

**Microscopic theory of dielectric screening and lattice dynamics. I. Local-field corrections and dielectric constants\***

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We show how local-field corrections in solids may be treated by a very general factorization scheme for  $\epsilon(\vec{Q}, \vec{Q}')$  from which practically all existing models of dielectric screening and lattice dynamics may be derived as special cases, including the shell model, the breathing-shell model, and the bond-charge model, as well as generalizations of these models which result from the introduction of a "screening medium." The latter arise naturally in our formalism from a portion of  $\epsilon(\vec{Q}, \vec{Q}')$  which is purely diagonal. It is shown that the formalism also allows for charge-transfer and multipole effects. In this first paper we derive explicit expressions for the elements of  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  and its inverse and show that they have the correct analytic behavior as  $\vec{q} \rightarrow 0$ . For insulators of cubic and tetrahedral symmetry, explicit microscopic expressions are derived for the high-frequency dielectric constant  $\epsilon_\infty$ , thus realizing a generalization of the Lorentz-Lorenz formula, and for the local field produced by an applied field.

I. INTRODUCTION

The formal microscopic theory of dielectric screening in insulators has been fairly extensively discussed in recent years.<sup>1-7</sup> For such solids as well as for non-free-electron-like metals, it is well known that a correct treatment of the response of the electrons to an external potential must take into account the so-called local-field corrections. These will exist whenever the electrons are properly described in terms of Bloch states rather than single plane waves. The phonon spectrum of a crystal is intimately related to the nature of the dielectric screening in the crystal and provides a sensitive test of the model used to describe the screening. A unified theoretical description of the lattice dynamics of crystals must therefore start with a unified description of dielectric screening in solids.

The formal theory of dielectric screening may be expressed in terms of the dielectric or screening matrix given by

$$\epsilon(\vec{Q}, \vec{Q}') = \delta_{\vec{Q}\vec{Q}'} - v(\vec{Q})\chi^{(0)}(\vec{Q}, \vec{Q}'), \tag{1}$$

where  $v(\vec{Q})$  is the Fourier transform of the effective electron-electron interaction given by

$$v(\vec{Q}) = \frac{4\pi e^2}{\Omega Q^2} [1 - f_{xc}(\vec{Q})], \tag{2}$$

where  $\Omega$  is the unit-cell volume and  $f_{xc}(\vec{Q})$  approximately allows for exchange and correlation effects.<sup>8-10</sup> [We shall assume unit volume for the crystal and always define our Fourier transforms to be of the form (2) with the unit-cell volume in the denominator.]

$\chi^{(0)}(\vec{Q}, \vec{Q}')$  is the so-called irreducible-polarization part of the density-response matrix and is defined by

$$\chi^{(0)}(\vec{Q}, \vec{Q}') = 2 \sum'_{kk'} \frac{n_k - n_{k'}}{E_k - E_{k'}} \times \langle \Psi_k | e^{-i\vec{Q}\cdot\vec{r}} | \Psi_{k'} \rangle \langle \Psi_{k'} | e^{i\vec{Q}'\cdot\vec{r}} | \Psi_k \rangle, \tag{3}$$

where  $k, k'$  label the actual Bloch states and represent both the Bloch wave vector and the band indices.  $\Psi_k$  represents the wave function of the Bloch state  $k$ , with energy  $E_k$  and occupation number  $n_k$  exclusive of spin. The prime over the summation in Eq. (3) implies the case  $k = k'$  is to be excluded.

The static-electron-density-response matrix  $\chi(\vec{Q}, \vec{Q}')$  is defined by

$$\Delta\rho(\vec{Q}) = \sum_{\vec{Q}'} \chi(\vec{Q}, \vec{Q}') V_{\text{ext}}(\vec{Q}'), \tag{4}$$

where  $\Delta\rho(\vec{Q})$  is the Fourier transform of the electron-density perturbation induced by an external potential whose Fourier transform is given by  $V_{\text{ext}}(\vec{Q}')$ .  $\chi(\vec{Q}, \vec{Q}')$  is related to  $\epsilon(\vec{Q}, \vec{Q}')$  by

$$\chi(\vec{Q}, \vec{Q}') = -[1/v(\vec{Q})][\delta_{\vec{Q}\vec{Q}'} - \epsilon^{-1}(\vec{Q}, \vec{Q}')]. \tag{5}$$

Thus we have the problem of carrying out the inversion of the matrix  $\epsilon(\vec{Q}, \vec{Q}')$ , the off-diagonal elements of which give rise to the so-called local-field corrections. To carry out such an inversion exactly is clearly an impossible task since, except possibly for the free-electron metals,  $\epsilon(\vec{Q}, \vec{Q}')$  will contain a large number of off-diagonal elements. One must therefore resort to approximate methods. On the other hand, there exist quite a number of phenomenological models such as the shell model,

breathing-shell model, bond-charge model, deformable-shell model, and so forth,<sup>11-17</sup> which have been used with some degree of success to calculate the dielectric and lattice-dynamical properties of insulators. It is clear therefore that the physical assumptions about the nature of the screening that is being put into these models must correspond to an explicit evaluation of  $\epsilon^{-1}(\vec{Q}, \vec{Q}')$  in various approximations. In this first paper, we present a general factorization scheme for  $\epsilon(\vec{Q}, \vec{Q}')$  which enables the inversion to be carried out explicitly and which connects the formal theory of dielectric screening in solids to all of the various phenomenological models referred to above. We thus achieve a unified microscopic description of screening in solids from which the various models may be derived as special limiting cases. The formalism also leads to models more general than those used hitherto and these may be useful for treating the lattice dynamics of a wide variety of solids ranging from semiconductors to transition metals. We also derive the generalization of the Lorentz-Lorenz formula, relating the dielectric constant to the unit-cell polarizability for cubic and tetrahedral crystals, to the case of arbitrary local fields.

We discuss the application to lattice dynamics in the second paper (II) in this series and in a third paper (III) show how it can be extended to include intraband transitions.

Recently several authors have considered the justification of similar factorization schemes under quite general conditions, starting from Wannier representations.<sup>18-20</sup> In practical applications of this work an expression for  $\epsilon(\vec{Q}, \vec{Q}')$  is obtained which is formally similar to that derived in the present framework for the contribution from intraband transitions. For this reason it is convenient to postpone the discussion of these theories to the third paper in the series.

