

## Clausius-Mosotti limit of the quantum theory of the electronic dielectric constant

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It is shown that an unambiguous discussion of the limit of independent atoms in the theory of the dielectric constant has to be formulated in terms of asymptotic series in the ratio of the Bohr radius to the lattice spacing. In this sense, a derivation of the classical Clausius-Mosotti (or Lorentz-Lorenz) formula is given, starting from the quantum-mechanical theory including "local-field" corrections, at the self-consistent Hartree-Fock level. Our approach clarifies the origin of the many diverging results on the subject and eliminates most of the unnecessary approximations and/or assumptions.

### I. INTRODUCTION

The classical Clausius-Mosotti (or Lorentz-Lorenz, for nonzero frequency) relation for cubic crystals (and gases)

$$\frac{\epsilon}{\epsilon_0} - 1 = \frac{\kappa^{\text{at}}}{1 - \frac{1}{3}\kappa^{\text{at}}} \quad (1.1)$$

between the dielectric constant  $\epsilon$  and the atomic polarizability  $\kappa^{\text{at}}$  ( $\epsilon_0$  is the permittivity of the vacuum) was derived before the advent of quantum mechanics, from the model of independent neutral atoms assimilated to point dipoles whose magnitude is proportional to the local electric field. This field is given by the sum of the external field and the field of all the other atomic dipoles. In the textbook derivations the latter is evaluated in a hybrid manner, i.e., it is done microscopically within a finite sphere while the rest of the system is treated as a continuum. More recent treatments<sup>1,2</sup> perform the discrete summation over the whole lattice of atoms and compute the macroscopic field by taking the long-wavelength limit. These derivations contain again the essential ingredient of uncorrelated atoms, i.e., there is no overlap between the wave functions of electrons on different atoms.

On intuitive grounds one expects that as the ratio  $r_0/a$  of Bohr radius to the lattice spacing tends to zero, one should approach the limit of uncorrelated atoms. On the other hand, it was known for a long time that the well-known quantum-mechanical linear-response Kubo formula, which for crystals in the one-electron frame is equivalent to that derived in Refs. 3 and 4, leaves no hopes of recovering (1.1) for very large lattice spacing. Only after the refining of the quantum theory of the dielectric constant of crystals, due to Adler<sup>5</sup> and Wiser<sup>6</sup> the possibility of a deeper understanding of this problem evolved. They remarked that since the translational invariance is only discrete (and this is precisely the way the atomic structure enter the theory), specific "local-field" corrections appear.

Nevertheless, until now there has been a wide controversy in the literature with arguments both for and against the Clausius-Mosotti (Lorentz-Lorenz) limit. Some of these papers<sup>7,8</sup> use unnecessarily restrictive assumptions

and approximations, being at the same time mathematically nonconvincing. Other works,<sup>9-12</sup> under similar conditions obtain alternative results disagreeing with (1.1). A typical source of misunderstanding was the ambiguous definition of the atomic polarizability, as it was pointed out recently in Ref. 13. Generally speaking, most of the discussion was within the frame of self-consistent theories with respect to Coulomb interactions, however, it was felt that self-interaction is dangerous and therefore exchange and perhaps correlation effects should be essential. Another ingredient which is often used to simplify the calculations is some variant of a factorization assumption. Whereas there is a general agreement as to the necessity of taking the atoms sufficiently far apart, this idea is implemented in a mathematically imprecise manner, differing from author to author.

In this paper we will show that the Clausius-Mosotti problem must be formulated as an asymptotic series problem in the parameter  $r_0/a$ . This is the only mathematically reasonable formulation. It means that one should neglect only terms that vanish faster than any power. We restrict the discussion to the self-consistent potential or Hartree-Fock approximations and will prove that, in the above-mentioned sense, the Clausius-Mosotti formula is recovered in both cases. The only ingredients are the inclusion of local-field effects in the manner of Adler-Wiser<sup>5,6</sup> and certain assumptions about the asymptotic behavior (in  $r_0/a$ ) of the wave functions and spectrum. These plausible assumptions coincide with the commonly used ones.

In Sec. II the quantum theory of the macroscopic dielectric constant is described together with the basic approximation schemes. The quantum theory of the atomic polarizability is outlined in Sec. III in a way that facilitates our purposes. Our basic statement and its proof on the asymptotic validity of the Clausius-Mosotti relation, are contained in Sec. IV. The last section is devoted to the discussion of the results.

### II. QUANTUM THEORY OF THE MACROSCOPIC DIELECTRIC CONSTANT

With the use of linear-response theory with respect to an external potential  $V^{\text{ext}}$  of frequency  $\omega$ , in the

quantum-mechanical problem of the motion of electrons in a periodic potential at  $T=0$  K one may define the dielectric matrix  $[\hat{\epsilon}(\vec{k}, \omega)]_{\vec{k} \vec{k}'}$ , [ $\vec{k}$  belongs to the first Brillouin zone (BZ), while  $\vec{K}$  and  $\vec{K}'$  run through the reciprocal lattice] as relating the Fourier transforms of the total potential (created by the external and internal nonequilibrium charges) to the external one

$$\sum_{\vec{k}'} [\hat{\epsilon}(\vec{k}, \omega)]_{\vec{k} \vec{k}'} V^{\text{tot}}(\vec{k} + \vec{K}', \omega) = \epsilon_0 V^{\text{ext}}(\vec{k} + \vec{K}, \omega). \quad (2.1)$$

