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Microscopic Theory of Force Constants in the Adiabatic Approximation*

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The microscopic quantum-mechanical expressions for the Born–von Karman force constants in an arbitrary solid, crystalline or amorphous, are derived in terms of the complete inverse dielectric function $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$ of the electrons The many-body nature of the electrons is treated exactly; only the Born-Oppenheimer approximation is made. Born's translation and rotation invariance conditions are shown to be satisfied by the microscopic force constants. In the case of a perfect crystal, it is shown for the first time that the microscopic formulas recapture completely the phenomenological form of the dynamical matrix; in particular, the microscopic expression for the effective charge in an insulator is found. We prove that the charge neutrality of the system implies the "effective charge neutrality" condition and that, consequently, all acoustic-mode frequencies vanish at long wavelength. This condition may be stated as a useful property of ϵ^{-1} which we term the acoustic sum rule. Many results of the phenomenological theory, e.g., the generalized Lyddane-Sachs-Teller relation, carry over exactly to the microscopic theory.

I. INTRODUCTION

THE vibration of nuclei in solids in the harmonic approximation is described by the Born-von Karman force constants.[1,2] In the phenomenological approach the force constants are regarded as parameters adjusted to fit experimentally observed vibration frequencies. In order to make the parametrization both feasible and physically meaningful, one introduces for the various types of crystals different force-constant models which are at first sight unconnected. Recently, on the other hand, much effort has been applied to deriving the force constants from first principles based on the microscopic electronic configuration of the solid. These methods have been very successful in many metals[3] and have been applied to other materials in a few instances.[4–6]

Among the authors who have developed the microscopic theory of lattice dynamics of metals are Toya,[7] Baym,[8] Sham,[9] Harrison,[10] Cochran,[11] Sjölander and Johnson,[12] Vosko *et al.*,[13] and Joshi and Rajagopal.[3] The success of the theory applied to metals has in turn spurred the extension to other materials. The additional problems encountered in applying the general theory to insulators have been examined in a preliminary report of the present work,[14] by Keating,[15] and by Sham,[16] who has independently derived the important results of the present paper. Also, Sinha[17] has recently given a microscopic basis for the shell model.

The purpose of the present paper is to derive in a simple manner a microscopic theory applicable to a wide range of solids so that it may provide the relationship between the various methods and models used to describe the nuclear vibrations. We go on to analyze the results of the microscopic theory so that the connection to the familiar phenomenological theories can be made. Of particular importance is our analysis of the analytic properties of the microscopic functions involved which were not considered in the previous works.

In Sec. II the general expression for the force constants C_{AB} is derived from a microscopic examination of the forces in terms of the nuclear charges and the

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complete inverse dielectric response function ϵ^{-1} of the electrons, treating all electrons equivalently. The derivation assumes only the Born-Oppenheimer[1,18] approximation and the harmonic approximation for the nuclear displacements. Thus the force constants derived are essentially quasiharmonic force constants in that they are, in general, temperature-dependent because of thermal electronic excitation but do not include any lifetime effects or frequency renormalization due to phonon-phonon interaction.

The remainder of the paper is devoted to examining the consequences of the expressions derived in Sec. II. The invariance properties of the free energy of the system in the harmonic approximation can be expressed in terms of relations among the force constants which have been stated, for example, by Born.[1] In Sec. III it is shown that these conditions are indeed satisfied by the force constants of Sec. II.

In Sec. IV the specialization to a perfect infinite crystal is made and the formulas for the dynamical matrix are given. For comparison, we briefly review the phenomenological expressions for the dynamical matrix[19] and note that in the case of ionic insulators the long-range effective charge contribution to the dynamical matrix is identified by its analytic behavior as a function of wave vector $\mathbf{q}$ near $\mathbf{q}=0$.

The analytic behavior of the microscopic expression for the dynamical matrix is examined in Sec. V and it is shown that in the case of an insulator the phenomenological form of the dynamical matrix for an ionic crystal is obtained. In particular, the microscopic expression for the effective charge is found. In the case of a metal, there are no such effective charge terms.

The final step in making the identification with the phenomenological theory is accomplished in Sec. VI. There it is shown that the charge neutrality of the system implies the "effective charge neutrality" condition which must be assumed in the phenomenological approach.[19] From this condition it follows that all acoustic modes have vanishing frequencies at long wavelength. The condition may be stated as a useful property of ϵ^{-1} which we call the *acoustic sum rule* and which points out a crucial factor in the computational differences between metals and nonmetals. It is in the study of the analytic properties that the present work differs from that of Keating[15] (consequently, the acoustic sum rule derived here differs from the similar condition given by Keating).

Having completed the identification with the phenomenological theory, in Sec. VII we point out two results derived previously,[19] the generalized Lyddane-Sachs-Teller (LST) relation[20] and the expression for the total static dielectric tensor, which immediately carry over to the microscopic theory.

II. BORN-VON KARMAN FORCE CONSTANTS

The Born-von Karman theory[1,2] of atomic vibrations in solids and its direct descendants are formulated in terms of force constants relating the force on an atom to the displacement of any other atom from its equilibrium position. Strictly speaking, this description is valid only for insulators where the Born-Oppenheimer (BO) approximation[1,18] applies. In metals, on the other hand, the breakdown of the BO approximation leads to damping and retardation effects not included in the Born-von Karman theory. With the exception of degenerate semiconductors and semimetals in which the Fermi or plasma energies and phonon frequencies can become comparable, the effects of damping and retardation are not important numerically.[21] We therefore confine ourselves to insulators and ordinary metals and make the BO approximation.

It is convenient to generalize the BO approximation to apply to the system of nuclei and electrons at finite temperature. We assume that the electrons are always in thermal equilibrium as the ions move. Then we can define a free-energy function F, computed for infinite nuclear mass, which is a function of the nuclear positions only. It is this free energy that provides the potential in which the nuclei vibrate.

We suppose our system to be arbitrary in structure and in composition and to consist of nuclei labeled by $a, b, \ldots$, and of electrons labeled by $t, u, \ldots$. The nuclear positions are given by R_A where the Cartesian component α and the nuclear index a are subsumed in a composite index A. The displacements of the nuclei from the equilibrium positions $R_A{}^0$,

$$u_A = R_A - R_A{}^0, \qquad (2.1)$$

are assumed to be sufficiently small that F may be expanded in powers of the u_A and the expansion truncated after the quadratic terms:

$$F = F_0 + \tfrac{1}{2} \sum_{AB} \left[\frac{\partial^2 F}{\partial R_A \partial R_B} \right]_0 u_A u_B , \qquad (2.2)$$

where the symbol $[\ ]_0$ means that the bracketed expression is evaluated with all nuclear coordinates at the equilibrium positions. Equation (2.2) is the basis of the present work. Our theory does not encompass lifetime effects and cannot be used when anharmonic effects in the nuclear motions appear; the truncation is then invalid. Quantum solids[22] such as He^3 and He^4 are entirely excluded since the truncation is invalid even at absolute zero because of the magnitude of the zero-point motion.

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The Hamiltonian governing the nuclear motion is

$$H_N=F_0+\sum_a \frac{\mathbf{P}_a^2}{2M_a}+\tfrac{1}{2}\sum_{AB} C_{AB}u_Au_B\,, \tag{2.3}$$

where $\mathbf{P}_a$ is the nuclear momentum, M_a is the nuclear mass, and the Born-von Karman force constants C_{AB} are given by

$$C_{AB}=\left[\frac{\partial^2 F}{\partial R_A\partial R_B}\right]_0. \tag{2.4}$$

We now express Eq. (2.4) in terms of well-defined microscopic quantities.