A preliminary report of this work has been published earlier.<sup>21</sup>

## II. FACTORIZATION ANSATZ

In an earlier paper by one of the authors<sup>22</sup> it was shown that for a crystal with a set of completely full bands separated by a finite gap from a set of completely empty bands, i. e., an insulator or a semiconductor, the generalized oscillator strength matrix element for allowed transitions could be written as

$$\langle \Psi_k | e^{-i\vec{Q}\cdot\vec{r}} | \Psi_{k'} \rangle = \sum_{\alpha} Q_{\alpha} f_{kk',\alpha}(\vec{Q}), \quad (6)$$

where

$$f_{kk',\alpha}(\vec{Q}) = (\hbar/m) \langle \Psi_k | e^{-i\vec{Q}\cdot\vec{r}} p_{\alpha} | \Psi_{k'} \rangle / [E_k - E_{k'} + (\hbar^2/2m)Q^2], \quad (7)$$

where  $p_{\alpha}$  is the Cartesian component of the electron-momentum operator and  $m$  is the electron mass. The  $f_{kk',\alpha}(\vec{Q})$  tend to finite values as  $\vec{Q} \rightarrow 0$  so that for an insulating crystal, Eq. (6) has the correct analytic structure as  $\vec{Q} \rightarrow 0$ .

Substituting in Eq. (3), we see that

$$\chi^{(0)}(\vec{Q}, \vec{Q}') = - \sum_{\alpha\beta} Q_{\alpha} a'_{\alpha\beta}(\vec{Q}, \vec{Q}') Q'_{\beta}, \quad (8)$$

where

$$a'_{\alpha\beta}(\vec{Q}, \vec{Q}') = -2 \sum_{kk'} \frac{n_k - n_{k'}}{E_k - E_{k'}} f_{kk',\alpha}(\vec{Q}) f_{k'k,\beta}^*(\vec{Q}'). \quad (9)$$

At this stage, the natural approximation which suggests itself is that  $a'_{\alpha\beta}(\vec{Q}, \vec{Q}')$  is of separable form. In fact, for the extreme tight-binding limit with only two bands of importance (this situation may, however, violate crystal symmetry; see the discussion in III), it was shown in Ref. 22 that  $a'_{\alpha\beta}(\vec{Q}, \vec{Q}')$  could be written as

$$a'_{\alpha\beta}(\vec{Q}, \vec{Q}') = \sum_{\kappa\kappa'} f^{\kappa}(\vec{Q}) a_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) f^{*\kappa'}(\vec{Q}') \times e^{-i(\vec{Q}\cdot\vec{r}_{\kappa} - \vec{Q}'\cdot\vec{r}_{\kappa'})}, \quad (10)$$

where  $\kappa, \kappa'$  denote the basis atoms in the unit cell, the functions  $f^{\kappa}(\vec{Q})$  are generalized form factors associated with the sites  $\vec{r}_{\kappa}$  (which we may normalize to unity as  $\vec{Q} = 0$ ), and  $\vec{q}$  is the vector  $\vec{Q}$  or  $\vec{Q}'$  reduced to the first Brillouin zone. (It is obvious from the Bloch symmetry of the wave functions that  $\vec{Q}, \vec{Q}'$  in  $\chi^{(0)}$  can differ only by a vector of the reciprocal lattice.) The  $a_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$  is then a generalized  $\vec{q}$ -dependent polarizability tensor which includes "interference" or cross-polarizabilities between atoms  $\kappa \neq \kappa'$  in the unit cell. The general expressions for the  $f^{\kappa}(\vec{Q})$  and  $a_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$  in terms of the tight-binding orbitals in the valence and conduction states were given in Eqs. (59), (A7), and (A8) of Ref. 22. [We should point out here, however, that in order to conform to conventional phase conventions for Fourier transforms, the quantities in Eq. (10) are the complex conjugates of the quantities defined in Refs. 21 and 22.] We may postulate the approximation in Eq. (10) to be valid in the more general case also, and the important fact which results from this approximation is that an explicit inversion of  $\epsilon(\vec{Q}, \vec{Q}')$  is then possible and we arrive at a form for the density-response matrix  $\chi(\vec{Q}, \vec{Q}')$  which may be evaluated in practical cases.

First, in order to conform to the usual phase convention for lattice-dynamical applications, let us absorb the phase factor  $e^{-i\vec{q}\cdot(\vec{r}_{\kappa} - \vec{r}_{\kappa'})}$  into  $a_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$ . Then  $\epsilon(\vec{Q}, \vec{Q}')$  is given by

$$\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \delta_{\vec{q}\vec{q}'} + v(\vec{q} + \vec{G}) \sum_{\alpha\beta}^{\kappa\kappa'} (\vec{q} + \vec{G})_{\alpha} \times f^{\kappa}(\vec{q} + \vec{G}) a_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) f^{*\kappa'}(\vec{q} + \vec{G}')$$

$$\times (\vec{q} + \vec{G}')_{\beta} e^{-i(\vec{G} \cdot \vec{r}_{\kappa} - \vec{G}' \cdot \vec{r}_{\kappa'})} \quad (11)$$

from which it may be verified by direct matrix multiplication that the inverse matrix  $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  may be written as

$$\begin{aligned} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \delta_{\vec{G}\vec{G}'} - v(\vec{q} + \vec{G}) \sum_{\substack{\alpha\beta \\ \kappa\kappa'}} (\vec{q} + \vec{G})_{\alpha} \\ &\times f^{\kappa}(\vec{q} + \vec{G}) S_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) f^{*\kappa'}(\vec{q} + \vec{G}') \\ &\times (\vec{q} + \vec{G}')_{\beta} e^{-i(\vec{G} \cdot \vec{r}_{\kappa} - \vec{G}' \cdot \vec{r}_{\kappa'})}, \quad (12) \end{aligned}$$

where the matrix  $S_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$  is the *inverse* of the  $3r \times 3r$  matrix ( $r$  is the number of basis sites in the unit cell)  $[V_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) + a_{\alpha\beta}^{-1\kappa\kappa'}(\vec{q})]$ , or in matrix form,

$$\underline{S} = [\underline{V} + \underline{a}^{-1}]^{-1}, \quad (13)$$

where the matrix  $\underline{V}$  is defined by

$$\begin{aligned} V_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) &= \sum_{\vec{G}} (\vec{q} + \vec{G})_{\alpha} (\vec{q} + \vec{G})_{\beta} f^{*\kappa}(\vec{q} + \vec{G}) \\ &\times f^{\kappa'}(\vec{q} + \vec{G}) v(\vec{q} + \vec{G}) e^{i\vec{G} \cdot \vec{r}_{\kappa\kappa'}}. \quad (14) \end{aligned}$$