In terms of the perturbation theory diagrams (see, for example, Ref. 14) with respect to the electron-electron Coulomb interaction it can be shown that  $[\hat{\epsilon}(\vec{k}, \omega)]_{\vec{k} \vec{k}'}$  is related to the so-called polarization part  $\Pi$ :

$$\begin{aligned} & [\hat{\epsilon}(\vec{k}, \omega)]_{\vec{k} \vec{k}'} \\ &= \epsilon_0 \delta_{\vec{k}, \vec{k}'} - \frac{e^2}{v |\vec{k} + \vec{K}|^2} \\ & \times \sum_{\Gamma, \Gamma'} \langle \vec{K} | u_{\Gamma}(\vec{k}) \rangle \Pi_{\Gamma\Gamma'}(\omega, \vec{k}) \langle u_{\Gamma'}(\vec{k}) | \vec{K}' \rangle, \end{aligned} \quad (2.2)$$

where

$$\langle \vec{K} | u_{\Gamma}(\vec{k}) \rangle = \int_v d\vec{x} e^{i(\vec{k} + \vec{K}) \cdot \vec{x}} \varphi_n^* (\vec{x}) \varphi_{m\vec{p}} (\vec{x}) \quad (2.3)$$

with  $\varphi_{n\vec{p}}(\vec{x})$  being the Bloch functions [of band index  $n$  and quasimomentum  $\vec{p} \in \text{BZ}$  (Brillouin zone)] of the self-consistent Hartree-Fock (HF) problem in the absence of the external potential. (The self-consistency being achieved for the ground-state.) Here  $\Gamma$  denotes the ensemble of indexes  $(n, m, \vec{p})$  and  $v$  is the volume of the elementary cell.

According to Alder<sup>5</sup> and Wiser<sup>6</sup> the macroscopic dielectric constant  $\epsilon(\vec{k}, \omega)$  is defined as

$$\begin{aligned} \frac{\epsilon(0, \omega)}{\epsilon_0} - 1 = & - \frac{e^2}{\epsilon_0 v} \sum_{\Gamma, \Gamma'} \left[ \vec{e} \cdot \vec{v}_{\Gamma}^{(1)} \left[ \frac{1}{1 - \Pi^{(0)}(\omega) \zeta^{(0)}} \Pi^{(0)}(\omega) \right]_{\Gamma\Gamma'} \vec{e} \cdot \vec{v}_{\Gamma'}^{(1)*} + \vec{e} \cdot \vec{v}_{\Gamma}^{(1)} \left[ \frac{1}{1 - \Pi^{(0)}(\omega) \zeta^{(0)}} \vec{\Pi}^{(1)}(\omega) \cdot \vec{e} \right]_{\Gamma\Gamma'} v_{\Gamma'}^{(0)*} \right. \\ & + v_{\Gamma}^{(0)} \left[ \vec{\Pi}^{(1)}(\omega) \cdot \vec{e} \frac{1}{1 - \zeta^{(0)} \Pi^{(0)}(\omega)} \right]_{\Gamma\Gamma'} \vec{e} \cdot \vec{v}_{\Gamma'}^{(1)*} \\ & \left. + v_{\Gamma}^{(0)} \left[ \vec{e} \cdot \hat{\Pi}^{(2)}(\omega) \cdot \vec{e} + \vec{e} \cdot \vec{\Pi}^{(1)}(\omega) \zeta^{(0)} \frac{1}{1 - \Pi^{(0)}(\omega) \zeta^{(0)}} \vec{e} \cdot \vec{\Pi}^{(1)}(\omega) \right]_{\Gamma\Gamma'} v_{\Gamma'}^{(0)*} \right], \end{aligned} \quad (2.8)$$

where

$$\vec{e} \equiv \frac{\vec{k}}{|\vec{k}|}.$$

In the following sections we will restrain the generality of the discussion by resorting to approximations for the

$$\epsilon(\vec{k}, \omega) = \frac{1}{[\hat{\epsilon}^{-1}(\vec{k}, \omega)]_{00}}. \quad (2.4)$$

Use of Eq. (2.2) here gives

$$\begin{aligned} \frac{\epsilon(\vec{k}, \omega)}{\epsilon_0} - 1 = & - \frac{e^2}{\epsilon_0 v \vec{k}^2} \sum_{\Gamma, \Gamma'} \langle 0 | u_{\Gamma}(\vec{k}) \rangle \left[ \frac{1}{1 - \Pi \zeta} \Pi \right] \\ & \times \langle u_{\Gamma'}(\vec{k}) | 0 \rangle, \end{aligned} \quad (2.5)$$

where a matrix notation is used with respect to the indexes  $\Gamma, \Gamma'$  with

$$\zeta_{\Gamma\Gamma'} \equiv \frac{e^2}{\epsilon_0 v} \sum_{\vec{K} (\neq \vec{0})} \frac{\langle u_{\Gamma}(\vec{k}) | \vec{K} \rangle \langle \vec{K} | u_{\Gamma'}(\vec{k}) \rangle}{(\vec{k} + \vec{K})^2}. \quad (2.6)$$

We are interested in the  $\vec{k} \rightarrow \vec{0}$  limit of Eq. (2.5).

The existence of this limit is assured due to the fact that the polarization part has no singularity at  $\vec{k} = \vec{0}$  and obeys the identities

$$\sum_{n, \vec{p}} [\Pi(\omega, 0)]_{nm\vec{p}, n'm'\vec{p}'} = \sum_{n', \vec{p}'} [\Pi(\omega, 0)]_{nm\vec{p}, n'n'\vec{p}'} = 0, \quad (2.7a)$$

$$\sum_{n, \vec{p}, n', \vec{p}'} \left[ \frac{\partial}{\partial k_{\mu}} [\Pi(\omega, \vec{k})]_{nm\vec{p}, n'n'\vec{p}'} \right]_{\vec{k} = \vec{0}} = 0, \quad (2.7b)$$

which are a consequence of the charge conservation. Using these identities, the expansion in powers of  $\vec{k}$

$$\begin{aligned} \Pi(\omega, \vec{k}) = & \Pi^{(0)}(\omega) + k^{\mu} \Pi_{\mu}^{(1)}(\omega) \\ & + k^{\mu} k^{\nu} \Pi_{\mu\nu}^{(2)}(\omega) + \dots, \\ \langle 0 | u(\vec{k}) \rangle = & v(\vec{k}) = v^{(0)} + k^{\mu} v_{\mu}^{(1)} + \dots, \\ \zeta(\vec{k}) = & \zeta^{(0)} + \dots, \end{aligned}$$

and also that

$$v_{nm\vec{p}}^{(0)} = \delta_{n,m},$$

one can derive

polarization part  $\Pi$ ; nevertheless some comments will be made also with regard to these general formulas.