The total microscopic Hamiltonian is

$$H_e=\sum_t \frac{\mathbf{p}_t^2}{2m}+\tfrac{1}{2}\sum_{a,b}{}' \frac{Z_aZ_be^2}{R_{ab}} -\sum_{at}\frac{Z_ae^2}{|\mathbf{r}_t-\mathbf{R}_a|}+\tfrac{1}{2}\sum_{tu}{}'\frac{e^2}{r_{tu}} \tag{2.5}$$

for infinite nuclear mass, where $\mathbf{p}_t$ is the momentum of electron t and $\mathbf{r}_t$ is its position, and where Z_a is the charge of nucleus a. The corresponding free energy is

$$F=-(1/\beta)\ln[\operatorname{tr}(e^{-\beta H_e})],\quad \beta=1/k_BT. \tag{2.6}$$

Let us define the electron density

$$\rho(\mathbf{r})=\sum_t \delta(\mathbf{r}-\mathbf{r}_t)\,, \tag{2.7}$$

the nuclear potential

$$V_N(\mathbf{r})=-\sum_a \frac{Z_ae^2}{|\mathbf{r}-\mathbf{R}_a|}\,, \tag{2.8}$$

the electron-nuclear interaction

$$\mathcal{V}=\int V_N(\mathbf{r})\rho(\mathbf{r})d^3r\,, \tag{2.9}$$

and the bare nuclear interaction

$$W=\tfrac{1}{2}\sum_{ab}{}'\frac{Z_aZ_be^2}{R_{ab}}\,. \tag{2.10}$$

We now expand H_e formally in powers of u_A through the second:

$$H_e=H_e^{(0)}+H_e^{(1)}+H_e^{(2)}\,, \tag{2.11a}$$

where

$$H_e^{(0)}=[H_e]_0\,, \tag{2.11b}$$

$$H_e^{(1)}=\sum_A\left[\frac{\partial H_e}{\partial R_A}\right]_0 u_A=W^{(1)}+\mathcal{V}^{(1)}\,, \tag{2.11c}$$

and so forth. Correspondingly, F may be expanded in powers of u_A by standard perturbation theory[23]:

$$F=F_0+\langle H_e^{(1)}\rangle+\langle H_e^{(2)}\rangle -\frac{1}{2}\int_0^\beta d\tau[\langle\mathcal{V}^{(1)}(\tau)\mathcal{V}^{(1)}(0)\rangle-\langle\mathcal{V}^{(1)}\rangle^2]\,, \tag{2.12}$$

where

$$\mathcal{O}(\tau)=e^{\tau H_e^{(0)}}\mathcal{O}e^{-\tau H_e^{(0)}} \tag{2.13}$$

and

$$\langle\mathcal{O}\rangle=\operatorname{tr}(e^{-\beta H_e^{(0)}}\mathcal{O})/\operatorname{tr}(e^{-\beta H_e^{(0)}})\,. \tag{2.14}$$

The term $\langle H_e^{(2)}\rangle$ in (2.12), derived from the expansion of the Hamiltonian to second order, has often been omitted in treating the electron-phonon interaction[24]; however, it is essential to preserve the translation invariance of the free energy.

From (2.12) the microscopic equilibrium condition, which expresses the requirement that the force F_A on each nucleus a vanishes, can be seen to be

$$F_A=\left[\frac{\partial F}{\partial R_A}\right]_0=Z_ae^2\left[\frac{\partial}{\partial R_A}\left(\sum_b{}'\frac{Z_b}{R_{ab}} -\int\frac{\langle\rho(\mathbf{r})\rangle}{|\mathbf{r}-\mathbf{R}_a|}d^3r\right)\right]_0=0\,. \tag{2.15}$$

Finally, the force constants can be put in the microscopic form

$$\begin{aligned}C_{AB}=\left[\frac{\partial^2 F}{\partial R_A\partial R_B}\right]_0=\Bigg[&(1-\delta_{ab})\frac{\partial^2}{\partial R_A\partial R_B}\frac{Z_aZ_be^2}{R_{ab}} -\int\frac{\partial V_N}{\partial R_A}(\mathbf{r})D(\mathbf{r},\mathbf{r}')\frac{\partial V_N}{\partial R_B}(\mathbf{r}')d^3rd^3r'\\ &+\delta_{ab}\left(\int\langle\rho(\mathbf{r})\rangle\frac{\partial^2V_N(\mathbf{r})}{\partial R_A\partial R_B}d^3r +\sum_c{}'\frac{\partial^2}{\partial R_A\partial R_B}\frac{Z_aZ_c}{R_{ac}}\right)\Bigg]_0\,,\end{aligned} \tag{2.16}$$

where we have defined the density-density correlation function

$$D(\mathbf{r},\mathbf{r}')=\int_0^\beta d\tau[\langle\rho(\mathbf{r},\tau)\rho(\mathbf{r}',0)\rangle-\langle\rho(\mathbf{r})\rangle\langle\rho(\mathbf{r}')\rangle]\,. \tag{2.17}$$

Using the symmetry of $D(\mathbf{r},\mathbf{r}')$ in $\mathbf{r}$ and $\mathbf{r}'$, it is easy to show that C_{AB} is symmetric, $C_{AB}=C_{BA}$, as it must be from (2.4). The form (2.16) is neither physically appealing nor perspicuous. A more appealing form is achieved by introduction of the microscopic dielectric function.

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Let a static external potential $V_{\mathrm{ext}}(\mathbf{r})$ with which only the electrons interact be applied to the system; it results in the additional term $\int V_{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r})d^3r$ in H_e. If V_{ext} is sufficiently small the change $V(r)$ in the total potential experienced by an external test charge is linear in V_{ext}:

$$V(\mathbf{r})=\int \epsilon^{-1}(\mathbf{r},\mathbf{r}')V_{\mathrm{ext}}(\mathbf{r}')d^3r'. \tag{2.18}$$

A perturbation calculation analogous to that of the preceding derivation immediately yields, for the inverse dielectric function,

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')-\int \frac{1}{|\mathbf{r}-\mathbf{r}''|}D(\mathbf{r}'',\mathbf{r}')d^3r''. \tag{2.19}$$

Returning to C_{AB} in Eq. (2.16), we see that Eq. (2.19) leads to

$$\begin{aligned}C_{AB}=\bigg[&\frac{\partial^2}{\partial R_A\partial R_B}\bigg(\int \epsilon^{-1}(\mathbf{R}_a,\mathbf{r})\frac{Z_aZ_be^2}{|\mathbf{r}-\mathbf{R}_b|}d^3r\bigg)(1-\delta_{ab})\\&+\delta_{ab}\bigg(\int \langle\rho(\mathbf{r})\rangle\frac{\partial^2V_N(\mathbf{r})}{\partial R_A\partial R_B}d^3r+\sum_c{}'\frac{\partial^2}{\partial R_A\partial R_B}\frac{Z_aZ_ce^2}{R_{ac}}\\&+\frac{\partial^2}{\partial R_A\partial R_B}\int[\epsilon^{-1}(\mathbf{R}_a,\mathbf{r})-\delta(\mathbf{R}_a-\mathbf{r})]\frac{Z_aZ_be^2}{|\mathbf{r}-\mathbf{R}_b|}d^3r\bigg)\bigg]_0.\end{aligned} \tag{2.20}$$

The first term in (2.20) is evidently the bare nuclear interaction screened by the total dielectric function of the electrons, including core as well as valence electrons. As we shall see in Sec. III, the remaining terms guarantee the translation invariance of the free energy (2.2) and can be transformed so as to combine directly with the first term.

III. INVARIANCE PROPERTIES OF THE FREE ENERGY

The free energy of the system defined in Eq. (2.6) with the Hamiltonian H_e given by (2.5) is obviously translationally and rotationally invariant because H_e is a function of relative coordinates only. However, the truncated expression (2.12) for the free energy involves the absolute coordinates of the nuclei at equilibrium $R_A{}^0$. We now proceed to demonstrate that in the microscopic theory, translation and rotation invariance is indeed maintained in the truncated free energy.