(The vector  $\vec{r}_{\kappa\kappa'}$  is used to denote  $[\vec{r}_{\kappa} - \vec{r}_{\kappa'}]$ .) From Eqs. (5) and (12) we see that the electron-density-response function is given by

$$\begin{aligned} \chi(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= - \sum_{\kappa\alpha} (\vec{q} + \vec{G})_{\alpha} f^{\kappa}(\vec{q} + \vec{G}) \sum_{\kappa'\beta} S_{\alpha\beta}^{\kappa\kappa'}(\vec{q}) \\ &\times f^{*\kappa'}(\vec{q} + \vec{G}') (\vec{q} + \vec{G}')_{\beta} e^{-i(\vec{G} \cdot \vec{r}_{\kappa} - \vec{G}' \cdot \vec{r}_{\kappa'})}. \quad (15) \end{aligned}$$

An examination of Eq. (15) shows that the electron-density response in this approximation corresponds to the appearance of a set of dipole distributions centered on the sites  $\vec{r}_{\kappa}$  and characterized by the set of form factors  $f^{\kappa}(\vec{Q})$ . This is reminiscent of the dipole models of lattice dynamics such as the shell model, deformation-dipole model, and so on. In fact, in Ref. 22 it was shown that Eq. (15) led to a lattice-dynamical model that was formally equivalent to the dipole models referred to above. However, we note that it is already more general in that (conceptually at least) the above models were *point-dipole* models, whereas the appearance of *dipole distributions* in the above equation does lead to an approximate inclusion of higher multipole effects (and charge-transfer effects, as we shall see in III). An inspection of Eq. (14) reveals that  $\underline{V}$  is the coupling coefficient between dipole distributions with form factors  $f^{\kappa}(\vec{Q})$ ,  $f^{\kappa'}(\vec{Q})$  situated on the sublattices  $\kappa$ ,  $\kappa'$  and interacting via the effective electron-electron interaction  $v(\vec{Q})$ . Equations (13)–(15) are really equivalent to the “shell equilibrium condition” of the shell model.

We note that the main point of the “factorization *ansatz*” represented by Eq. (10) is that it reduces the problem of formally inverting an infinite matrix to that of inverting the  $(3r \times 3r)$  matrix  $[\underline{V} + \underline{a}^{-1}]$ . We also note that the matrices  $V_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$  and  $a_{\alpha\beta}^{-1\kappa\kappa'}(\vec{q})$  must be periodic in  $\vec{q}$  space and transform under symmetry operations of the crystal in exactly the

same way as a general dynamical matrix between sublattices  $\kappa$ ,  $\kappa'$  in order that  $\epsilon(\vec{Q}, \vec{Q}')$  possess the correct symmetry. This implies that, if necessary,  $a_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$  can be parameterized in terms of constants in exactly the same way that the dynamical matrix may be parametrized in terms of force constants.

Although the factorization *ansatz* represented by Eq. (11) may be reasonable for ionic crystals, it is unnecessarily restrictive in that it fails to describe  $\epsilon(\vec{Q}, \vec{Q}')$  for a material which contains a large diagonal component of  $\epsilon(\vec{Q}, \vec{Q}')$  such as a semiconductor or a material containing free electrons in addition to the tightly bound electrons. In the case of semiconductors, Phillips<sup>3</sup> proposed an intuitively based model in which he split the electron-density response into a “diagonal” part and a part associated with “bond charges” situated at the midpoints of the covalent bonds. Martin<sup>15</sup> used this idea to set up a lattice-dynamical bond-charge model with which he calculated the phonon-dispersion relations for silicon. We shall discuss his model in more detail in II.

In this paper we show that we may incorporate the above models also in our scheme if we make a suitable generalization of our factorization *ansatz*. First, we note that there is no reason to restrict the sites  $\kappa$ ,  $\kappa'$  in Eq. (11) to be atomic sites, so long as they are chosen consistent with crystal symmetry. {We may just as well choose them as the bond charge sites if this in fact provides a better representation of the actual  $\epsilon(\vec{Q}, \vec{Q}')$ , or a combination of both types of sites and possibly other sites as well. Obviously, the more sites we choose in the unit cell, the better becomes our approximation, but of course the matrix  $[\underline{V} + \underline{a}^{-1}]$  grows larger and so we gain less. In the limit, of course, we simply obtain the real-space double Fourier transform of  $a'_{\alpha\beta}(\vec{Q}, \vec{Q}')$ .}

We could, in principle, represent a large purely diagonal contribution to  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  in the form given in Eq. (11) where the  $\kappa$ ,  $\kappa'$  are now replaced by sites  $s$ ,  $s'$  which can be anywhere in the unit cell. Unfortunately, such a representation would be poorly convergent, since in principle a purely diagonal contribution can only be represented if (a)  $s$ ,  $s'$  sum over *all* points in the cell and (b)  $a_{\alpha\beta}^{ss'}(\vec{q})$  has the form  $a_{\alpha\beta}(\vec{q})\delta_{ss'}$ . In such a case there will be only nonvanishing contributions for  $\vec{G} = \vec{G}'$ . Thus a large number of sites would be required, whereas for the off-diagonal components, which are small anyway, we expect on physical grounds that dipolar distributions on only a few sites are likely to provide a reasonable approximation for the density response. Fortunately, the purely diagonal part can be easily handled by separating it out explicitly from the start and writing our generalized factorization *ansatz* as

$$\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \epsilon_0(\vec{q} + \vec{G})\delta_{\vec{G}\vec{G}'} + v(\vec{q} + \vec{G}) \sum_{\substack{\alpha\beta \\ ss'}} (\vec{q} + \vec{G})_\alpha f^s(\vec{q} + \vec{G}) a_{\alpha\beta}^{ss'}(\vec{q}) f^{*s'}(\vec{q} + \vec{G}') (\vec{q} + \vec{G}')_\beta e^{-i(\vec{G} \cdot \vec{r}_s - \vec{G}' \cdot \vec{r}_{s'})}, \quad (16)$$

where the  $\vec{r}_s$  denote the positions of the  $r$  chosen sites in the unit cell. It may be readily verified that, in this approximation, the inverse matrix becomes

$$\epsilon^{-1}(q + G, q + G') = \frac{1}{\epsilon_0(\vec{q} + \vec{G}')} \left( \delta_{\vec{G}\vec{G}'} - \frac{v(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} \sum_{\substack{\alpha\beta \\ ss'}} (\vec{q} + \vec{G})_\alpha f^s(\vec{q} + \vec{G}) S_{\alpha\beta}^{ss'}(\vec{q}) f^{*s'}(\vec{q} + \vec{G}') (\vec{q} + \vec{G}')_\beta e^{-i(\vec{G} \cdot \vec{r}_s - \vec{G}' \cdot \vec{r}_{s'})} \right), \quad (17)$$

where the matrix  $\underline{S}$  is now the inverse of the  $(3r \times 3r)$  matrix  $[\underline{V} + \underline{a}^{-1}]$ , with

$$V_{\alpha\beta}^{ss'}(\vec{q}) = \sum_{\vec{G}} (\vec{q} + \vec{G})_\alpha (\vec{q} + \vec{G})_\beta f^{*s}(\vec{q} + \vec{G}) f^s(\vec{q} + \vec{G}) \frac{v(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} e^{i\vec{G} \cdot \vec{r}_{ss'}}. \quad (18)$$