The time-dependent, self-consistent Hartree-Fock approximation in the presence of the external potential is equivalent to the summation of all ladder diagrams for  $\Pi$  giving

$$[\Pi^{\text{HF}}(\vec{k}, \omega)]_{\Gamma\Gamma'} = -2 \left[ \frac{1}{1 - \mathcal{X}(\vec{k}, \omega) \mathcal{C}^e(\vec{k})} \mathcal{X}(\vec{k}, \omega) \right]_{\Gamma\Gamma'} \quad (2.9)$$

$$[\mathcal{X}(\vec{k}, \omega)]_{\Gamma\Gamma'} = -\delta_{\Gamma\Gamma'} \frac{\Theta(\mu - E_{n\vec{p}}) - \Theta(\mu - E_{m, \vec{p} - \vec{k}})}{E_{n\vec{p}} - E_{m, \vec{p} - \vec{k}} + \hbar\omega - i0}, \quad (2.10)$$

with

where  $E_{n\vec{p}}$  is the band-energy,  $\mu$  is the chemical potential and

$$[\mathcal{C}^e(\vec{k})]_{\Gamma\Gamma'} = \frac{e^2}{4\pi\epsilon_0} \int d\vec{x} \int_v d\vec{x}' \varphi_{n\vec{p}}(\vec{x}) \varphi_{m, \vec{p} - \vec{k}}^*(\vec{x}') \frac{1}{|\vec{x} - \vec{x}'|} \varphi_{n\vec{p}}^*(\vec{x}) \varphi_{m, \vec{p} - \vec{k}}(\vec{x}') \quad (2.11)$$

is a type of exchange Coulomb matrix. [The factor of 2 in Eq. (2.9) comes from the spin.]

Introducing Eq. (2.9) in Eq. (2.5), one finds

$$\frac{\epsilon^{\text{HF}}(\vec{k}, \omega)}{\epsilon_0} - 1 = \frac{2e^2}{\epsilon_0 v k^2} \sum_{\Gamma, \Gamma'} \langle 0 | u_{\Gamma}(\vec{k}) \rangle \left[ \frac{1}{1 + \mathcal{X}(\vec{k}, \omega) [2\xi(\vec{k}) - \mathcal{C}^e(\vec{k})]} \mathcal{X}(\vec{k}, \omega) \right]_{\Gamma\Gamma'} \langle u_{\Gamma'}(\vec{k}) | 0 \rangle. \quad (2.12)$$

The time-dependent self-consistent potential approximation is equivalent to omitting all the exchange effects, i.e., ignoring  $\mathcal{C}^e$  in Eq. (2.9) and considering the Bloch functions  $\varphi_{n\vec{p}}$  as solutions of the unperturbed self-consistent potential problem. This is nothing but the random-phase approximation (RPA) for the polarization diagram, not to be confused with the RPA approximation for the dielectric constant itself, which implies ignoring also  $\xi$ . The appearance of  $\xi$ , due to the inversion procedure (2.4), is often referred to as the “local-field” correction.

Within the HF approximation we are interested again in the  $\vec{k} \rightarrow 0$  limit. It can be shown that Eq. (2.8) becomes

$$\begin{aligned} \frac{\epsilon^{\text{HF}}(0, \omega)}{\epsilon_0} - 1 = & \frac{2e^2}{v\epsilon_0} \sum_{\Gamma, \Gamma'} \left[ \vec{e} \cdot \vec{v}_{\Gamma}^{(1)} \left[ \frac{1}{1 + \mathcal{X}^{(0)}(\omega) (2\xi^{(0)} - \mathcal{C}^e(0))} \mathcal{X}^{(0)}(\omega) \right]_{\Gamma\Gamma'} \vec{e} \cdot \vec{v}_{\Gamma'}^{(1)*} \right. \\ & + \vec{e} \cdot \vec{v}_{\Gamma}^{(1)} \left[ \frac{1}{1 + \mathcal{X}^{(0)}(\omega) (2\xi^{(0)} - \mathcal{C}^e(0))} \vec{\mathcal{X}}^{(1)}(\omega) \cdot \vec{e} \right]_{\Gamma\Gamma'} v_{\Gamma'}^{(0)*} \\ & + v_{\Gamma}^{(0)} \left[ \vec{\mathcal{X}}^{(1)}(\omega) \cdot \vec{e} \frac{1}{1 + \mathcal{X}^{(0)}(\omega) (2\xi^{(0)} - \mathcal{C}^e(0))} \right] \vec{e} \cdot \vec{v}_{\Gamma'}^{(1)*} \\ & \left. + v_{\Gamma}^{(0)} \left[ \vec{e} \cdot \hat{\mathcal{X}}^{(2)}(\omega) \cdot \vec{e} - 2\vec{e} \cdot \vec{\mathcal{X}}^{(1)}(\omega) \xi^{(0)} \frac{1}{1 + \mathcal{X}^{(0)}(\omega) (2\xi^{(0)} - \mathcal{C}^e(0))} \vec{e} \cdot \vec{\mathcal{K}}^{(1)}(\omega) \right]_{\Gamma\Gamma'} v_{\Gamma'}^{(0)*} \right], \quad (2.13) \end{aligned}$$