The invariance of the system against any uniform displacement is guaranteed by 18 relations[1] among the set of force constants

$$C_{ab}{}^{\alpha\beta}\equiv C_{AB} \tag{3.1}$$

which involve an arbitrary nucleus a. Nine of these relations express the fact that no force is felt by nucleus a when the system undergoes a rigid translation:

$$\sum\nolimits_b C_{ab}{}^{\alpha\beta}=0. \tag{3.2}$$

The nine remaining conditions express that this force also vanishes when the system is rotated rigidly about an axis passing through $\mathbf{R}_a{}^0$. Utilizing (3.2), one finds

$$\sum\nolimits_b(C_{ab}{}^{\alpha\beta}R_b{}^\gamma-C_{ab}{}^{\alpha\gamma}R_b{}^\beta)=0 \tag{3.3}$$

for the desired relation. The brackets $[\;]_0$ will usually be omitted in the remainder of the paper with the understanding that all expressions are to be evaluated at the nuclear equilibrium positions.

To our knowledge none of these relations has been proved in general for the force constants derived in Sec. II. Sham[9] has previously derived (3.2) for a perfect crystal in the self-consistent field approximation. While the present work was in progress, Keating established (3.2) for a perfect crystal in a many-body framework, but in a way more cumbersome than that presented here.

The invariance conditions (3.2) and (3.3), as well as another condition discussed later in Sec. VI, are easily demonstrated using an identity which is proved in the Appendix. Let $\mathcal{O}_\mathbf{r}$ be an operator which acts on the variable $\mathbf{r}$ subject to the two conditions

$$[\mathcal{O}_\mathbf{r},\nabla_r{}^2]=0 \tag{3.4}$$

and

$$\mathcal{O}_\mathbf{r}g(|\mathbf{r}-\mathbf{r}'|)=-\mathcal{O}_{\mathbf{r}'}g(|\mathbf{r}-\mathbf{r}'|) \tag{3.5}$$

for any function $g(|r|)$. Then in the Appendix we demonstrate the following identity:

$$\sum_b\int f(\mathbf{r})D(\mathbf{r},\mathbf{r}')[\mathcal{O}_{\mathbf{R}_b},V_N(\mathbf{r}')]d^3rd^3r' +\int \langle\rho(\mathbf{r})\rangle[\mathcal{O}_\mathbf{r},f(\mathbf{r})]d^3r=0, \tag{3.6}$$

where $f(\mathbf{r})$ is an arbitrary function of $\mathbf{r}$. The physical import of (3.6) is that under any rigid displacement of the nuclei, the electron distribution is also rigidly displaced.

The translation invariance condition (3.2) is easily demonstrated. The part of the force constants (2.16) involving the bare nuclear interactions manifestly obeys (3.2). The proof is completed by using the identity (3.6) with

$$f(\mathbf{r})=(\partial/\partial R_a{}^\alpha)V_N(\mathbf{r}) \tag{3.7a}$$

and the translation operator

$$\mathcal{O}_\mathbf{r}=-\partial/\partial r^\beta. \tag{3.7b}$$

Proceeding to the rotation invariance, one may show that

$$\sum_b (C_{ab}{}^{\alpha\beta}R_b{}^{\gamma}-C_{ab}{}^{\alpha\gamma}R_b{}^{\beta})$$

$$=Z_a e^2\left(\delta_{\alpha\gamma}\frac{\partial}{\partial R_a{}^{\beta}}-\delta_{\alpha\beta}\frac{\partial}{\partial R_a{}^{\gamma}}\right)\sum_b{}' \frac{Z_b}{R_{ab}}$$

$$-\int\langle\rho(\mathbf{r})\rangle\left[\delta_{\alpha\gamma}\frac{\partial}{\partial R_a{}^{\beta}}-\delta_{\alpha\beta}\frac{\partial}{\partial R_a{}^{\gamma}}\right]\frac{Z_a e^2}{|\mathbf{r}-\mathbf{R}_a|}d^3r$$

$$-\int\frac{\partial}{\partial R_a{}^{\alpha}}V_N(\mathbf{r})D(\mathbf{r},\mathbf{r}')\sum_b \mathcal{O}_{\mathbf{R}_b}V_N(\mathbf{r}')d^3r d^3r'$$

$$-\int\langle\rho(\mathbf{r})\rangle\mathcal{O}_{\mathbf{r}}\frac{\partial}{\partial R_a{}^{\alpha}}V_N(\mathbf{r})d^3r, \quad (3.8)$$

where $\mathcal{O}_{\mathbf{r}}$ is the rotation operator

$$\mathcal{O}_{\mathbf{r}}=r^{\gamma}\frac{\partial}{\partial r^{\beta}}-r^{\beta}\frac{\partial}{\partial \gamma^{\gamma}}. \quad (3.9)$$

The coefficients of each of $\delta_{\alpha\beta}$ and $-\delta_{\alpha\gamma}$ are the components of the force $\mathbf{F}_a$ exerted on nucleus a at equilibrium which must vanish. The rotation invariance condition immediately follows from (3.8) by using the identity (3.6) with $f(\mathbf{r})$ given in (3.7a).

The translation and rotation invariance of the truncated free energy, expressed in (3.2) and (3.3), has been shown to follow from the exact microscopic expression for the force constants. The proof is valid for any arrangement of the nuclei and for both finite and infinite systems. The only requirement is that the infinite system must be electrically neutral so that the sums can be shown to be well defined.

The force constants may now be expressed in terms of $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$ only. From the translation invariance condition and (2.20), we find

$$C_{ab}{}^{\alpha\beta}=\bar{C}_{ab}{}^{\alpha\beta}-\delta_{ab}\sum_c \bar{C}_{ac}{}^{\alpha\beta}, \quad (3.10)$$

where

$$\bar{C}_{ab}{}^{\alpha\beta}=\left[\frac{\partial}{\partial R_a{}^{\alpha}\partial R_b{}^{\beta}}\int\epsilon^{-1}(\mathbf{R}_a,\mathbf{r})\frac{Z_a Z_b e^2}{|\mathbf{r}-\mathbf{R}_b|}d^3r\right]_0. \quad (3.11)$$

This is the form for the force constants that is used in the remainder of the paper.

IV. VIBRATIONS IN PERFECT CRYSTAL

We now specialize our attention to the perfect infinite crystal. The nuclear label a is divided into the unit cell index l and the label of the nucleus in the unit cell s, so that $R_A=R_a{}^{\alpha}=R_l{}^{\alpha}+R_s{}^{\alpha}$. The force constants then are

$$C_{AB}=C_{ss'}{}^{\alpha\beta}(l,l')=C_{ss'}{}^{\alpha\beta}(l-l'), \quad (4.1)$$

where the final equality expresses the periodicity of the crystal lattice.

Making use of the Born-von Karman periodic boundary conditions[1] the nuclear displacements are propagating waves

$$u_{sl}{}^{\alpha}(\mathbf{q})=u_s{}^{\alpha}(\mathbf{q})e^{i\mathbf{q}\cdot(\mathbf{R}_l+\mathbf{R}_s)-i\omega t}+\text{c.c.}, \quad (4.2)$$

with wave vector $\mathbf{q}$ and frequency ω, the square of which is an eigenvalue of the dynamical matrix

$$\frac{1}{(M_sM_{s'})^{1/2}}C_{ss'}{}^{\alpha\beta}(\mathbf{q})$$

$$=\frac{1}{(M_sM_{s'})^{1/2}}\sum_l C_{ss'}{}^{\alpha\beta}(l)e^{-i\mathbf{q}\cdot(\mathbf{R}_l+\mathbf{R}_s-\mathbf{R}_{s'})}. \quad (4.3)$$

It is convenient in the present work to deal with the matrix $C_{ss'}{}^{\alpha\beta}(\mathbf{q})$ instead of (4.3). Both the matrices C and $\bar{C}$ defined below will be referred to as the dynamical matrix when there is no danger of confusion.