The sum still runs over reciprocal-lattice vectors of the crystal, but the matrices  $\underline{V}$  and  $\underline{a}$  now transform according to the symmetry rules for a dynamical matrix appropriate to a hypothetical lattice with basis given by the set of  $\vec{r}_s$ . From Eqs. (5) and (17), the electron-density-response function now becomes

$$\chi(q + G, q + G') = -\frac{1}{v(\vec{q} + \vec{G})} \left( 1 - \frac{1}{\epsilon_0(\vec{q} + \vec{G})} \right) \delta_{\vec{G}\vec{G}'} - \sum_{s\alpha} (\vec{q} + \vec{G})_\alpha \frac{f^s(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} \times e^{-i\vec{G} \cdot \vec{r}_s} \sum_{s'\beta} \frac{S_{\alpha\beta}^{ss'}(\vec{q}) f^{*s'}(\vec{q} + \vec{G}') (\vec{q} + \vec{G}')_\beta}{\epsilon_0(\vec{q} + \vec{G}')} e^{i\vec{G}' \cdot \vec{r}_{s'}}. \quad (19)$$

Thus, the electron-density response splits into two parts—a purely diagonal part analogous to that in the case of the free-electron gas except that the free-electron dielectric function is replaced by  $\epsilon_0(\vec{Q})$ , and a part which corresponds to a set of dipole distributions centered on the sites  $\vec{r}_s$  and characterized by the set of form factors  $f^s(\vec{Q})$ . These dipole distributions in turn produce (via the electron-electron interaction) a polarization from the  $\epsilon_0(\vec{Q})$  part so that the form factors of the *overall* dipolar distributions on the sites  $s$  are  $f^s(\vec{Q})/\epsilon_0(\vec{Q})$  instead of simply  $f^s(\vec{Q})$ .  $\underline{V}$  is now the coupling coefficient between these dipolar distributions which now, however, interact not via the “bare” effective electron-electron interaction  $v(\vec{Q})$  but rather via  $v(\vec{Q})/\epsilon_0(\vec{Q})$ . The interpretation is that  $\epsilon_0(\vec{Q})$  acts in the same way as a screening function for the rest of the interaction. If  $\epsilon_0(\vec{Q})$  arises from the presence of additional free electrons in the system, we see that they provide a screening medium for the interaction between the other electrons, a result expected on intuitive grounds. We should emphasize for the sake of clarity that what we have termed the purely diagonal part  $\epsilon_0(\vec{Q})$  is not the *total* contribution to  $\epsilon(\vec{Q}, \vec{Q}')$ , since some contribution to these elements will obviously also come from the second term of Eq. (16).

Our point of view here is that with the availability of realistic  $\epsilon(\vec{Q}, \vec{Q}')$  from actual band-structure calculations, it should be possible to choose a suitable set of sites  $\vec{r}_s$  and a suitable set of functions  $\epsilon_0(\vec{Q})$ ,  $f^s(\vec{Q})$ , and  $a_{\alpha\beta}^{ss'}(\vec{q})$  to provide a convenient interpolation formula for  $\epsilon(\vec{Q}, \vec{Q}')$  which enables its inversion to be carried out explicitly. The physical

meaning of these functions, however, only becomes clear in certain limiting cases. For instance, for free-electron metals, we can neglect the  $a_{\alpha\beta}^{ss'}(\vec{q})$  and  $\epsilon_0(\vec{Q})$  becomes the free-electron dielectric function and conventional screening theory is retrieved in this limit. For tightly bound solids such as ionic crystals, we may choose the  $\vec{r}_s$  as the ion sites  $\vec{r}_\kappa$ , set  $\epsilon_0(\vec{Q})$  to unity, and then, as discussed above, the dipolar screening models are recovered with the  $a_{\alpha\beta}^{ss'}$  playing the role of ionic polarizability tensors. For metals such as the noble metals which contain fully occupied atomiclike states (e.g.,  $d$ -states) separated in energy from unoccupied states, together with free-electron-like bands,  $\epsilon_0(\vec{Q})$  may be taken to be the free-electron contribution while the interband contribution from the  $d$  states is in the form of the second term of Eq. (15) with the sites  $\vec{r}_s$  being the ion sites  $\vec{r}_\kappa$ . The physical model that results from Eq. (16) then is one of dipolar distributions forming on the ions and associated with the  $d$  electrons, the interaction between these being screened by the  $s$  electrons. The “screened-dipole” model we have termed the *generalized shell model* (GSM). For semiconductors, we may use either the GSM or choose the sites  $\vec{r}_s$  as the bond-charge sites at the centers of the covalent bonds. This screened-dipole model with dipole distributions developing on the bonds possesses the same qualitative features as the bond-charge model (BCM) proposed by Phillips<sup>3</sup> and Martin.<sup>15</sup> Thus which particular way we choose to represent  $\epsilon(\vec{Q}, \vec{Q}')$  within the very general framework of our *ansatz* Eq. (16) depends on the electronic structure of the solid in question.

### III. LOCAL FIELD-CORRECTIONS AND DIELECTRIC CONSTANTS OF INSULATORS

Since we now have an approximation which yields an explicit expression for the density-response function, we may use it to look closely at what is meant by the local field seen by an electron in a crystal. Such local-field effects have been hitherto calculated explicitly only for the point-dipole case, or else ignored altogether. We first look at local-field corrections to the dielectric constant  $\epsilon_\infty$  which is defined as the dielectric constant for frequencies much greater than lattice frequencies but much less than the frequencies of electronic excitations in the solid. Under these circumstances the rigorous expression for  $\epsilon_\infty$  is<sup>23,24</sup>

$$\epsilon_\infty = \lim_{\vec{q} \rightarrow 0} \frac{1}{\epsilon^{-1}(\vec{q}, \vec{q})}. \quad (20)$$