where

$$\mathcal{C}^e(0) \equiv \mathcal{C}^e(\vec{k}) \Big|_{\vec{k}=\vec{0}},$$

$\mathcal{X}^{(0)}$ ,  $\mathcal{X}_{\mu}^{(1)}$ ,  $\mathcal{X}_{\mu\nu}^{(2)}$  are the corresponding terms from the  $\vec{k}$  expansion of  $\mathcal{X}(\omega, \vec{k})$ , or explicitly

$$\begin{aligned} [\mathcal{X}^{(0)}(\omega)]_{\Gamma\Gamma'} &= \delta_{\Gamma\Gamma'} [\mathcal{X}^{(0)}(\omega)]_{\Gamma}, \\ [\mathcal{X}^{(0)}(\omega)]_{nm\vec{p}} &= -\frac{\Theta(\mu - E_{n\vec{p}}) - \Theta(\mu - E_{m\vec{p}})}{E_{n\vec{p}} - E_{m\vec{p}} + \hbar\omega - i0}, \\ \sum_{\Gamma} \vec{e} \cdot [\vec{\mathcal{X}}^{(1)}(\omega)]_{\Gamma\Gamma'} v_{\Gamma'}^{(0)*} &= \sum_{\Gamma} v_{\Gamma}^{(0)} \vec{e} \cdot [\vec{\mathcal{X}}^{(1)}(\omega)]_{\Gamma\Gamma'} \quad (2.14) \\ &= \frac{1}{\hbar\omega} \vec{e} \frac{\partial E_{n\vec{p}}}{\partial \vec{p}} \delta(\mu - E_{n\vec{p}}), \\ \sum_{\Gamma, \Gamma'} v_{\Gamma}^{(0)} \vec{e} \cdot \hat{\mathcal{X}}^{(2)}_{\Gamma\Gamma'} \vec{e} v_{\Gamma'}^{(0)*} &= -\frac{1}{(\hbar\omega)^2} \left[ \vec{e} \frac{\partial E_{n\vec{p}}}{\partial \vec{p}} \right]^2 \delta(\mu - E_{n\vec{p}}). \quad (2.14) \end{aligned}$$

In the case of the insulators, where the chemical potential  $\mu$  is situated in an energy gap, only the first term of

Eq. (2.13) survives; the others appear only in the case of metals, carrying a typical  $1/\omega^2$  singularity at  $\omega=0$ .

Although we are interested mostly in the insulator problem, where a static dielectric constant also exists, we cannot *a priori* ignore these spurious terms. Indeed, the gap of most real dielectrics is a so-called Bloch gap, i.e., it is not related to the atomic gap. When the lattice constant is increased, the gap disappears, reappearing later as an atomic gap. Correspondingly, the system may undergo several metal-insulator transitions (the chemical potential being in the band or the gap). Since we are interested in the study of the limit  $a \rightarrow \infty$ , we must keep all the terms and consider  $\omega \neq 0$ . Nevertheless, as we shall see later, other arguments help to eliminate these complications.

In the following sections we shall base our discussion on Eq. (2.13). On the other hand, since as we shall see, no specific role is played by the exchange terms, all the results hold also in the simple self-consistent potential approximation.

### III. QUANTUM THEORY OF THE ATOMIC POLARIZABILITY

If one considers the linear response of the system of interacting electrons belonging to a given atom with respect

to a homogeneous monochromatic external field  $\vec{\mathcal{E}} e^{i\omega t}$  at  $T=0$  K, one may compute the induced dipole moment

$$p_\mu = e \int d\vec{x} \bar{x}_\mu \langle n(\vec{x}, t) \rangle.$$

One defines then the atomic polarizability  $\kappa^{\text{at}}$  through the coefficient of proportionality between the density of induced dipole moments  $\vec{P} \equiv \bar{p}/v$ , where  $v$  is the volume attributed to one atom (in the crystalline arrangement of the atoms in a Bravais lattice it would correspond to the volume of the cell), and the external field

$$\vec{P}(t) = \epsilon_0 \kappa(\omega) \vec{\mathcal{E}} e^{i\omega t}. \quad (3.1)$$

The resulting formula is

$$\begin{aligned} \kappa(\omega) = & -\frac{e^2}{\epsilon_0 v} \int d\vec{x} \int d\vec{x}' (\vec{e} \cdot \vec{x})(\vec{e} \cdot \vec{x}') \frac{1}{i\hbar} \\ & \times \int_0^\infty dt e^{i(\omega+i0)t} \\ & \times \langle [n(\vec{x}, t)_H, n(\vec{x}')] \rangle_0, \end{aligned} \quad (3.2)$$

where  $\vec{e}$  is an arbitrary unit vector ( $\vec{e}^2=1$ ). The retarded Green function in Eq. (3.2) of course can be related to the Coulomb operator and the polarization diagram, giving rise to

$$\begin{aligned} \kappa^{\text{at}}(\omega) = & -\frac{e^2}{v\epsilon_0} \sum_{\gamma, \gamma'} \vec{e} \cdot \vec{v}_\gamma^{(1)} \left[ \frac{1}{1 - \Pi^{\text{at}}(\omega) \mathcal{C}^{\text{at}d}} \Pi^{\text{at}}(\omega) \right]_{\gamma\gamma'} \\ & \times (\vec{e} \cdot \vec{v}_{\gamma'}^{(1)})^*, \end{aligned} \quad (3.3)$$

where

$$\vec{v}_\gamma^{(1)} \equiv i \int d\vec{x} \varphi_i^*(\vec{x}) \vec{x} \varphi_j(\vec{x}) \quad (3.4)$$

$$\kappa^{\text{at HF}}(\omega) = \frac{2e^2}{\epsilon_0 v} \sum_{\gamma, \gamma'} \vec{e} \cdot \vec{v}_\gamma^{(1)} \left[ \frac{1}{1 + \mathcal{X}^{\text{at}}(\omega) (2\mathcal{C}^{\text{at}d} - \mathcal{C}^{\text{at}e})} \mathcal{X}^{\text{at}}(\omega) \right]_{\gamma\gamma'} \vec{e} \cdot \vec{v}_{\gamma'}^{(1)*}. \quad (3.9)$$

A comparison of the formulas of this section with those of the preceding one shows much similitude underlined by our choice of the notations. We were careful of course to introduce similar entities with similar (HF) approximations. This is a very important point to be emphasized.