The sum in (4.3) can be carried out using the general microscopic force constants given in (3.10) and (3.11), yielding

$$C_{ss'}{}^{\alpha\beta}(\mathbf{q})=\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})-\delta_{ss'}\sum_{s''}\bar{C}_{ss''}{}^{\alpha\beta}(0), \quad (4.4)$$

where[25]

$$\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})=Z_sZ_{s'}\frac{4\pi e^2}{\Omega}\sum_{\mathbf{K},\mathbf{K}'}\frac{(\mathbf{q}+\mathbf{K})^{\alpha}(\mathbf{q}+\mathbf{K}')^{\beta}}{|\mathbf{q}+\mathbf{K}'|^2}$$

$$\times\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}')e^{i(\mathbf{K}\cdot\mathbf{R}_s-\mathbf{K}'\cdot\mathbf{R}_{s'})}. \quad (4.5)$$

Here Ω is the unit cell volume, $\mathbf{K}$ and $\mathbf{K}'$ are reciprocal-lattice vectors, and $\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}')$ is the Fourier transform of the inverse dielectric function $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$,

$$\epsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}')$$

$$=\frac{1}{N\Omega}\int d^3r\, d^3r'\,\epsilon^{-1}(\mathbf{r},\mathbf{r}')e^{i[-(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}+(\mathbf{q}+\mathbf{K}')\cdot\mathbf{r}']}, \quad (4.6)$$

where $N\Omega$ is the volume of the system. Equations (4.4) and (4.5) for the dynamical matrix have been derived by Keating[15] through a more involved procedure and have previously been derived within the self-consistent field approximation by Sham.[9]

We note that the second term in (4.4) is by definition independent of $\mathbf{q}$ so that all $\mathbf{q}$ dependence of the elements of C are contained in $\bar{C}$. Also, we have formally included the infinite self-interaction term in $\bar{C}_{ss}$. In the following we shall examine the $\mathbf{q}$ dependence of $\bar{C}$ ignoring the infinite constant since it does not affect the final matrix C and in any actual calculation may simply be omitted.

Because the retardation of the electromagnetic field is neglected, the formulas for the dynamical matrix are invalid[26] for wave numbers $q<\omega/c$, where c is the velocity of light. Thus the $q\rightarrow 0$ limits of the elements

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[25] The Fourier transform of the Coulomb potential is $v(|q+K|)=4\pi Ze^2/|q+K|^2$ for $q+K\neq 0$. However, for $q+K=0$, the charge neutrality of the system allows us to set $v(0)=0$.

[26] K. Huang, Nature **167**, 779 (1951); Proc. Rov. Soc. (London) **A208**, 352 (1951).

of the dynamical matrix must be understood to be restricted to $q > \omega_{\text{optic}}/c$. However, in the following wherever the acoustic modes are explicitly projected out there is no such restriction since $q = \omega/v_s \gg \omega/c$, where v_s is the appropriate velocity of sound; then retardation of the field plays no role and the limits are exact.

Let us briefly recall the behavior of the dynamical matrix in the phenomenological theory (also neglecting retardation) in which the force constants are regarded as adjustable parameters. If the force constants $C_{ss'}{}^{\alpha\beta}(l)$ are required to be of finite range, as is assumed to be the case in metals and nonionic insulators, the dynamical matrix is an analytic function of $\mathbf{q}$. However, in ionic crystals there are long-range Coulombic forces which must be taken into account. In the phenomenological theory these forces are included through the effective charge tensor $Z_s{}^{\alpha\beta}$, assumed to incorporate all long-range effects of charge polarization in the distorted crystal. Cochran and Cowley[19] have shown that in an ionic crystal of arbitrary symmetry, the dynamical matrix takes the form

$$C_{ss'}{}^{\alpha\beta}(\mathbf{q}) = C_{ss'}{}^{N\alpha\beta}(\mathbf{q}) + \frac{4\pi e^2}{\Omega}\Big[\sum_\gamma \hat{q}^\gamma Z_s{}^{\gamma\alpha}(\mathbf{q})\Big]^* \frac{1}{\epsilon_0(\mathbf{q})}\Big[\sum_\gamma \hat{q}^\gamma Z_{s'}{}^{\gamma\beta}(\mathbf{q})\Big], \tag{4.7}$$

where $Z_s{}^{\alpha\beta} = Z_s{}^{\alpha\beta}(0)$ is the dynamical effective charge tensor and $\epsilon_0(\mathbf{q})$ is the electronic ("high-frequency" or "optic") macroscopic dielectric function. The two terms on the right-hand side of (4.7) are distinguished by their analytic properties as functions of $\mathbf{q}$ at $\mathbf{q}=0$; the part $C^N(\mathbf{q})$ is an analytic function, whereas the terms involving the effective charges are discontinuous at $\mathbf{q}=0$.

V. ANALYTIC PROPERTIES OF THE DYNAMICAL MATRIX

The analytic properties of ϵ^{-1} can be established using the results of Martin and Schwinger (MS)[27] (which have been stated more recently by Keating[15] in the reciprocal space representation) and following a procedure close to that of Ambegaokar and Kohn (AK).[28] In this section we consider only the $T \to 0$ limit of ϵ^{-1} in which case one finds[27]

$$\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \delta_{\mathbf{KK}'} - v(\mathbf{q}+\mathbf{K}) D(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'), \tag{5.1}$$

where $v(\mathbf{q}+\mathbf{K})$ is the Coulomb potential[25] and where

$$D(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = (1/N)\langle \rho_{\mathbf{q}+\mathbf{K}}[(1-P_0)/(H-E_0)]\rho_{\mathbf{q}+\mathbf{K}'}\rangle. \tag{5.2}$$

Here E_0 is the ground-state energy, $\langle\ \rangle$ means the expectation value in the ground state, P_0 is the ground-state projection operator, and

$$\rho_{\mathbf{q}+\mathbf{K}} = \sum\nolimits_t e^{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}_t}. \tag{5.3}$$

In terms of functional derivatives, D is

$$D(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \langle \delta\rho_{\mathbf{q}+\mathbf{K}}/\delta V_{\text{ext}}(\mathbf{q}+\mathbf{K}')\rangle, \tag{5.4}$$

i.e., the variation of the electronic charge density with respect to an external field. Let us define $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+K')$ to be the "proper part" of the screening function, which is

$$\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \langle \delta\rho_{\mathbf{q}+\mathbf{K}}/\delta V(\mathbf{q}+\mathbf{K}')\rangle, \tag{5.5}$$

where V is the total field seen by a test charge in the medium. In graphical language, π is that part of the total screening function D which remains when one omits all graphs which can be separated into two parts by cutting a single Coulomb interaction line of momentum $\mathbf{q}+\mathbf{K}''$, where $\mathbf{K}''$ is any reciprocal-lattice vector. (Note the difference from the definition of AK who require $\mathbf{K}''=0$.)

It was shown by MS that ϵ^{-1} satisfies the equation

$$\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \delta_{\mathbf{KK}'} + v(|\mathbf{q}+\mathbf{K}|) \times \sum\nolimits_{\mathbf{K}''} \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'')\epsilon^{-1}(\mathbf{q}+\mathbf{K}'', \mathbf{q}+\mathbf{K}'), \tag{5.6}$$

from which it follows that the dielectric function has the simple form

$$\epsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}') = \delta_{\mathbf{KK}'} - v(|\mathbf{q}+\mathbf{K}|)\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}'), \tag{5.7}$$

where ϵ is the matrix inverse of ϵ^{-1} viewed as a matrix in $\mathbf{K}$ and $\mathbf{K}'$. Because the analytical properties of π are straightforward to determine, we examine ϵ; the needed properties of ϵ^{-1} are then found using elementary arguments on the inversion of the ϵ matrix.

