κth subcell in the origin unit cell instead. We note that Eq. (A6) may now be generalized to obtain for the wave function ψ_k in the (l,κ) subcell,

$$\psi_k=(\Omega)^{-1/2}e^{i\mathbf{k}\cdot(\mathbf{r}_l+\mathbf{r}_\kappa)}\phi_k{}^\kappa(\mathbf{r}-\mathbf{r}_l-\mathbf{r}_\kappa).\quad(57)$$

In the tight-binding limit, $\phi_k{}^\kappa(\mathbf{r}-\mathbf{r}_l-\mathbf{r}_\kappa)$ represents the atomic orbital in the κth subcells for the state k and is negligible in other subcells for the same k. The generalization of **J** is

$$J_{\alpha\beta}{}^{\kappa\kappa'}(\mathbf{q})=-\frac{\hbar}{m}N\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\times e^{i\mathbf{H}\cdot(\mathbf{r}_\kappa-\mathbf{r}_{\kappa'})}(I_{\kappa,\alpha}{}^{k'k})^*\frac{1}{E_k-E_{k'}}\int_{(0,\kappa')}d\mathbf{r}\,\phi_k{}^{\kappa'}(\mathbf{r}-\mathbf{r}_{\kappa'})\times p_\alpha\phi_k{}^{\kappa'}(\mathbf{r}-\mathbf{r}_{\kappa'})\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}},\quad(58)$$

where the integral in the dipole matrix element is over the κ'th subcell in the origin unit cell, the $(I_{\kappa,\alpha}{}^{k'k})$ is evaluated from the surface integral over the surface of $V_0{}^\kappa$ in the κth subcell, and $-\mathbf{H}$ is the reciprocal lattice vector needed to connect $(\mathbf{k}'-\mathbf{k})$ to $\mathbf{q}$. (Note that $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{q}$ are all defined in the reduced-zone scheme.)

Finally the polarizability matrix $\mathbf{a}'$ defined in Eq. (A8) must be generalized to

$$(a')_{\alpha\beta}{}^{\kappa\kappa'}(\mathbf{q})=N^2\frac{\hbar^2}{m^2}\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\times e^{i\mathbf{H}\cdot(\mathbf{r}_\kappa-\mathbf{r}_{\kappa'})}r_{\kappa,\alpha}{}^{kk'}r_{\kappa',\beta}{}^{k'k}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}},\quad(59)$$

where $r_{\kappa,\alpha}{}^{k'k}$ is the α component of the dipole matrix element for the κth subcell, similar to the one entering Eq. (58) above. Note that there are, in general, interference or cross terms between different subcells in this polarizability matrix, except in the extreme tight-binding limit. At $\mathbf{q}\to 0$, the static polarizability per unit cell is obtained from Eq. (27) as

$$a_{\alpha\beta}(0)=\frac{1}{N}\sum_{k,k'}(a')_{\alpha\beta}{}^{kk'}(0),\quad(60)$$

so that if the interference terms are appreciable, we will not get additivity of ionic polarizabilities in the crystal. For $\mathbf{q}=0$, in fact, Eqs. (59) and (60) provide a rigorous expression for the static polarizability of a crystal in terms of the actual crystal wave functions (which are, in general, different from those of the free ions).

V. RELATION TO QUANTUM THEORY OF DIELECTRIC CONSTANT

We now discuss the relation between the dielectric constant obtainable from the SM and that obtainable from a band-structure calculation. We present here an extension of the ideas put forward by Cochran and Phillips.[29]

Let us consider the case where there is no motion of the cores, i.e., we discuss only the electronic part of the dielectric constant. Suppose that there is a weak external potential $V(\mathbf{r})$ acting on the system with only one slowly varying Fourier component, so that

$$V(\mathbf{r})=V(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}.\quad(61)$$