We note that some of the components of the matrix  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  become singular in the limit of  $\vec{q} \rightarrow 0$  as may be seen directly from Eq. (16) if we remember that  $v(\vec{q}) \sim 4\pi e^2 / \Omega q^2$  as  $\vec{q} \rightarrow 0$ . This has been discussed from more general considerations by Pick, Cohen, and Martin.<sup>25</sup> We see that by selecting the appropriate factorization scheme for interband transitions we have obtained the correct analytical behavior of the dielectric matrix for an insulator in the small- $\vec{q}$  limit. In order to handle the singular behavior of this matrix, it is convenient to follow Pick *et al.* in partitioning  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  as

$$\underline{\epsilon} = \begin{pmatrix} \underline{A} & \underline{B} \\ \underline{C} & \underline{D} \end{pmatrix}, \quad (21)$$

where  $\underline{A}$  is the scalar  $\epsilon(\vec{q}, \vec{q})$ ,  $\underline{B}$  is the row vector  $\epsilon(\vec{q}, \vec{q} + \vec{G})$ ,  $\underline{C}$  is the column vector  $\epsilon(\vec{q} + \vec{G}, \vec{q})$ , and  $\underline{D}$  is the matrix  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  ( $\vec{G}, \vec{G}' \neq 0$ ). Then

$$\underline{\epsilon}^{-1} = \begin{pmatrix} \underline{W} & \underline{X} \\ \underline{Y} & \underline{Z} \end{pmatrix}, \quad (22)$$

where

$$\underline{W} = (\underline{A} - \underline{B} \underline{D}^{-1} \underline{C})^{-1}, \quad (23a)$$

$$\underline{X} = -\underline{W} \underline{B} \underline{D}^{-1}, \quad (23b)$$

$$\underline{Y} = -\underline{D}^{-1} \underline{C} \underline{W}, \quad (23c)$$

$$\underline{Z} = \underline{D}^{-1} + \underline{Y} \underline{W}^{-1} \underline{X}. \quad (23d)$$

We note that  $\underline{A}$ ,  $\underline{B}$ ,  $\underline{C}$ ,  $\underline{D}$ ,  $\underline{W}$ ,  $\underline{X}$ ,  $\underline{Y}$ ,  $\underline{Z}$  are all matrices in  $(\vec{G}, \vec{G}')$  space.

Now  $\underline{D}^{-1}$ , which is the inverse of the matrix  $\bar{\epsilon}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  [where  $\bar{\epsilon}$  stands for the matrix  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  with  $\vec{G}, \vec{G}' \neq 0$ ] is readily verified to be given by an expression similar to Eq. (17), except that  $S_{\alpha\beta}^{ss'}(\vec{q})$  in that equation is replaced by  $\bar{S}_{\alpha\beta}^{ss'}(\vec{q})$ , where  $\bar{S}$  is now the inverse of  $[\bar{V} + \underline{a}^{-1}]$  and

$$\begin{aligned} \bar{V}_{\alpha\beta}^{ss'}(\vec{q}) &= \sum_{\vec{G}}' (\vec{q} + \vec{G})_{\alpha} (\vec{q} + \vec{G})_{\beta} f^{*s}(\vec{q} + \vec{G}) \\ &\times f^{s'}(\vec{q} + \vec{G}) \frac{v(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} e^{i\vec{G} \cdot \vec{r}_{ss'}}, \end{aligned} \quad (24)$$

where the prime over the sum indicates the *exclusion of  $\vec{G} = 0$*  from the sum. It is this which causes  $\bar{S}$  to be different from  $\underline{S}$ . Note that the matrices  $\bar{V}$  and  $\bar{S}$  are perfectly regular as  $\vec{q} \rightarrow 0$ . We may now substitute in Eqs. (23) to obtain the elements of  $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  and proceed to the limit  $\vec{q} \rightarrow 0$ . We obtain

$$\begin{aligned} \epsilon_\infty &= \lim_{\vec{q} \rightarrow 0} \frac{1}{\epsilon^{-1}(\vec{q}, \vec{q})} = \lim_{\vec{q} \rightarrow 0} \left( \epsilon(\vec{q}, \vec{q}) \right. \\ &\left. - \sum_{\vec{G}, \vec{G}'}' \epsilon(\vec{q}, \vec{G}) \bar{\epsilon}^{-1}(\vec{G}, \vec{G}') \epsilon(\vec{G}', \vec{q}) \right). \end{aligned} \quad (25)$$

Using Eqs. (16) and (17), noting that  $f^s(\vec{q}) \rightarrow 1$  as  $\vec{q} \rightarrow 0$ , and defining  $\epsilon_0$  to be  $\epsilon_0(\vec{Q} = 0)$ , we get

$$\epsilon_\infty = \epsilon_0 + \sum_{\substack{\alpha\beta \\ ss'}} [ \underline{a} \underline{P} - \underline{a} \bar{V} \underline{a} \underline{P} + \underline{a} \bar{V} \bar{S} \bar{V} \underline{a} \underline{P} ]_{\alpha\beta}^{ss'}, \quad (26)$$

where the matrices  $\underline{a}$ ,  $\bar{V}$  are all evaluated at  $\vec{q} = 0$  and

$$P_{\alpha\beta}^{ss'}(\vec{q}) = \lim_{\vec{q} \rightarrow 0} \frac{4\pi e^2}{\Omega} \frac{q_\alpha q_\beta}{q^2}. \quad (27)$$

Now, since

$$\underline{S} = [\bar{V} + \underline{a}^{-1}]^{-1}, \quad (28)$$

we have

$$\bar{S} = (\underline{1} - \bar{S} \bar{V}) \underline{a} = \underline{a} (\underline{1} - \bar{V} \bar{S}); \quad (29)$$

$$\begin{aligned} \epsilon_\infty &= \epsilon_0 + \sum_{\substack{\alpha\beta \\ ss'}} [ \underline{1} - \underline{a} \bar{V} (\underline{1} - \bar{S} \bar{V}) ] \underline{a} \underline{P} ]_{\alpha\beta}^{ss'} \\ &= \epsilon_0 + \sum_{\substack{\alpha\beta \\ ss'}} [ \bar{S} \underline{P} ]_{\alpha\beta}^{ss'} \\ &= \epsilon_0 + \lim_{\vec{q} \rightarrow 0} \sum_{\substack{\alpha\beta \\ ss'}} \bar{S}_{\alpha\beta}^{ss'} \frac{q_\alpha q_\beta}{q^2} \frac{4\pi e^2}{\Omega}. \end{aligned} \quad (30)$$