A. Dielectric Function Matrix

We now proceed to show that in the exact theory the analytic form of $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ for $\mathbf{q}$ near zero are the same as in the familiar self-consistent field (SCF)[29–31] form for π. Despite the difference in their definition of the proper part, the methods of AK for establishing the properties of $\pi(\mathbf{q},\mathbf{q})$ can immediately be taken over to the study of $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$. Here we give the essence of their argument.

The proper part π is so defined that the momenta of all internal Coulomb lines are integrated over all reciprocal space. This means that any possible nonanalytic behavior in $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ as a function of $\mathbf{q}$ can enter in only two ways: (1) the factors $\rho_{\mathbf{q}+\mathbf{K}}$ or $\rho_{\mathbf{q}+\mathbf{K}'}$ or (2) the vanishing of the energy denominators in the expression for π, where the energy denominators

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[27] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1392 (1959).

[28] V. Ambegaokar and W. Kohn, Phys. Rev. **117**, 423 (1960).

[29] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, No. 8 (1954); H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

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

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

are simply the energies for production of electronic excitations above the ground state of the system.

In the case of an insulator, we need consider only (1) because the electronic excitation energies never vanish for any wave vector. It follows that every element of $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ may be expanded in a power series in $\mathbf{q}$. Here we need to keep only the first nonvanishing term. For $\mathbf{K}\neq 0$ and $\mathbf{K}'\neq 0$, the lowest-order term is the constant $\pi(\mathbf{K},\mathbf{K}')$ evaluated at $\mathbf{q}=0$. But for $\mathbf{K}$ or $\mathbf{K}'=0$, the leading terms are

$$\begin{aligned} \pi(\mathbf{q}, \mathbf{q}+\mathbf{K}) &\rightarrow \mathbf{q}\cdot\mathbf{A}(\mathbf{K}), \\ \pi(\mathbf{q}+\mathbf{K}, \mathbf{q}) &\rightarrow \mathbf{q}\cdot\mathbf{A}^*(\mathbf{K}), \\ \pi(\mathbf{q},\mathbf{q}) &\rightarrow \mathbf{q}\cdot\mathbf{B}\cdot\mathbf{q}, \end{aligned} \tag{5.8}$$

where the vectors $\mathbf{A}(\mathbf{K})$ and the tensor $\mathbf{B}$ are well-defined quantities independent of $\mathbf{q}$. Thus, in the case of an insulator ϵ has precisely the same form as $\mathbf{q}\rightarrow 0$ as is given by the SCF formulas.[14,30,31]

Consider now a metal. In addition to the excitations of finite energy found in the insulator, there are excitations of vanishing energy as $\mathbf{q}\rightarrow 0$. However, our assumption of the validity of the BO approximation in the metal is equivalent to assuming that the electrons near the Fermi surface are long-lived Landau quasiparticles. That is, under the present assumptions the SCF approximation is valid for the description of any characteristically metallic excitations. For $q\rightarrow 0$ we may immediately adopt the SCF form for the dielectric function matrix in which $\pi(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ has a well-defined finite limit for all $\mathbf{K}$ and $\mathbf{K}'$. Therefore, in every case in which the BO approximation is valid, metal or insulator, the exact ϵ matrix has the same analytic properties as in the SCF approximation.

B. Inverse Dielectric Function

In order to determine the analytic properties of ϵ^{-1}, we must examine the inversion of the ϵ matrix.[32] Let a square matrix M and its inverse be written in the forms

$$M=\begin{bmatrix} P & Q \\ R & S \end{bmatrix}, \quad M^{-1}=\begin{bmatrix} W & X \\ Y & Z \end{bmatrix}, \tag{5.9}$$

where P and S are square matrices assumed to be nonsingular. It is easy to verify that

$$\begin{aligned} X&=-WQS^{-1}, \\ Y&=-S^{-1}RW, \\ W&=(P-QS^{-1}R)^{-1}, \end{aligned} \tag{5.10}$$

and that the remaining elements of the inverse matrix may be expressed as

$$Z=S^{-1}+YW^{-1}X. \tag{5.11}$$

The needed properties of ϵ^{-1} are obtained by identifying P with the 1×1 matrix $\epsilon(\mathbf{q},\mathbf{q})$, W with $\epsilon^{-1}(\mathbf{q},\mathbf{q})$, S with $\epsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ for $\mathbf{K}$ and $\mathbf{K}'\neq 0$, and so forth. The discussion in Sec. V A shows that S, and thus S^{-1}, are always analytic functions of $\mathbf{q}$ at $\mathbf{q}=0$. In the case of a metal it follows from (5.10) and (5.11) that each element of the $\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ matrix is an analytic function of $\mathbf{q}$ and that each has a finite limit at $\mathbf{q}=0$ except for $\epsilon^{-1}(\mathbf{q},\mathbf{q})$ and $\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q})$ which go as q^2.

However, in the case of an insulator, using (5.7), (5.8), and (5.10), we find for $\mathbf{q}\rightarrow 0$,

$$[1/\epsilon^{-1}(\mathbf{q},\mathbf{q})]\rightarrow \hat{q}\cdot\mathbf{B}'\cdot\hat{q}, \tag{5.12}$$

$$\frac{\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q})}{\epsilon^{-1}(\mathbf{q},\mathbf{q})}\rightarrow -\frac{4\pi e^2}{\Omega}\frac{|\mathbf{q}|\hat{q}\cdot\mathbf{A}'^*(\mathbf{K})}{K^2}, \tag{5.13a}$$

$$\frac{\epsilon^{-1}(\mathbf{q}, \mathbf{q}+\mathbf{K})}{\epsilon^{-1}(\mathbf{q},\mathbf{q})}\rightarrow -\frac{4\pi e^2}{\Omega}\frac{1}{|\mathbf{q}|}\hat{q}\cdot\mathbf{A}'(\mathbf{K}) \tag{5.13b}$$

for $\mathbf{K}\neq 0$, where

$$\mathbf{A}'(\mathbf{K})=\textstyle\sum_{\mathbf{K}'} \mathbf{A}(\mathbf{K}')S^{-1}(\mathbf{K}',\mathbf{K}), \tag{5.14}$$

and $\mathbf{B}'$ is easily derived. Thus the first term on the right-hand side of (5.11) is analytic but the second term is, in general, nonanalytic at $\mathbf{q}=0$ and has a direct product form analogous to the second term of (4.7).

C. Dynamical Matrix and Effective Charges in Insulators

The analytic form of the dynamical matrix $\bar{C}$ defined in (4.5) now may be easily displayed. In the case of a metal, the above analysis shows that every element of $\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})$ is always an analytic function of $\mathbf{q}$. Thus the separation of the terms in ϵ^{-1} in (5.11) has no particular interest and the form for $\bar{C}$ as given in (4.5) is sufficient.