The self-consistency equation (12) becomes in this case

$$\Delta\rho_d(\mathbf{q}+\mathbf{H})=\sum_{\mathbf{H}'}[\Omega v(\mathbf{q}+\mathbf{H}')\Delta\rho_d(\mathbf{q}+\mathbf{H}')+V(\mathbf{q})\delta_{\mathbf{H}'0}]\times\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}').\quad(62)$$

Let $V_t(\mathbf{K})$ be the Fourier transform of the total self-consistent potential in the crystal including the electron response,

$$V_t(\mathbf{K})=V(\mathbf{q})\delta_{\mathbf{K},\mathbf{q}}+\Omega v(\mathbf{K})\Delta\rho_d(\mathbf{K}).\quad(63)$$

Adler[36] and Wiser[37] have shown that the $\mathbf{K}=\mathbf{q}$ component of $V_t(\mathbf{K})$ describes the macroscopic or "average" total potential, and that we may define a $\mathbf{q}$-dependent

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[36] S. Adler, Phys. Rev. **126**, 413 (1962).

[37] N. Wiser, Phys. Rev. **129**, 62 (1963).

macroscopic dielectric constant $\bar{\epsilon}(\mathbf{q})$ such that

$$V_t(\mathbf{q})=V(\mathbf{q})/\bar{\epsilon}(\mathbf{q}). \tag{64}$$

On the other hand, a rigorous self-consistent solution of of Eq. (62) may be shown[36,37] to yield

$$V_t(\mathbf{q})=\sum_{\mathbf{H}'}\epsilon^{-1}(\mathbf{q},\mathbf{q}+\mathbf{H}')V(\mathbf{q}+\mathbf{H}')=\epsilon^{-1}(\mathbf{q},\mathbf{q})V(\mathbf{q}), \tag{65}$$

so that we have the relation

$$\bar{\epsilon}(\mathbf{q})=1/\epsilon^{-1}(\mathbf{q},\mathbf{q}) \tag{66}$$

derived by Adler and by Wiser.

We may also write from Eqs. (63) and (65)

$$\Delta\rho_d(\mathbf{q})=\frac{V_t(\mathbf{q})-V(\mathbf{q})}{\Omega v(\mathbf{q})}=\frac{V(\mathbf{q})}{\Omega v(\mathbf{q})}[\epsilon^{-1}(\mathbf{q},\mathbf{q})-1]. \tag{67}$$

If $\mathbf{P}(\mathbf{q})$ is the transform of the macroscopic polarization wave associated with $\Delta\rho_d(\mathbf{r})$, then by Eqs. (19) and (66) we have

$$-i\sum_\alpha q_\alpha P_\alpha(\mathbf{q})=-\frac{V(\mathbf{q})}{\Omega v(\mathbf{q})}\frac{\bar{\epsilon}(\mathbf{q})-1}{\bar{\epsilon}(\mathbf{q})}. \tag{68}$$

This equation is satisfied if

$$\begin{aligned}P_\alpha(\mathbf{q})&=-i[q_\alpha V(\mathbf{q})/q^2\Omega v(\mathbf{q})][\bar{\epsilon}(\mathbf{q})-1]/\bar{\epsilon}(\mathbf{q})\\&=[E_\alpha(\mathbf{q})/q^2\Omega v(\mathbf{q})][\bar{\epsilon}(\mathbf{q})-1]/\bar{\epsilon}(\mathbf{q}),\end{aligned} \tag{69}$$