The quantity  $\epsilon_\infty$  represents the longitudinal component

$$\sum_{\alpha\beta} \epsilon_{\alpha\beta}(\infty) \frac{q_\alpha q_\beta}{q^2}$$

of the full high-frequency dielectric tensor which is given by

$$\epsilon_{\alpha\beta}(\infty) = \epsilon_0 \delta_{\alpha\beta} + \frac{4\pi e^2}{\Omega} \sum_{ss'} \bar{S}_{\alpha\beta}^{ss'}. \quad (30a)$$

For noncubic crystals,  $\epsilon_\infty$  as defined in Eq. (20) depends on the direction in which  $\vec{q} \rightarrow 0$ . For crystals of tetrahedral or cubic symmetry  $\epsilon_\infty$  is defined uniquely. In this case, lattice symmetry requires that

$$\sum_{ss'} \bar{S}_{\alpha\beta}^{ss'} = \delta_{\alpha\beta} \sum_{ss'} \bar{S}_{\alpha\alpha}^{ss'}$$

and is independent of  $\alpha$ . Thus, finally,

$$\epsilon_\infty = \epsilon_0 + \frac{4\pi e^2}{\Omega} \sum_{ss'} \bar{S}_{\alpha\alpha}^{ss'}. \quad (31)$$

(Unless the argument  $\vec{q}$  of matrices such as  $\bar{S}$ ,  $\bar{V}$ ,  $\underline{a}$ ,

etc., appears explicitly in this paper, the matrices will be understood to be evaluated at  $\vec{q}=0$ .)

Equation (31) constitutes a generalization of the Lorentz-Lorentz formula, which may be obtained in the appropriate limit as discussed below. The expression for  $\epsilon(\vec{q}, \vec{q})$  in the limit  $\vec{q} \rightarrow 0$  is, on the other hand, by Eq. (16), for cubic crystals,

$$\epsilon(0, 0) = \epsilon_0 + \frac{4\pi e^2}{\Omega} \sum_{ss'} a_{\alpha\alpha}^{ss'}. \quad (32)$$

The difference between expressions (31) and (32) is due to the so-called local-field corrections. In order to see whether these enhance or decrease the value of  $\epsilon_\infty$ , we have to examine whether

$$\sum_{ss'} \bar{S}_{\alpha\alpha}^{ss'} \geq \sum_{ss'} a_{\alpha\alpha}^{ss'}.$$

Consider an ionic crystal and let us suppose it is well described by a model where  $\epsilon_0(\vec{Q})=1$ , and the form factors  $f^s(\vec{Q})$  are situated on the ionic sites with negligible overlap in real space. Let us further suppose that the effect of exchange and correlation corrections to  $v(\vec{Q})$  is simply to remove the interaction of a distribution on a particular ion site with itself but to leave it as pure Coulombic between different sites. In such a case the matrix  $\bar{V}_{\alpha\beta}^{\kappa\kappa'}$  becomes the  $\vec{q}=0$  limit of the ordinary Coulomb-coupling coefficient between point dipoles on sublattices  $\kappa, \kappa'$  with the self-interaction removed<sup>26</sup> and for cubic and tetrahedral crystals it is well-known that

$$\bar{V}_{\alpha\beta}^{\kappa\kappa'} = -\frac{4\pi e^2}{3\Omega} \delta_{\alpha\beta} \text{ for all } \kappa, \kappa'. \quad (33)$$

Further, since the sites  $\vec{r}_s$  are now the ionic sites  $\vec{r}_\kappa$ , by crystal symmetry,

$$a_{\alpha\beta}^{\kappa\kappa'} = \delta_{\alpha\beta} a^{\kappa\kappa'}. \quad (34)$$

Thus

$$\bar{S}_{\alpha\beta}^{\kappa\kappa'} = \delta_{\alpha\beta} \left[ \hat{a}^{-1} - (4\pi e^2/3\Omega) \underline{I} \right]_{\kappa\kappa'}^{-1}, \quad (35)$$

where  $\hat{a}$  is the  $(r \times r)$  matrix  $a^{\kappa\kappa'}$  and  $\underline{I}$  is the  $(r \times r)$  matrix, each of whose elements is unity. It may be shown that

$$\left( \hat{a}^{-1} - \frac{4\pi e^2}{3\Omega} \underline{I} \right)_{\kappa\kappa'}^{-1} = a^{\kappa\kappa'} + \left[ \frac{4\pi e^2}{3\Omega} / \left( 1 - \frac{4\pi e^2}{3\Omega} \sum_{\kappa\kappa'} a^{\kappa\kappa'} \right) \right] P_{\kappa\kappa'}, \quad (36)$$

where

$$P_{\kappa\kappa'} = \sum_{\lambda\lambda'} a_{\kappa\lambda} a_{\lambda\kappa'}. \quad (37)$$

It follows that

$$\sum_{\kappa\kappa'} \bar{S}_{\alpha\beta}^{\kappa\kappa'} = \delta_{\alpha\beta} \times \left[ \sum_{\kappa\kappa'} a^{\kappa\kappa'} / \left( 1 - \frac{4\pi e^2}{3\Omega} \sum_{\kappa\kappa'} a^{\kappa\kappa'} \right) \right]. \quad (38)$$

Now  $\sum_{\kappa\kappa'} a^{\kappa\kappa'}$  is related to the total polarizability  $\alpha$  of the unit cell by<sup>22</sup>

$$\alpha = \frac{e^2}{\Omega} \sum_{\kappa\kappa'} a^{\kappa\kappa'}. \quad (39)$$

Using Eqs. (38) and (39) in Eq. (31), we obtain finally

$$\epsilon_\infty = (1 + \frac{8}{3}\pi\alpha) / (1 - \frac{4}{3}\pi\alpha), \quad (40)$$

which is exactly the Lorentz-Lorenz formula, but a little more general in the sense that  $\alpha$  is here rigorously the polarizability of the unit cell and we have not assumed additivity of individual ionic polarizabilities. We note here that since  $v(\vec{Q})$  has the interaction of the distribution on one ion with itself removed, the  $a^{\kappa\kappa'}$  above are related to the *many-electron polarizabilities* of the ions themselves and should include the effects of exchange and correlation between electrons on the same ion. This point has recently also been discussed explicitly by Onodera.<sup>27</sup>

In the opposite limit, we may imagine a crystal in which the dipole distributions are so delocalized that the  $f^s(\vec{Q})$  are negligible by the time  $\vec{Q}$  equals a reciprocal-lattice vector. In such a case  $\bar{V}_{\alpha\beta}^{\kappa\kappa'}$  vanishes, and  $\epsilon_\infty$  becomes identical with  $\epsilon(0, 0)$  as given by Eq. (32), and we retrieve the so-called Drude limit,  $\epsilon_\infty = \epsilon_0 + 4\pi\alpha$ , where local-field corrections are completely neglected.