In our opinion, in comparing crystalline entities with atomic ones, one must stick to the same approximation. A striking example is given by the case of the mono-electronic atom. In this case we know exactly the atomic polarizability as given by the dipole formula

$$\frac{e^2}{\epsilon_0 v} \sum_{\gamma, \gamma'} \vec{e} \cdot \vec{v}_\gamma^{(1)} [\mathcal{X}^{\text{at}}(\omega)]_{\gamma\gamma'} \vec{e} \cdot \vec{v}_{\gamma'}^{(1)}$$

(where, however, the true one-electronic wave functions and energies appear). The time-dependent HF approximation Eq. (3.9) for this problem as can be shown, would give the same result for spinless electrons (in spite of the

with  $\varphi_i(\vec{x})$  being the atomic wave functions of the self-consistent Hartree-Fock problem in the absence of the external potential (the self-consistency being achieved for the ground state). Here  $\gamma$  denotes the ensemble of atomic indexes  $(i, j)$ , and

$$\begin{aligned} \mathcal{C}_{ij:i'j'}^{\text{at}d} = & \frac{e^2}{4\pi\epsilon_0} \int d\vec{x} \int d\vec{x}' \varphi_i(\vec{x}) \varphi_j^*(\vec{x}) \frac{1}{|\vec{x} - \vec{x}'|} \\ & \times \varphi_{i'}^*(\vec{x}') \varphi_{j'}(\vec{x}') \end{aligned} \quad (3.5)$$

is the direct Coulomb matrix. (Actually the Feynman graph technique applies only for the non-degenerate ground state—in the atomic case it means full shell occupation.)

The time-dependent, self-consistent Hartree-Fock approximation in the presence of the external potential is given, similarly to the crystalline case, by

$$[\Pi^{\text{at HF}}(\omega)]_{\gamma\gamma'} = -2 \left[ \frac{1}{1 - \mathcal{X}^{\text{at}}(\omega) \mathcal{C}^{\text{at}e}} \mathcal{X}^{\text{at}}(\omega) \right]_{\gamma\gamma'} \quad (3.6)$$

with

$$[\mathcal{X}^{\text{at}}(\omega)]_{\gamma\gamma'} \equiv -\delta_{\gamma\gamma'} \frac{\Theta(\mu - \epsilon_i) - \Theta(\mu - \epsilon_j)}{\epsilon_i - \epsilon_j + \hbar\omega - i0}, \quad (3.7)$$

where  $\epsilon_i$  is the atomic energy and

$$\begin{aligned} \mathcal{C}_{\gamma\gamma'}^{\text{at}e} = & \frac{e^2}{4\pi\epsilon_0} \int d\vec{x} \int d\vec{x}' \varphi_i(\vec{x}) \varphi_j^*(\vec{x}') \frac{1}{|\vec{x} - \vec{x}'|} \\ & \times \varphi_{i'}^*(\vec{x}') \varphi_{j'}(\vec{x}') \end{aligned} \quad (3.8)$$

is the Coulomb exchange matrix.

Introducing Eq. (3.6) into Eq. (3.3) gives

formal differences), but it introduces a spurious Coulomb interaction for spinning electrons. The same approximation may become quantitatively a good one in the crystal (where no exact solution is available), but from our point of view these qualities are irrelevant for our discussion. It would be meaningful, of course, to compare the exact results, but it is meaningless to compare entities from different approximation schemes and levels.

An important feature of the atomic polarizability is that its dependence on the average distance between the atoms is only through the factor  $1/v$  in front of Eqs. (3.3) or (3.9). It can be shown through a dimensional analysis that

$$\kappa^{\text{at}}(\omega) = \left[ \frac{r_0}{a} \right]^3 \bar{\kappa}^{\text{at}} \left[ \frac{\hbar\omega}{e^2/4\pi\epsilon_0 r_0} \right], \quad (3.10)$$

where  $\bar{\kappa}^{\text{at}}(x)$  is a universal function (not depending on any

physical constant except  $Z$ —the number of electrons per atom).

Here the case of a simple cubic arrangement of atoms was considered where  $v=a^3$  and  $r_0$  denotes the Bohr radius. Equation (3.10) shows that increasing  $a$  or decreasing  $r_0$  are equivalent only for the zero-frequency case. In what follows, we shall vary the parameter  $r_0/a$  only through the increase of the lattice constant  $a$ .

#### IV. CLAUSIUS-MOSOTTI LIMIT

With the use of Eq. (3.10), the Clausius-Mosotti formula for crystals of cubic symmetry can be written as

$$\frac{\epsilon^{\text{CM}}}{\epsilon_0} - 1 = \frac{(r_0/a)^3 \bar{\kappa}^{\text{at}}}{1 - \frac{1}{3}(r_0/a)^3 \bar{\kappa}^{\text{at}}}. \quad (4.1)$$

Then one is confronted with the dilemma of how to reconcile the idea that this nonlinear relation supposedly holds for  $r_0/a \rightarrow 0$ , with the obvious relation

$$\lim_{r_0/a \rightarrow 0} \left[ \frac{\epsilon^{\text{CM}}}{\epsilon_0} - 1 \right] \left[ \frac{a}{r_0} \right]^3 = \bar{\kappa}^{\text{at}}$$

that forbids the discernibility of the nonlinearity in the same limit.