where $\mathbf{E}(\mathbf{r})$ is the applied electric field associated with $V(\mathbf{r})$. (We are here working in units such that $e=1$.) This solution assumes that $\mathbf{P}$ is parallel to $\mathbf{E}$. Note that we are considering here only longitudinal fields, i.e., $\mathbf{E}(\mathbf{q})\|\mathbf{q}$. The self-consistent field equation (62) relates the charge density response to the externally applied longitudinal field, and by Eq. (18) we see that the only relevant component of $\mathbf{P}$ is the longitudinal component $P_{\|}(\mathbf{q})$, since the transverse component automatically satisfies the equation $\nabla\cdot P_\perp(\mathbf{q})=0$.[30] Hence, as far as Eq. (69) is concerned, $\mathbf{P}$ is arbitrary to the extent of any $P_\perp(\mathbf{q})$. This arbitrariness does not matter, since in the electrostatic approximation the lattice equations of motion are determined only by $\Delta\rho(\mathbf{r})$ and hence only by $P_{\|}(\mathbf{q})$. Therefore, no particular significance is to be attached to apparent components of $\mathbf{P}(\mathbf{q})$ perpendicular to $\mathbf{q}$ which come out of the SM formalism, since the model has only been fitted to the lattice-dynamical data. Alternatively, we may say that the lattice equations of motion are determined purely by the longitudinal component of the general dielectric tensor.[36] The transverse components have to be determined in terms of the electron response to an external electromagnetic transverse field as discussed by Pines[32] and Adler.[36] (At $\mathbf{q}=0$, these two components are of course equal.) Thus, it would seem difficult to ascribe any physical significance to the $\bar{\epsilon}_\perp(\mathbf{q})$ derived by Cochran and Phillips[29] for germanium on the basis of the lattice-dynamical data alone.

We thus concentrate on the longitudinal microscopic dielectric constant $\bar{\epsilon}_\mathbf{H}(\mathbf{q})$. An alternative definition of $\bar{\epsilon}_H(\mathbf{q})$ is

$$P_\alpha(\mathbf{q})=E_\alpha(\mathbf{q})(1/4\pi)[\bar{\epsilon}_H(\mathbf{q})-1]/\bar{\epsilon}_H(\mathbf{q}). \tag{70}$$

Comparing Eqs. (69) and (70), we see that $\bar{\epsilon}_H(\mathbf{q})$ is the same as $\bar{\epsilon}(\mathbf{q})$ defined in Eq. (64) only if $\Omega v(\mathbf{q})=4\pi/q^2$, i.e., if we consider only Hartree screening in the RPA and neglect exchange and correlation corrections to $v(\mathbf{q})$. This is the case considered by Adler and by Wiser.

If we now solve Eq. (62) by making the dipolar approximation as in Eq. (28) we obtain, exactly as we obtained the shell response to the lattice motion in Sec. III,

$$\sum_{\beta\kappa'}\tilde{S}_{\alpha\beta}{}^{\kappa\kappa'}w_{\kappa'\beta}=f^\kappa(\mathbf{q})E_\alpha(\mathbf{q}), \tag{71}$$

where $\tilde{S}$ stands for the shell-shell bonding coefficient $[\mathbf{V}+\mathbf{a}^{-1}]$, and we have assumed the $f^\kappa(\mathbf{q})$ are real. Equation (71) is just the "condition of equilibrium" for the shells in an external field, apart from the factor $f^\kappa(\mathbf{q})$.

Using Eq. (23), which relates $\mathbf{P}(\mathbf{K})$ to the $\mathbf{w}$, we obtain

$$P_\alpha(\mathbf{q})=\sum_{\kappa\kappa'}f^\kappa(\mathbf{q})[\tilde{S}^{-1}]_{\alpha\beta}{}^{\kappa\kappa'}f^{\kappa'}(\mathbf{q})E_\beta(\mathbf{q}). \tag{72}$$

Now let us assume $f^\kappa(\mathbf{q})$ is independent of subcell κ, as in a crystal where each subcell contained the same kind of atom. Then we have

$$P_\alpha(\mathbf{q})=f^2(\mathbf{q})\sum_{\kappa\kappa'}\{[\tilde{S}^{-1}]_{\alpha\beta}{}^{\kappa\kappa'}\}E_\beta(\mathbf{q}). \tag{73}$$