It is worth pointing out that a true microscopic calculation of local-field corrections in an insulator necessarily involves knowing the exchange and correlation corrections to the effective electron-electron interaction  $v(\vec{Q})$  which enters into the calculation of the self-consistent response. Unfortunately, these are at present not known accurately for real insulating crystals. As stated, when the appropriate dipolar distributions are nonoverlapping, a crude approximation is to assume that the "exchange and correlation hole" around each electron simply removes the self-interaction between electrons on the same sites when the electrons respond to an external field. Residual effects may be then formally included in the  $a_{\alpha\beta}^{\kappa\kappa'}$  corresponding to that site, so that it is the total polarizability associated with that site. Exchange and correlation corrections to the Coulomb interaction between electrons on different sites may be ignored on the basis that such effects are short-range in nature. When the dipolar distributions are extended, however, the above procedure breaks down. Obviously exchange and correlation corrections will still have a general tendency to remove some of the short-range part of the direct Coulomb interaction between electrons. A crude procedure would be to assume that the effective electron-electron interaction is pure Coulomb-like for  $r$  greater than some cut-off radius  $r_{xc}$  and zero for  $r < r_{xc}$ . For a

semiconductor, a somewhat better prescription would be to use  $v(\vec{Q})$  as given by Eq. (2) with  $f_{xc}(\vec{Q})$  taken over from recent estimates for a free-electron gas of equivalent average density.<sup>8-10</sup>

It is to be noted that the local-field corrections in the Lorentz-Lorenz limit [Eq. (40)] tend to *enhance*  $\epsilon_\infty$  above  $\epsilon(0, 0)$  and hence it has been customary to estimate local-field corrections in the intermediate case approximately by multiplying  $\epsilon(0, 0)$  by a number between 1 and that obtained from Eq. (38). However, as we shall see in the case of our calculations on silicon described below, it is quite possible to get models for which  $\epsilon_\infty$  comes out to be *less* than  $\epsilon(0, 0)$  as has also been found by Van Vechten and Martin.<sup>28</sup> Thus local-field corrections to  $\epsilon_\infty$  could go either way, determined principally by the detailed form of the ex-

change and correlation corrections to  $v(\vec{Q})$  and the form factors  $f^s(\vec{Q})$ . The experimental situation is that  $\epsilon_\infty$  is in general larger than the  $\epsilon(0, 0)$  calculated from electronic structure.

A more explicit expression for  $\epsilon_\infty$  in the case of arbitrary local field may be derived for crystals of the NaCl or zinc-blende structure from Eq. (31) if the sites  $\vec{r}_s$  are chosen as the ionic sites  $\vec{r}_\kappa$ . In that case, crystal symmetry still requires that Eq. (34) be true and that

$$\bar{V}_{\alpha\beta}^{\kappa\kappa'} = \delta_{\alpha\beta} \bar{V}^{\kappa\kappa'}, \quad (41)$$

where

$$\bar{V}^{\kappa\kappa'} = \frac{1}{3} \sum_{\vec{G}} G^2 f^{*\kappa}(\vec{G}) f^{\kappa'}(\vec{G}) \frac{v(\vec{G})}{\epsilon_0(\vec{G})} e^{i\vec{G} \cdot \vec{r}_{\kappa\kappa'}}. \quad (42)$$

In this case, Eq. (31) yields

$$\epsilon_\infty = \epsilon_0 + \frac{4\pi e^2}{\Omega} \left[ \left( \sum_{\kappa\kappa'} a^{\kappa\kappa'} + (\bar{V}^{11} + \bar{V}^{22} - \bar{V}^{12} - \bar{V}^{*12}) \Delta \right) / \left( 1 + \sum_{\kappa\kappa'} \bar{V}^{\kappa\kappa'} a^{\kappa\kappa'} + \bar{\Delta} \Delta \right) \right] \quad (43)$$

where

$$\Delta = a^{11} a^{22} - |a^{22}|^2 \quad (44a)$$

and

$$\bar{\Delta} = \bar{V}^{11} \bar{V}^{22} - |\bar{V}^{12}|^2. \quad (44b)$$

For a bond-charge model, on the other hand, the

symmetry of the "bond-charge lattice" does not require the  $a_{\alpha\beta}^{ss'}$  and the  $\bar{V}_{\alpha\beta}^{ss'}$  to be diagonal in  $(\alpha, \beta)$  space and one must in general invert a  $12 \times 12$  matrix to obtain  $\epsilon_\infty$  using Eq. (31).

We now return to Eqs. (23) to obtain the behavior of the remaining elements of  $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  as  $\vec{q} \rightarrow 0$ .

From these, it may be verified that

$$\lim_{\vec{q} \rightarrow 0} \epsilon^{-1}(\vec{q}, \vec{G}) = \lim_{\vec{q} \rightarrow 0} - \frac{4\pi e^2}{\Omega \epsilon_\infty} \frac{1}{\epsilon_0(\vec{G})} \sum_{\alpha\beta} \frac{q_\alpha G_\beta}{q^2} f^{*s'}(\vec{G}) \bar{S}_{\alpha\beta}^{ss'} e^{i\vec{G} \cdot \vec{r}_{s'}}, \quad (45)$$

$$\lim_{\vec{q} \rightarrow 0} \epsilon^{-1}(\vec{G}, \vec{q}) = \lim_{\vec{q} \rightarrow 0} - \frac{1}{\epsilon_\infty} \frac{v(\vec{G})}{\epsilon_0(\vec{G})} \sum_{\alpha\beta} G_\alpha q_\beta f^s(\vec{G}) \bar{S}_{\alpha\beta}^{ss'} e^{-i\vec{G} \cdot \vec{r}_s}, \quad (46)$$

$$\lim_{\vec{q} \rightarrow 0} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')(\vec{G}, \vec{G}' \neq 0) = \lim_{\vec{q} \rightarrow 0} \frac{1}{\epsilon_0(\vec{G}')} \left[ \delta_{\vec{G}\vec{G}'} - \frac{v(\vec{G})}{\epsilon_0(\vec{G})} \sum_{\alpha\beta} G_\alpha f^s(\vec{G}) \right. \\ \left. \times \left( \bar{S}_{\alpha\beta}^{ss'} - \sum_{\gamma\delta} \frac{4\pi e^2}{\Omega \epsilon_\infty} \frac{q_\gamma q_\delta}{q^2} \bar{S}_{\alpha\gamma}^{s\sigma} \bar{S}_{\delta\beta}^{\sigma's'} \right) f^{*s'}(\vec{G}') G'_\beta e^{-i(\vec{G} \cdot \vec{r}_s - \vec{G}' \cdot \vec{r}_{s'})} \right]. \quad (47)$$

It may be verified that the expressions (45)–(47) have the correct analytic behavior as  $\vec{q} \rightarrow 0$  as discussed in the formal theory of Pick *et al.*<sup>25</sup> for the inverse dielectric matrix of insulators. [If  $\epsilon_0(\vec{Q})$  contains a free-electron contribution,  $\epsilon_0$  becomes infinite and hence so, by Eq. (31), does  $\epsilon_\infty$ . It may also be seen from Eqs. (45)–(47) that the elements of  $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  then vanish as  $\vec{q} \rightarrow 0$  when  $\vec{G}$  or  $\vec{G}' = 0$ , as expected. In the case  $\vec{G}, \vec{G}' \neq 0$ ,  $\lim_{\vec{q} \rightarrow 0} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  is given by Eq. (17) with  $\underline{S}$  replaced by  $\bar{S}$ .]