In an insulator, on the other hand, the form of ϵ^{-1} given in (5.11)–(5.14) allows $\bar{C}$ to be separated into two parts which in general have different analytic behavior:

$$\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})=\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q},1)+\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q},2). \tag{5.15}$$

Here $\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q},1)$ is the analytic part

$$\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q},1)=\frac{4\pi e^2}{\Omega}Z_sZ_{s'}\sum_{\mathbf{K}\pm 0,\ \mathbf{K}'\pm 0}\frac{(\mathbf{q}+\mathbf{K})^\alpha(\mathbf{q}+\mathbf{K}')^\beta}{|\mathbf{q}+\mathbf{K}'|^2}\times S^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')e^{i(\mathbf{K}\cdot\mathbf{R}_s-\mathbf{K}'\cdot\mathbf{R}_{s'})}, \tag{5.16}$$

where S^{-1} is the inverse of the matrix $\epsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ for $\mathbf{K}$ and $\mathbf{K}'\neq 0$. The remaining term contains all

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[32] The essence of this inversion procedure was first applied to ϵ for the special case of the diamond structure by A. A. Maradudin and L. J. Sham (private communication). More recently, Sham (Ref. 16) has also derived the results given in this subsection for an arbitrary crystal structure.

possibly nonanalytic behavior and may be written

$$\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q},2)=\frac{\Omega}{4\pi\epsilon^{-1}(\mathbf{q},\mathbf{q})}\sum_{\gamma}E_s{}^{\gamma\alpha}(\mathbf{q})^*E_{s'}{}^{\gamma\beta}(\mathbf{q}),\qquad(5.17)$$

where $E_s{}^{\gamma\alpha}(\mathbf{q})$ is the long-wavelength component of the electric field (macroscopic field) per unit displacement of the nuclei of type s for a phonon of wave vector $\mathbf{q}$:

$$E_s{}^{\gamma\alpha}(\mathbf{q})=-\frac{4\pi|e|}{\Omega}q^{\gamma}\times\sum_{\mathbf{K}}\epsilon^{-1}(\mathbf{q},\,\mathbf{q}+\mathbf{K})\frac{(\mathbf{q}+\mathbf{K})^{\alpha}}{|\mathbf{q}+\mathbf{K}|^2}Z_se^{-i\mathbf{K}\cdot\mathbf{R}_s}.\qquad(5.18)$$

The dynamical matrix in the microscopic theory of an insulator now may be cast in exactly the form (4.7) of the phenomenological theory. First, we note that the high-frequency macroscopic dielectric function is given by[30,31]

$$\epsilon_0(\mathbf{q})=1/\epsilon^{-1}(\mathbf{q},\mathbf{q}).\qquad(5.19)$$

The identification is completed with the formulas for the effective charge tensor generalized to finite $\mathbf{q}$,

$$\sum_{\alpha}\hat{q}^{\alpha}Z_s{}^{\alpha\beta}(\mathbf{q})=\frac{\Omega}{4\pi|e|}\Big[\sum_{\alpha}\hat{q}^{\alpha}E_s{}^{\alpha\beta}(\mathbf{q})/\epsilon^{-1}(\mathbf{q},\mathbf{q})\Big],\qquad(5.20)$$

and the analytic part

$$C_{ss'}{}^{N\alpha\beta}(\mathbf{q})=\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q};1)-\delta_{ss'}\sum_{s''}C_{ss''}{}^{\alpha\beta}(0).\qquad(5.21)$$

The form of ϵ^{-1} given in (5.13) shows that the microscopic effective charge defined by

$$Z_s{}^{\alpha\beta}=\lim_{\mathbf{q}\to0}Z_s{}^{\alpha\beta}(\mathbf{q})\qquad(5.22)$$

has the proper tensor character and is well-defined independent of the direction $\hat{q}$ in which the limit is taken.

The meaning of the effective charge is clarified by rewriting Eq. (5.20) as

$$\lim_{\mathbf{q}\to0}\epsilon^{-1}(\mathbf{q},\mathbf{q})\sum_{\alpha}\hat{q}^{\alpha}Z_s{}^{\alpha\beta}|e|=\frac{\Omega}{4\pi}\lim_{\mathbf{q}\to0}\sum_{\alpha}\hat{q}^{\alpha}E_s{}^{\alpha\beta}(\mathbf{q}).\qquad(5.23)$$

Equation (5.23) shows that $Z_s{}^{\alpha\beta}\times|e|$ is the charge which when screened by only the macroscopic screening gives rise to the exact macroscopic electric field. This means that $Z_s{}^{\alpha\beta}$ is a "bare" charge tensor which incorporates all of the effects of the nonlocal screening, i.e., it is the Born effective charge[33,34] which is also called the dynamic effective charge.[34]

The derivation of the analytic properties of the dynamical matrix could have been given more economically without introducing the ϵ matrix. However, it was felt that because ϵ is the quantity that would actually be computed in a calculation to any degree of approximation, it is the quantity in terms of which the derivation should be given. Moreover, in the present approach the relation to the familiar SCF theory is manifestly apparent.

VI. ACOUSTIC SUM RULE

In a long-wavelength acoustic mode all the nuclei in the unit cell are displaced rigidly independent of s to order q, i.e.,

$$u_s{}^{\alpha}(\mathbf{q})=u^{\alpha}(\mathbf{q})+\mathcal{O}(|\mathbf{q}|).\qquad(6.1)$$

Projecting out the acoustic modes, we find that to order q the acoustic frequencies are eigenvalues of the 3×3 matrix

$$\frac{1}{M}\sum_{ss'}\big[\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})-\bar{C}_{ss'}{}^{\alpha\beta}(0)\big],\qquad(6.2)$$

where M is the mass of the unit cell. We are only interested in the long-wavelength limit of the acoustic-mode frequencies, so that (6.2) is sufficient.

From (6.2) it follows that the condition that all acoustic-mode frequencies go to zero at long wavelength is

$$\lim_{\mathbf{q}\to0}\sum_{ss'}\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})=\sum_{ss'}\bar{C}_{ss'}{}^{\alpha\beta}(0),\qquad(6.3)$$

i.e., $\sum_{ss'}\bar{C}_{ss'}{}^{\alpha\beta}(\mathbf{q})$ must be a continuous function of $\mathbf{q}$ at $\mathbf{q}=0$. In the case of a metal we have seen that (6.3) is trivially satisfied. However, in the case of an insulator, the form of the dynamical matrix (4.7) shows that a necessary and sufficient condition for (6.3) is the *effective charge neutrality* condition

$$\textstyle\sum_s Z_s{}^{\alpha\beta}=0.\qquad(6.4)$$

This requirement has been recognized[1,19] in the phenomenological theory where it is imposed as an additional constraint. Because the effective charges there are purely phenomenological and have magnitudes which must reflect the polarizability of the electrons, this condition cannot be regarded as directly equivalent to a statement of charge neutrality of the system.

In the microscopic theory, however, the definition of the effective charge tensor is fixed [Eq. (5.22)], and we must verify that (6.4) is satisfied to show that the acoustic modes always have the proper zero-frequency limit. We shall prove that (6.4) is a consequence of the charge neutrality of the system.

From the microscopic expression (5.20) for $Z_s{}^{\alpha\beta}$,

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[33] M. Born and M. Goppert-Meyer, Handbuch Physik **24**, 638 (1933).

[34] E. Burstein, *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press Ltd., London, 1965), p. 315; Int. J. Quantum Chem. **1s**, 759 (1967).

we find that the charge neutrality condition (6.4) is

$$\sum_s\left(\delta_{\alpha\beta}Z_s-\sum_{\mathbf{K}\neq 0,\ \mathbf{K}'\neq 0} A^\alpha(\mathbf{K}')S^{-1}(\mathbf{K}',\mathbf{K})\times\frac{\mathbf{K}^\beta}{K^2}Z_s e^{-i\mathbf{K}\cdot\mathbf{R}_s}\right)=0. \qquad (6.5)$$