Since $f(\mathbf{q})=1$ for $\mathbf{q}=0$, this equation leads to the same value of the electronic contribution to the dielectric constant as calculated from the original SM.[38] For nonzero values of $\mathbf{q}$, Cochran and Phillips have defined a $\mathbf{q}$-dependent logitudinal dielectric function obtained from the original point-dipole form of the SM from the relations

$$P_\alpha(\mathbf{q})=\sum_{\kappa\kappa'}[\tilde{S}^{-1}]_{\alpha\beta}{}^{\kappa\kappa'}E_\beta(\mathbf{q})$$

by picking out the longitudinal part,

$$\mathbf{P}^{\|}(\mathbf{q})=\sum_{\kappa\kappa'}(\tilde{S}^{-1})_{\mathrm{long}}{}^{\kappa\kappa'}\mathbf{E}(\mathbf{q}). \tag{74}$$

Let us define their dielectric function as $\bar{\epsilon}_{cp}(\mathbf{q})$. Then from Eq. (70), by comparing Eqs. (73) and (74), we have

$$f^2(\mathbf{q})\frac{\bar{\epsilon}_H(\mathbf{q})-1}{\bar{\epsilon}_H(\mathbf{q})}=\frac{\bar{\epsilon}_{cp}(\mathbf{q})-1}{\bar{\epsilon}_{cp}(\mathbf{q})}. \tag{75}$$

Equation (75) gives the rigorous relation between the macroscopic longitudinal Hartree dielectric function $\bar{\epsilon}_H(\mathbf{q})$ [defined by Eq. (70)] as calculated from our generalized SM, and the dielectric function $\bar{\epsilon}_{cp}(\mathbf{q})$ calculated in the point-dipole approximation. It may be seen that they are equal for $\mathbf{q}=0$.

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[38] R. A. Cowley, Proc. Roy. Soc. (London) **A268**, 121 (1962).

Finally, let us relate exactly the dielectric function $\bar{\epsilon}_{cp}(\mathbf{q})$ which Cochran and Phillips obtained to the general dielectric matrix $\epsilon(\mathbf{q}+\mathbf{H}, \mathbf{q}+\mathbf{H}')$ entering into Eq. (65) and obtained from a band-structure calculation.

From Eqs. (66), (69), (70), and (75), we obtain

$$\frac{1}{\bar{\epsilon}_{cp}(\mathbf{q})}-1=\frac{4\pi f^2(\mathbf{q})}{q^2\Omega v(\mathbf{q})}\{\epsilon^{-1}(\mathbf{q},\mathbf{q})-1\}. \tag{76}$$

Exchange and correlation corrections to $v(\mathbf{q})$ render it approximately of the form[1]

$$v(\mathbf{q})=\frac{4\pi}{\Omega q^2}\left(1-\frac{1}{2}\frac{q^2}{q^2+\xi^2}\right). \tag{77}$$

From Eqs. (84) and (85), since $f(\mathbf{q})\rightarrow 1$ as $\mathbf{q}\rightarrow 0$, we see that $\bar{\epsilon}_{cp}(\mathbf{q})\rightarrow 1/\epsilon^{-1}(\mathbf{q},\mathbf{q})$. We note that Cochran and Phillips identified their dielectric function with $1/\epsilon^{-1}(\mathbf{q},\mathbf{q})$ for all $\mathbf{q}$. They also compared $\bar{\epsilon}_{cp}(\mathbf{q})$ with $\epsilon(\mathbf{q},\mathbf{q})$, the diagonal element of the dielectric matrix as calculated for germanium on a simple band model by Penn[39] and found agreement at $\mathbf{q}=0$, but about 30% disagreement at the zone boundary. Penn actually fitted the parameters in his model so that $\epsilon(\mathbf{q},\mathbf{q})$ agreed with the experimentally observed static dielectric constant $\epsilon^{-1}(\mathbf{q},\mathbf{q})$ at $\mathbf{q}=0$. The disagreement for $\mathbf{q}\neq 0$ may therefore be attributed to (a) off-diagonal elements of $\epsilon(\mathbf{q}+\mathbf{H}, \mathbf{q}+\mathbf{H}')$, so that $\epsilon^{-1}(\mathbf{q},\mathbf{q})\neq 1/\epsilon(\mathbf{q},\mathbf{q})$; (b) the factors $f^2(\mathbf{q})$ and $q^2\Omega v(\mathbf{q})$ in Eq. (76); (c) neglect of the exchange and correlation effects in Penn's dielectric constant; and (d) breakdown of the dipolar assumption for nonzero $\mathbf{q}$.