Let us consider the case of a weak externally applied potential

$$V_{\text{ext}}(\vec{r}) = V_{\text{ext}}(\vec{q}) e^{i\vec{q} \cdot \vec{r}}, \quad (48)$$

where we regard  $\vec{q}$  as tending to zero in the limit. The externally applied electric field corresponding to this is given by

$$\vec{D}(\vec{q}) = -i\vec{q} V_{\text{ext}}(\vec{q}). \quad (49)$$

Let  $V_{\text{tot}}$  be the Fourier transform of the total (self-consistent) change in potential seen by an electron due to the applied field, and let us expand the *total* local field seen by an electron as

$$E(\vec{r}) = \sum_{\vec{G}} \vec{E}(\vec{q} + \vec{G}) e^{i(\vec{q} + \vec{G}) \cdot \vec{r}}. \quad (50)$$

Now

$$\begin{aligned}\vec{E}(\vec{q} + \vec{G}) &= -i(\vec{q} + \vec{G})V_{\text{tot}}(\vec{q} + \vec{G}) \\ &= -i(\vec{q} + \vec{G})\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q})V_{\text{ext}}(\vec{q}).\end{aligned}\quad (51)$$

In the limit  $\vec{q} \rightarrow 0$ , using Eq. (46), we get, for  $\vec{G} \neq 0$ ,

$$\vec{E}(\vec{G}) = \frac{i}{\epsilon_{\infty}} \vec{G} \frac{v(\vec{G})}{\epsilon_0(\vec{G})} \lim_{\vec{q} \rightarrow 0} \sum_{\alpha\beta} G_{\alpha} f^{\alpha}(\vec{G}) e^{-i\vec{G} \cdot \vec{r}_{\alpha}} \bar{S}_{\alpha\beta}^{ss'} D_{\beta}.\quad (52)$$

For tetrahedral or cubic crystals where the sites  $\vec{r}_{\alpha}$  are chosen as the atomic sites  $\vec{r}_{\kappa}$ ,  $\bar{S}_{\alpha\beta}^{ss'}$  becomes  $\bar{S}_{\alpha\beta}^{\kappa\kappa'} \delta_{\alpha\beta}$  and Eq. (52) may be written

$$\vec{E}(\vec{G}) = -\frac{1}{\epsilon_{\infty}} \vec{G} \frac{v(\vec{G})}{\epsilon_0(\vec{G})} \sum_{\kappa\kappa'} f^{\kappa}(\vec{G}) e^{-i\vec{G} \cdot \vec{r}_{\kappa}} \bar{S}_{\alpha\beta}^{\kappa\kappa'} (\vec{G} \cdot \vec{D}).\quad (53)$$

For  $\vec{G} = 0$ , on the other hand, from Eqs. (49) and (51) we get

$$\vec{E}(0) = (1/\epsilon_{\infty})\vec{D}\quad (54)$$

for the *macroscopic* local field.

Equations (50), (53), and (54) thus provide, within the framework of our model, a detailed description of the spatial dependence of the local field.

We note that the microscopic local field can have components which are *normal* to the applied field, although these are periodic with respect to the unit cell and average out to zero.

#### IV. SUMMARY AND DISCUSSION

We have presented in this paper a rather general scheme for calculating the local-field corrections to the dielectric screening in any solid for which the screening matrix  $\epsilon(\vec{Q}, \vec{Q}')$  is not diagonal, by representing  $\epsilon(\vec{Q}, \vec{Q}')$  as a part  $\epsilon_0(\vec{G}) \delta_{\vec{Q}\vec{Q}'}$ , which is completely diagonal and a part which may be written down in a very general separable form. The "diagonal part"  $\epsilon_0(\vec{Q})$ , which may include the contribution of free electrons also, if they are present in the solid, acts as a general screening function for the interaction of the rest of the induced-charge distribution with the lattice and with itself, and gives rise to contributions to the induced-charge distribution and to the dynamical matrix exactly analogous to those valid for a free-electron gas. For insulators, the structure of the interband matrix elements leads naturally to a factorization

scheme which yields the physical result that the induced-charge distribution produced by an external potential consists of distributions of dipoles centered on a particular set of sites in the unit cell. If these sites coincide with the ionic sites, then a kind of generalized shell model results which reduces to the ordinary shell model under further restrictions, but is more general in the sense that it allows for screening effects due to the "diagonal" part  $\epsilon_0(\vec{Q})$ , and since it avoids the point-dipole picture, it also allows for charge-transfer effects and multipole effects. It is interesting to note in this connection that Kuhner *et al.*<sup>29</sup> have found that the vibronic spectra in a number of crystals of the fluor spar type can only be explained by giving the "shell" of the shell model a spread-out distribution in space to decrease the effect of the local field. The above model may, for instance, be applied to treat the screening associated with the *d* electrons in the noble metals. If, on the other hand, the sites are chosen at the centers of the bonds in a covalently bonded crystal, a general kind of bond-charge model similar in concept to that introduced earlier by Phillips<sup>3</sup> and Martin<sup>15</sup> results. Obviously a combination of the two types is also possible for ionic-covalent solids within the framework of our model.

Explicit expressions are derived for the analytic behavior of  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$  and its inverse at small  $\vec{q}$  based on the model and it is shown that this behavior is in accordance with that predicted by a completely general theory.<sup>1,25</sup> For insulators, an explicit expression is given for  $\epsilon_{\infty}$  which corresponds to a generalization of the Lorentz-Lorenz formula for arbitrary local fields, and thus corresponds to the first such microscopic expression for this quantity valid also in the limit of covalent solids. An explicit microscopic expression is also derived for the local field produced by an applied macroscopic field.

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