The proof of (6.5) involves two essential steps. First, we show that for $\mathbf{K}$ and $\mathbf{K}'\neq 0$,

$$S^{-1}(\mathbf{K},\mathbf{K}')=\epsilon^{-1}(\mathbf{K},\mathbf{K}'), \qquad (6.6)$$

where the right-hand side is evaluated at $\mathbf{q}\equiv 0$. This identity follows because for an electrically neutral system the $\mathbf{q}+\mathbf{K}=0$ Fourier component of the Coulomb potential is zero,[25,35] so that $\epsilon(0,\mathbf{K})=\epsilon^{-1}(0,\mathbf{K})=\delta_{0\mathbf{K}}$. Formula (5.11) then establishes (6.6). Second, using (6.6) and the definition of $A(\mathbf{K})$ in (5.8), we find

$$\sum_s Z_s{}^{\alpha\beta}=\delta_{\alpha\beta}\sum_s Z_s+\sum_{s,\mathbf{K}',\mathbf{K}\neq 0}\left[\int r^\alpha\left(\frac{\nabla_{\mathrm{r}}{}^2}{4\pi}\right)\epsilon(\mathbf{r},\mathbf{r}')e^{(i\mathbf{K}'\cdot\mathbf{r}')}d^3r\,d^3r'\right]\times\epsilon^{-1}(\mathbf{K},\mathbf{K}')(K^\beta/K^2)Z_s e^{(-i\mathbf{K}\cdot\mathbf{R}_s)}, \qquad (6.7)$$

which is easily transformed to

$$\sum_s Z_s{}^{\alpha\beta}=\delta_{\alpha\beta}\sum_s Z_s+N^{-1}\int r^\alpha\left(\frac{\nabla_{\mathrm{r}}{}^2}{4\pi}\right)\epsilon(\mathbf{r},\mathbf{r}')\epsilon^{-1}(\mathbf{r}',\mathbf{r}'')\times\left(\sum_{s,l}\frac{\partial}{\partial R_{s,l}{}^\beta}\frac{Z_s}{|\mathbf{r}''-\mathbf{R}_{s,l}|}\right)d^3r\,d^3r'd^3r''=\delta_{\alpha\beta}\sum_s(Z_s-Z_s), \qquad (6.8)$$

from which (6.4) follows.

Because the effective charges are defined in terms of ϵ^{-1}, the charge neutrality condition places an important constraint on the inverse dielectric function. For an arbitrary insulator and for any direction $\hat{q}$ and any component β, Eq. (6.4) implies

$$\lim_{\mathbf{q}\to 0}\sum_{s,\mathbf{K}}\epsilon^{-1}(\mathbf{q},\mathbf{q}+\mathbf{K})\frac{|\mathbf{q}|\,(\mathbf{q}+\mathbf{K})^\beta}{|\mathbf{q}+\mathbf{K}|^2}Z_s e^{-i\mathbf{K}\cdot\mathbf{R}_s}=0. \qquad (6.9)$$

We call the condition (6.9) the acoustic sum rule[14] on ϵ^{-1}.

An important consequence of the acoustic sum rule is that ϵ^{-1} cannot be a diagonal matrix for an insulator. It follows from (5.19) that the first term in the sum over $\mathbf{K}$ in (6.9) is always nonzero for some direction β. Therefore, (6.9) can be satisfied only if there is a cancellation between the diagonal and off-diagonal elements of ϵ^{-1}. In terms of the calculation of the phonon dispersion curves of an insulator from the dielectric function, the acoustic sum rule implies that the off-diagonal elements of ϵ^{-1} must be included and must satisfy the sum rule if the acoustic modes are to vanish at long wavelength. In a metal, on the other hand, there is no such requirement. Any ϵ^{-1} matrix with the characteristic metallic behavior ($\epsilon_0\sim 1/q^2$ as $q\to 0$) yields acoustic modes with the proper long-wavelength limit. This distinction demonstrates the large computational differences between metals and insulators and the difficulty of any first-principles calculation in an insulator.

Note that in the discussion of analytic properties no restriction to ionic crystals was made. The results must also apply to nonionic insulators for which $Z_s{}^{\alpha\beta}=0$ for all s, which may be regarded as a special case of (6.4), in which all the effective charges are equal. In this case the effective charge terms vanish in the dynamical matrix, but the acoustic sum rule (6.9) is nevertheless a necessary requirement on ϵ^{-1}.

The division of charges in the crystal in the manner proposed by Phillips[36] in his bond-charge model can be given a fundamental basis in the microscopic theory presented above. The effective charge in the microscopic theory can be divided into "diagonal" and "off-diagonal" parts coming, respectively, from the $\mathbf{K}=0$ and $\mathbf{K}\neq 0$ terms in the sum in (5.20). These new effective charges correspond directly to the charges in the Phillips model. The connection is discussed in detail elsewhere by one of us.[5]

VII. ADDITIONAL RESULTS FOR CRYSTALS

In the previous sections it was shown that the dynamical matrix for an insulator has the same form as the phenomenological expression of Cochran and Cowley (CC).[19] In addition, the form of the dynamical matrix (4.4) and the effective charge neutrality condition were found to hold in the microscopic theory. Therefore, all results derived by CC extend also to the exact microscopic theory for any material, assuming only the adiabatic approximation. [We may formally extend the form (4.7) of the dynamical matrix to metals with $Z_s{}^{\alpha\beta}=0$ and with the proper definition of C^N.]

One of the results of CC is the demonstration that the total static dielectric tensor that describes the response of the system, including the nuclear response, to a static long-wavelength potential is given by

$$\epsilon_s(\hat{q})=\lim_{\mathbf{q}\to 0}\left\{1/\epsilon^{-1}(\mathbf{q},\mathbf{q})+\frac{4\pi}{\Omega}\sum_{\alpha\beta,\gamma\delta,ss'}\hat{q}^\alpha Z_s{}^{\alpha\beta}[C^N(0)]_{ss'}{}^{-1\beta\gamma}Z_{s'}{}^{\gamma\delta}\hat{q}^\delta\right\}, \qquad (7.1)$$

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[35] There is an ambiguity in the definition of $\epsilon^{-1}(K,K')$ for K or $K'=0$. The form obtained here follows from Ref. 25, in which we noted that the Hamiltonian itself is invariant to the choice of $v(0)$. All observable quantities must be unaffected by the choice $v(0)=0$. However, we note that $\epsilon^{-1}(0,K)$ as defined here does *not* describe the change in the average total potential as the external field is varied.

[36] J. C. Phillips, Phys. Rev. **168**, 917 (1968).

where the limit is taken along the $\hat{q}$ direction. Because $C^N(\mathbf{q})$ is an analytic function of $\mathbf{q}$, its limiting value has been taken in (7.1). The matrix $[C^N(0)]^{-1}$ is defined by (see CC) (1) inverting the $3(n-1)\times 3(n-1)$ matrix formed by deleting the rows and columns of $C^N(0)$ corresponding to any atom s' and (2) inserting zeros in the rows and columns of the inverse matrix corresponding to atom s'.

The first term on the right-hand side of (7.1) is the dielectric tensor given by Adler[31] and by Wiser.[30] Their result gives the complete static dielectric tensor only in the case of metals or nonionic insulators. Equation (7.1) provides the extension of their formula to give the exact expression (within the harmonic approximation) for the total response of any crystal to an external field which is sufficiently slowly varying that both the nuclei and the electrons respond adiabatically.

A second result derived by CC is the generalization of the LST relation[20] to include crystals of arbitrary symmetry. Let us simply quote here the most general form of the LST relation,

$$\lim_{\mathbf{q}\to 0}\prod_{\lambda=4}^{3n}\omega_\lambda^2(\mathbf{q})=\kappa\frac{\epsilon_s(\hat{q})}{\epsilon_0(\hat{q})}, \tag{7.2}$$

where the left-hand side of (7.2) denotes the product of all the optic frequencies and κ is a constant independent of $\hat{q}$. The LST relation (7.2) thus follows from the microscopic theory; the only point remaining to complete the interpretation of (7.2) is to demonstrate that $\epsilon_0(\hat{q})$, originally introduced as a longitudinal dielectric function, can in general be identified with the optical (or transverse) dielectric tensor.