ACKNOWLEDGMENTS

The author wishes to express his gratitude for helpful discussions with Dr. R. Fuchs and Dr. K. Kliewer.

APPENDIX

In this Appendix we discuss the justification of the basic approximation made in Eq. (28) to derive the SM equations. Let us write the wave functions ψ_k in the lth unit cell in the general form

$$\psi_k(\mathbf{r})=(\Omega)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}_l}\phi_k(\mathbf{r}-\mathbf{r}_l), \tag{A1}$$

where $\phi_k(\mathbf{r})$ is a function defined only in the unit cell but is the same for all unit cells for a given state k. For the case of nonoverlapping tight-binding wave functions, $\phi_k(\mathbf{r})$ is simply the atomic orbital $\phi_b(\mathbf{r})$ associated with the state k, but in the general case $\phi_k(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_k(\mathbf{r})$, where $u_k(\mathbf{r})$ is the periodic or Bloch part of the wave function $\psi_k(\mathbf{r})$. Then we have

$$\langle\psi_k|p_\beta e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle =N\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}\phi_{k'}(\mathbf{r}), \tag{A2}$$

where the integral is over the origin unit cell only. Let us write

$$\frac{\langle\psi_k|p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle}{E_k-E_{k'}+\hbar^2(\mathbf{q}+\mathbf{H})^2/2m}$$

in the form

$$N\left[\frac{E_k-E_{k'}}{E_k-E_{k'}+\dfrac{\hbar^2(\mathbf{q}+\mathbf{H})^2}{2m}}\frac{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}\phi_{k'}(\mathbf{r})}{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}\right]$$
$$\times\frac{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}{E_k-E_{k'}}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}. \tag{A3}$$

The central approximation of the SM is to take the factor in large parenthesis in Eq. (A3) as independent of the states k and k' but depending only on $(\mathbf{q}+\mathbf{H})$. Let us call it $f(\mathbf{q}+\mathbf{H})$ since, as we shall see, it will be consistent to take the $f(\mathbf{q}+\mathbf{H})$ introduced in Eq. (23) as the same function, thus defining a form factor for the shells.

Thus we have in this approximtion,

$$\frac{E_k-E_{k'}}{E_k-E_{k'}+(\hbar^2/2m)(\mathbf{q}+\mathbf{H})^2}$$
$$\times\frac{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}\phi_{k'}(\mathbf{r})}{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}=f(\mathbf{q}+\mathbf{H}), \tag{A4}$$

and combining Eqs. (25), (A3), and (A4),

$$\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle=-N\frac{\hbar}{m}f(\mathbf{q}+\mathbf{H})\sum_\alpha(\mathbf{q}+\mathbf{H})_\alpha$$
$$\times\frac{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}{(E_k-E_{k'})}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}, \tag{A5}$$

and

$$\langle\psi_k|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle=N\frac{\hbar}{m}f^*(\mathbf{q}+\mathbf{H})\sum_\alpha(\mathbf{q}+\mathbf{H})_\alpha$$
$$\times\frac{\displaystyle\int_0 dr\,\phi_k^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}{(E_k-E_{k'})}\Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}}. \tag{A6}$$

Note that $f(0)=1$. $f(\mathbf{K})$ is not, however, simply the Fourier transform of the charge density in the shell (i.e., the valence charge density) as assumed by Cochran