The only conceivable conjecture is that the quantum-mechanical expression of the dielectric constant of a simple cubic crystal has the same asymptotic series in the parameter  $r_0/a$  as that given by Eq. (4.1). Otherwise stated

$$\epsilon \sim \epsilon^{\text{CM}},$$

where  $\sim$  stands for equality up to terms that decrease faster than any power of  $r_0/a$ . This is a meaningful mathematical statement that we shall try to prove in the frame of the approximations described in the previous sections.

Unfortunately, the straightforward proof must be sup-

$$\mathcal{E}_{\Gamma\Gamma'}^{e(0)} \equiv \frac{e^2}{4\pi\epsilon_0} \sum_{\vec{\Gamma}} \int_v d\vec{x} \int_v d\vec{x}' \varphi_{n\vec{p}}(\vec{x}) \varphi_{m\vec{p}'}^*(\vec{x}') \frac{e^{i(\vec{p}-\vec{p}')\cdot\vec{r}}}{|\vec{x}-\vec{x}'+\vec{r}|} \varphi_{n'\vec{p}'}^*(\vec{x}) \varphi_{m'\vec{p}}(\vec{x}'). \quad (4.2)$$

Then

$$\mathcal{E}_{\Gamma\Gamma'}^{e(0)} \sim \frac{e^2}{4\pi\epsilon_0} \sum_{\vec{\Gamma}} \int d\vec{x} \int d\vec{x}' \varphi_n^{\text{at}}(\vec{x}) \varphi_m^{\text{at}*}(\vec{x}') \frac{e^{i(\vec{p}-\vec{p}')\cdot\vec{r}}}{|\vec{x}-\vec{x}'+\vec{r}|} \varphi_{n'}^{\text{at}*}(\vec{x}) \varphi_{m'}^{\text{at}}(\vec{x}') \quad (4.3)$$

and also

$$\zeta_{\Gamma\Gamma'}^{(0)} \sim \frac{e^2}{\epsilon_0 v} \sum_{\vec{\kappa} \neq 0} \frac{1}{\vec{\kappa}^2} \int d\vec{x} e^{i\vec{\kappa}\cdot\vec{x}} \varphi_n^{\text{at}}(\vec{x}) \varphi_m^{\text{at}*}(\vec{x}) \int d\vec{x}' e^{-i\vec{\kappa}\cdot\vec{x}'} \varphi_{n'}^{\text{at}}(\vec{x}')^* \varphi_{m'}^{\text{at}}(\vec{x}') \equiv \zeta_{\gamma\gamma'}^{\text{at}}, \quad (4.4)$$

$$\vec{v}_{\Gamma}^{(1)} \sim i \int d\vec{x} \varphi_n^{\text{at}*}(\vec{x}) \vec{x} \varphi_m^{\text{at}}(\vec{x}) \equiv \vec{v}_{\gamma}^{(1)}. \quad (4.5)$$

Here after the introduction of the atomic wave functions the integration over the cell has been extended to the whole space. Such an extension is allowed due to the faster-than-power-law decay of the atomic wave functions.

Now we see that the dependence on the quasimomenta survives only in  $\mathcal{E}^{e(0)}$  according to Eq. (4.3). On the other hand, since the summation symbol is

$$\sum_{\Gamma} \cdots \equiv \sum_{n,m} \frac{v}{(2\pi)^3} \int_{\text{BZ}} d\vec{p} \cdots \quad (4.6)$$

while

plemented with some assumptions about the properties of the unperturbed (equilibrium) Hartree-Fock solution, which is not explicitly known. These assumptions (generally accepted in the literature) are the following:

(a) The bands tend to the atomic levels faster than a power law.

(b) The restrictions of the Bloch functions on the cell tend to the atomic functions faster than a power law. Under this form they are acceptable for those bands that correspond to the negative part of the atomic spectrum (bound states). The analysis of simple Kronig-Penney models shows that they hold for the negative spectrum, while for the positive part of the atomic spectrum these statements are meaningless. For these states a much more sophisticated mathematical property should hold, which we are unable to formulate. We are compelled therefore to ignore that part of the spectrum. In this respect, however, our state of the art is identical with that of all the other approaches, where these assumptions are brought in under the form of the tight-binding scheme.

Under the assumptions (a) and (b), for our asymptotic purpose we may consider  $\partial\varphi_{n\vec{p}}/\partial\vec{p}$  and  $\partial E_{n\vec{p}}/\partial\vec{p}$  as vanishing. As a consequence Eq. (2.13) reduces to the first term. Therefore, irrespective of the position of the Fermi level, for nonvanishing frequencies, we remain only with the expression that is typical for insulators.