The tensor $\epsilon_0(\hat{q})$ [Eq. (5.19)] represents the total long-wavelength response of the system to an external scalar potential of frequency much higher than any phonon frequency but small compared to any energy required to excite an electron from a filled to an unfilled state. For a cubic material it has also been shown by Ambegaokar and Kohn[28] that $\epsilon_0(\hat{q})=\epsilon_0$ is also the square of the refractive index at the given frequency. The same result can be inferred from Adler's[30] arguments. But for arbitrary symmetry the identification must be demonstrated. That is, one must show that there exists the tensor $\epsilon_0{}^{\alpha\beta}$ such that

$$\epsilon_0(\hat{q})=\sum_{\alpha\beta}\hat{q}^\alpha\epsilon_0{}^{\alpha\beta}\hat{q}^\beta, \tag{7.3}$$

and that the dispersion relation for a transverse electromagnetic wave (with frequency ω in the above-mentioned range) is given by

$$\det|(\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta)-(\omega^2/c^2q^2)\epsilon_0{}^{\alpha\beta}|=0. \tag{7.4}$$

The demonstration of the required properties of $\epsilon_0{}^{\alpha\beta}$ will be given elsewhere.[37] Establishing Eq. (7.4) constitutes a microscopic derivation of the transverse dielectric tensor and completes the derivation of the generalized LST relation.

VIII. SUMMARY AND CONCLUSIONS

The theory of lattice dynamics has been examined from a microscopic quantum-mechanical point of view within the harmonic and adiabatic approximations. The results fall into two categories. In the first category are the microscopic expressions for the force constants and their interrelations—the invariance conditions—which were derived for an arbitrary solid, crystalline, amorphous, or molecular, in the absence of any external forces. The second category of results applies to crystals only. We have pointed out the primary difference between metals and insulating materials and have succeeded in reconstructing completely the usual phenomenological theory of lattice dynamics from the microscopic expressions.

In Sec. II it was shown that the force constants which determine the equations of motion in the harmonic and adiabatic approximations are the second derivatives of the total free energy of the system with respect to the nuclear coordinates. It is then a matter of ordinary perturbation theory to carry out the differentiation and obtain the exact expressions for the force constants. The identification of the inverse dielectric response function of the electrons ϵ^{-1} in the formulas then yielded a simple and concise derivation of the force constants in terms of ϵ^{-1}. The expressions for the force constants are valid for any solid regardless of the arrangement of the nuclei and treat the electrons in an exact many-body framework.

In Sec. III, it was shown that the force constants derived there satisfy the translation and rotation conditions given by Born.[1] Thus the necessary invariance of the truncated expression for the free energy was explicitly proved.

In Secs. IV–VI it was shown that the analytic properties of the dielectric function matrix $\epsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}')$ as a function of $\mathbf{q}$ are sufficient to establish the connection of the dynamical matrix in the microscopic theory to that assumed in the phenomenological theory of lattice dynamics. The analytic properties of ϵ near $\mathbf{q}=0$ in the general many-body theory were shown to be exactly the same as in the well-known SCF approximation for ϵ.[30,31] It then followed that in the case of a metal every element of the dynamical matrix is an analytic function of $\mathbf{q}$ as has been previously recognized.[3,7–13] In an insulator, on the other hand, the present analysis has provided the first microscopic derivation of the dynamical matrix (4.7) derived for ionic crystals by Cochran and Cowley[19] from a purely phenomenological point of view. In particular, the microscopic theory provides exact expressions for the dynamical effective charge tensor $Z_s{}^{\alpha\beta}$ and for the

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[37] R. M. Pick (to be published).

analytic part of the dynamical matrix $C^N(\mathbf{q})$ in terms of the dielectric function matrix $\epsilon(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$.

Examination of the acoustic modes at long wavelength showed that for an insulator a necessary and sufficient condition that all acoustic-mode frequencies vanish as $q \rightarrow 0$ is the effective charge neutrality condition (6.4). In the phenomenological approach the condition (6.4) is imposed as a constraint on the otherwise arbitrary effective charges. Here we have shown that in the microscopic theory, the effective charge neutrality condition is implied by the real charge neutrality of the system.

The effective charge neutrality shows that the inverse dielectric function satisfies a requirement for $q \rightarrow 0$ which we call the *acoustic sum rule*. From the point of view of calculating dispersion curves, the necessity of fulfilling the acoustic sum rule in calculations for insulators represents a constraint of great practical importance, which does not exist for metals. In the case of a metal, no special requirements are placed on ϵ^{-1} as long as it exhibits the metallic behavior at long wavelength. Then the crudest approximations such as restricting $\epsilon^{-1}(\mathbf{q}+\mathbf{K}, \mathbf{q}+\mathbf{K}')$ to be diagonal, are allowed. This explains the wide, and rather successful, use of such approximations for simple metals.[7–13] But for insulators the acoustic sum rule implies a necessary cancellation between diagonal and off-diagonal elements of ϵ^{-1}. A high degree of accuracy in the computation of the entire inverse dielectric function matrix is required merely to satisfy the sum rule. An alternative to the calculation of the entire ϵ^{-1} matrix is to make use of the acoustic sum rule to derive information about the off-diagonal elements of ϵ^{-1}. A discussion of one such approximation procedure utilizing the sum rule as a justification for the Phillips model[36] has been given by one of us[5] along with results of calculations in the case of silicon.

In closing, we point out the two most important limitations of the present work. First, the Born-Oppenheimer approximation forced us to exclude from our analysis semimetals and degenerate semiconductors with low plasma frequencies. Second, the retardation effects of the electromagnetic fields inside the solid were completely omitted so that the coupling of the electromagnetic field with the optic phonons did not appear. A unified treatment including the nonadiabatic and retardation effects would complete the microscopic formulation of lattice dynamics in the harmonic approximation.

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APPENDIX

The proof of the identity (3.6) involves several steps but is straightforward. First, the second term in (3.6) may be written

$$\langle \textstyle\sum_t [\mathcal{O}_{\mathbf{r}_t}, f(\mathbf{r}_t)] \rangle = \langle [\mathcal{O}, f] \rangle , \tag{A1}$$

where

$$\mathcal{O} = \textstyle\sum_t \mathcal{O}_{\mathbf{r}_t} \tag{A2}$$

and

$$f = \textstyle\sum_t f(\mathbf{r}_t) . \tag{A3}$$

Next, the order of the operators in the trace on the right-hand side of (A1) may be rearranged to give

$$\langle [\mathcal{O}, f] \rangle = -\mathrm{tr}\{ f [\mathcal{O}, e^{-\beta H_e^{(0)}}] \} / \mathrm{Tr}\{ e^{-\beta H_e^{(0)}} \} . \tag{A4}$$

The commutator may be transformed using a formula given by Kubo[23]

$$[\mathcal{O}, e^{-\beta H_e^{(0)}}] = -\int_0^\beta d\tau\, e^{-\tau H_e^{(0)}} [\mathcal{O}, H_e^{(0)}] e^{-(\beta-\tau) H_e^{(0)}} . \tag{A5}$$

But because of the conditions (3.4) and (3.5), $\mathcal{O}$ commutes with electronic kinetic energy and electron-electron interaction energy operators in $H_e^{(0)}$, so that

$$[\mathcal{O}, H_e^{(0)}] = [\mathcal{O}, \mathcal{V}] . \tag{A6}$$

Substituting (A5) and (A6) in (A1) and using the definition (2.17) of $D(\mathbf{r},\mathbf{r}')$, we find that (A1) is the negative of the first term in (3.6) except for the term in $D(\mathbf{r},\mathbf{r}')$ involving the product of the average charge densities

$$\beta \left(\int f(\mathbf{r}) \langle \rho(\mathbf{r}) \rangle d^3r \right) \times \left(\int \langle \rho(\mathbf{r}') \rangle \textstyle\sum_b [\mathcal{O}_{\mathbf{R}_b}, V_N(\mathbf{r}')] d^3r' \right) . \tag{A7}$$

However, the second term in large parentheses in (A7) may be shown to be

$$-\mathrm{Tr}\{ e^{-\beta H_e^{(0)}} [\mathcal{O}, e^{-\beta H_e^{(0)}}] \} / \mathrm{tr}\{ e^{-\beta H_e^{(0)}} \} , \tag{A8}$$

which vanishes by the cyclic invariance of the trace. Thus the identity (3.6) is established.