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[39] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

and Phillips.[29] Let us now discuss the validity of the approximation in Eq. (A4). The assumption of a form-factor independent of the states k and k' is, strictly speaking, inconsistent with the generalized f sum rule.[32] Substitution of Eq. (A5), which is a consequence of Eq. (A4), in the f sum rule shows that $f(\mathbf{K})$ must be independent of $\mathbf{K}$. However, we note that the relevant transitions in the matrix elements that enter into the lattice-dynamical problem are only those from occupied to unoccupied states, and that hopefully only a few transitions are important. In this restricted sense, Eq. (A4) may not be a bad approximation. Consider, for example, the case where only two bands are of importance—an occupied valence band and an unoccupied conduction band. Let us also assume that the tight-binding limit is satisfied in the sense that E_k is independent of the Bloch wave vector $\mathbf{k}$ and depends only on the band index, and that ϕ_k is also independent of k and is simply the atomic orbital associated with the band in question. In this case

$$f(\mathbf{q}+\mathbf{H})=\frac{E_g}{E_g+(\hbar^2/2m)(\mathbf{q}+\mathbf{H})^2}\times\frac{\int_0 dr\,\phi_v{}^*(\mathbf{r})p_\alpha e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}\phi_c(\mathbf{r})}{\int_0 dr\,\phi_v{}^*(\mathbf{r})p_\alpha\phi_c(\mathbf{r})},\qquad\text{(A7)}$$

where E_g is the energy gap, and subscripts v and c refer to the valence and conduction bands, respectively. Since there is now only one effective interband transition, Eq. (A7) shows that Eq. (A4) becomes rigorously true in this case. In general, we might still hopefully neglect the k and k' dependence of the left-hand side of Eq. (A4) by defining $f(\mathbf{q}+\mathbf{H})$ as some kind of average over the important allowed transitions in the case of insulators. For metals, the assumption obviously breaks down. Needless to say, the validity of the central assumption in Eq. (A4) can only be checked from an actual calculation of the oscillator strengths in question. Note that the point-dipole assumption requires that $f(\mathbf{K})=1$ for all K [see Eq. (22)]. This assumption is valid only in the case where (a) for all relevant values of $(\mathbf{q}+\mathbf{H})$, $(\hbar^2/2m)(\mathbf{q}+\mathbf{H})^2$ is much less than the typical band gap to the unoccupied states, and (b) the functions $\phi_k(\mathbf{r})$ are extremely localized. These are more restrictive assumptions than are necessary for deducing the SM equations. We should point out that the approximation in Eq. (A4) obviously gets better as $(\mathbf{q}+\mathbf{H})$ becomes smaller. Hence it is important to choose a formulation which is rapidly convergent in terms of its reciprocal lattice sums. This has been achieved partly by the use of our residual-potential formalism. In particular we should choose V_0 such that both $W'(\mathbf{q}+\mathbf{H})$ and $M_{k'k}\times\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle$ are rapidly damped for increasing $(\mathbf{q}+\mathbf{H})$ [see Eq. (12)]. This may not necessarily be the whole unit cell (or subcell in the case of lattices with basis).

Now substituting Eqs. (A5) and (A6) into Eq. (13), and defining a q-dependent polarizability tensor

$$a'_{\alpha\beta}(\mathbf{q})=N^2\frac{\hbar^2}{m^2}\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\frac{\int_0 d\mathbf{r}\,\phi_k{}^*(\mathbf{r})p_\alpha\phi_{k'}(\mathbf{r})}{E_k-E_{k'}}\times\frac{\int_0 d\mathbf{r}\,\phi_{k'}{}^*(\mathbf{r})p_\beta\phi_k(\mathbf{r})}{E_k-E_{k'}}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}},\qquad\text{(A8)}$$

we get

$$\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')=-\sum_{\alpha\beta}(\mathbf{q}+\mathbf{H})_\alpha f(\mathbf{q}+\mathbf{H})\times a'_{\alpha\beta}(\mathbf{q})f^*(\mathbf{q}+\mathbf{H}')(\mathbf{q}+\mathbf{H}')_\beta.\qquad\text{(A9)}$$