We may also replace the crystal energies  $E_{n\vec{p}}$  and wave functions  $\varphi_{n\vec{p}}(\vec{x})$  by the corresponding atomic energies and wave functions  $\epsilon_n$  and  $\varphi_n^{\text{at}}(\vec{x})$ . (It is understood that the lattice constant is already so big that we encounter no more band crossings.) In applying this procedure we must be careful, however, to put the expression under a form in which only restrictions of the wave functions on the elementary cell appear. Therefore we must rewrite the definition of  $\mathcal{E}^{e(0)}$  [see Eq. (2.11)] in the form

$$\frac{v}{(2\pi)^3} \int_{\text{BZ}} d\vec{p} = 1, \quad (4.7)$$

$$\frac{v}{(2\pi)^3} \int_{\text{BZ}} d\vec{p} e^{i\vec{p}\cdot\vec{r}} = \delta_{\vec{r},\vec{0}},$$

we may replace the summation symbol (in all the matrix manipulations) with

$$\sum_{\gamma} \equiv \sum_{n,m}$$

simultaneously with the replacement of  $\mathcal{E}_{\Gamma\Gamma'}^{e(0)}$  with

$$\mathcal{C}_{\gamma\gamma'}^{\text{ate}} \equiv \frac{e^2}{4\pi\epsilon_0} \int d\vec{x} \int d\vec{x}' \varphi_n^{\text{at}}(\vec{x}) \varphi_m^{\text{at}*}(\vec{x}') \frac{1}{|\vec{x} - \vec{x}'|} \varphi_n^{\text{at}*}(\vec{x}) \varphi_m^{\text{at}}(\vec{x}') . \quad (4.8)$$

Therefore we arrive at the formula

$$\frac{\epsilon^{\text{HF}}(0, \omega)}{\epsilon_0} - 1 \sim \frac{2e^2}{v\epsilon_0} \sum_{\gamma, \gamma'} \vec{e} \cdot \vec{v}_{\gamma}^{(1)} \left[ \frac{1}{1 + \mathcal{X}^{\text{at}}(\omega)(2\zeta^{\text{at}} - \mathcal{C}^{\text{ate}})} \mathcal{X}^{\text{at}}(\omega) \right] \vec{e} \cdot \vec{v}_{\gamma'}^{(1)*} , \quad (4.9)$$

which resembles Eq. (3.9) for the atomic polarizability. The only difference is the appearance of  $\zeta^{\text{at}}$  instead of the direct Coulomb matrix  $\mathcal{C}^{\text{at}d}$ . On the other hand, it is obvious from the inspection of its definition Eq. (4.4) that

$$\lim_{a \rightarrow \infty} \zeta^{\text{at}} = \mathcal{C}^{\text{at}d} . \quad (4.10)$$

A hasty superficial conclusion would be then, that actually we obtained a linear relationship between the dielectric constant and the atomic polarizability. However, this is not so. Equation (4.10) says nothing about how fast is the limit achieved and this is crucial for the discussion of the Clausius-Mosotti limit. Actually we shall prove the following lemma,

$$\zeta_{\gamma\gamma'}^{\text{at}} \sim \mathcal{C}_{\gamma\gamma'}^{\text{at}d} - \frac{e^2}{3v\epsilon_0} \vec{v}_{\gamma}^{(1)*} \cdot \vec{v}_{\gamma'}^{(1)} , \quad (4.11)$$

which says that  $\zeta^{\text{at}}$  tends toward  $\mathcal{C}^{\text{at}d}$  faster than any power of  $r_0/a$  only after the subtraction of a term that falls as  $(r_0/a)^3$ .

From the Poisson formula

$$\frac{1}{a^3} \sum_{\vec{K}} \hat{g}(\vec{K}) = \frac{1}{(2\pi)^3} \sum_{\vec{r}} g(\vec{r}) \quad (4.12)$$

(where

$$g(\vec{x}) \equiv \int d\vec{k} e^{-i\vec{k} \cdot \vec{x}} \hat{g}(\vec{k})$$

and the limits on the summation signs mean that the summations are performed over the lattice of constant  $a$  and the reciprocal lattice of constant  $1/a$ ) we may conclude that

$$\frac{1}{a^3} \sum_{\vec{K}} \hat{g}(\vec{K}) \sim \frac{1}{(2\pi)^3} \int d\vec{k} \hat{g}(\vec{k}) \quad (4.13)$$

if  $g(\vec{x})$  decreases faster than any power law, or equivalent-

$$\frac{1}{a^3} \sum_{\vec{K} (\neq \vec{0})} \frac{\hat{F}(\vec{K})}{\vec{K}^2} \sim \frac{1}{(2\pi)^3} \int d\vec{k} \left[ \frac{\hat{F}(\vec{k}) - \vec{k} \cdot \hat{A} \cdot \vec{k}}{\vec{k}^2} e^{-\alpha \vec{k}^2} + \frac{\hat{F}(\vec{k})}{\vec{k}^2} (1 - e^{-\alpha \vec{k}^2}) + \frac{1}{3} (\text{tr} \hat{A}) e^{-\alpha \vec{k}^2} \right] - \frac{1}{3a^3} \text{tr} \hat{A} .$$

But due to the spherical symmetry of integration

$$\int d\vec{k} \frac{\vec{k} \cdot \hat{A} \cdot \vec{k}}{\vec{k}^2} e^{-\alpha \vec{k}^2} = \frac{1}{3} (\text{tr} \hat{A}) \int d\vec{k} e^{-\alpha \vec{k}^2} ,$$

we may regroup the terms and we have finally

ly if  $\hat{g}(\vec{k})$  is continuous, indefinitely differentiable, decreasing together with its derivatives faster than any power. On the other hand, we have for  $\zeta_{\gamma\gamma'}^{\text{at}}$  an expression of the form

$$\frac{1}{a^3} \sum_{\vec{K} (\neq \vec{0})} \frac{\hat{F}(\vec{K})}{\vec{K}^2} ,$$

where  $\hat{F}(\vec{k})$  is continuous, indefinitely differentiable in  $\vec{k}$ , decreasing together with its derivatives faster than any power and vanishing quadratically at the origin. Owing to the singularity of the summand in the origin, we cannot apply directly Eq. (4.13). Let us subtract the behavior  $\vec{k} \hat{A} \vec{k}$  of  $\hat{F}(\vec{k})$  around the origin in the following way:

$$\frac{\hat{F}(\vec{k})}{\vec{k}^2} = \frac{\vec{k} \cdot \hat{A} \cdot \vec{k}}{\vec{k}^2} e^{-\alpha \vec{k}^2} + \frac{[\hat{F}(\vec{k}) - \vec{k} \cdot \hat{A} \cdot \vec{k}] e^{-\alpha \vec{k}^2}}{\vec{k}^2} + \frac{\hat{F}(\vec{k})}{\vec{k}^2} (1 - e^{-\alpha \vec{k}^2}) ,$$

where  $\alpha$  is an arbitrary positive number. Only the first term does not satisfy the required conditions. However, due to the cubic symmetry,

$$\begin{aligned} \frac{1}{a^3} \sum_{\vec{K} (\neq \vec{0})} \frac{\vec{K} \cdot \hat{A} \cdot \vec{K}}{\vec{K}^2} e^{-\alpha \vec{K}^2} &= \frac{1}{3a^3} (\text{tr} \hat{A}) \sum_{\vec{K} (\neq \vec{0})} e^{-\alpha \vec{K}^2} \\ &= \frac{1}{3a^3} (\text{tr} \hat{A}) \sum_{\vec{K}} e^{-\alpha \vec{K}^2} \\ &\quad - \frac{1}{3a^3} \text{tr} \hat{A} , \end{aligned}$$

where the function under the sum again satisfies all the conditions.

Therefore

$$\frac{1}{a^3} \sum_{\vec{K} (\neq \vec{0})} \frac{\hat{F}(\vec{K})}{\vec{K}^2} \sim \frac{1}{(2\pi)^3} \int d\vec{k} \frac{\hat{F}(\vec{k})}{\vec{k}^2} - \frac{1}{3a^3} \text{tr} \hat{A} , \quad (4.14)$$

which gives immediately Eq. (4.11).

Now let us use Eq. (4.11) in Eq. (4.9). To this end it is

important to observe that the asymptotic difference between  $\xi^{\text{at}}$  and  $\mathcal{C}^{\text{at}d}$  is a factorized matrix, therefore the formula expanded in formal powers of this matrix gives rise to products of the  $3 \times 3$  matrix

$$\kappa_{\mu\nu}^{\text{at HF}} = \frac{2e^2}{v\epsilon_0} \sum_{\gamma, \gamma'} v_{\gamma}^{(1)\mu} \left( \frac{1}{1 + \mathcal{K}^{\text{at}(\omega)}(2\mathcal{C}^{\text{at}d} - \mathcal{C}^{\text{at}e})} \times \mathcal{K}^{\text{at}(\omega)} \right)_{\gamma\gamma'} v_{\gamma'}^{(1)*\nu} \quad (\mu, \nu = 1, 2, 3).$$

But, owing to the spherical symmetry of the atom

$$\kappa_{\mu\nu}^{\text{at HF}} = \delta_{\mu\nu} \kappa^{\text{at HF}},$$

and therefore we have after resummation

$$\frac{\epsilon^{\text{HF}}(0, \omega)}{\epsilon_0} - 1 \sim \frac{\kappa^{\text{at HF}}}{1 - \frac{1}{3}\kappa^{\text{at HF}}}, \quad (4.15)$$

which is exactly the proof of our conjecture.

## V. DISCUSSION

We have seen how the formulation of the problem in terms of asymptotic series in  $r_0/a$  leads in a natural way to the Clausius-Mosotti formula. While the plausible assumptions about the asymptotic behavior of the Bloch functions and band widths are the same as generally accepted in the literature, a crucial point of our proof is the lemma [contained in Eq. (4.11)] about the asymptotic behavior of a certain lattice sum. In the absence of the guiding criterion of asymptotic equivalence, one could derive the most contradictory results, since ignoring terms that vanish only as a power law would modify completely the results. Therefore, those papers that accidentally ignored only terms that according to our lemma decrease faster than a power law have obtained the Clausius-Mosotti relation, while the others have not. Of course, in the identification of the Clausius-Mosotti relation it was important also to use the appropriate definition of the atomic polarizability. As we have shown, one must compare similar approximations for the crystal dielectric constant and atomic polarizability.

Our discussion was limited to the self-consistent, time-dependent Hartree-Fock and the simple self-consistent po-

tential approximations. All the results hold in both approximations, irrespective to the presence or absence (in the spinless HF scheme) of a spurious self-interaction. We think that this is natural since only for pointlike charge distributions is self-interaction dangerous.

We expect that the Clausius-Mosotti relation in the above described asymptotic sense holds also between the exact crystal dielectric constant and the exact atomic polarizability, however no proof of such a general statement seems available. Moreover, an order by order perturbative argument for the irreducible polarization diagram  $\Pi$  leads to immediate difficulties. Indeed, a succession of second-order photon self-energy diagrams (electron loop with two external potential lines) within will give rise to crystal convolutions of the exchange Coulomb terms and not products of atomic exchange Coulomb terms.

A weak point of our discussion is that it ignores the part of the spectrum that tends toward the positive atomic spectrum (not bound states). This is a serious shortcoming, but again it is common for all approaches in the literature. The inclusion of this part of the spectrum would require an adequate formulation of the asymptotic properties, which obviously will be less intuitive and even harder to prove.

We would like to mention here also our results on the analysis of the Clausius-Mosotti problem within an exactly solvable hopping model with self-consistent potential.<sup>15</sup> In that lattice problem the role of the atoms was played by the elementary cell to which were confined the "bound electrons." The Clausius-Mosotti relation (for zero frequency) was obtained in the limit, when the dimension of the cell goes to zero, while the total electronic charge on the cell increases, in such a way that their product is constant. (The existence of this limit unfortunately implied a regularization of the Coulomb interaction at the origin.)

It can be shown however, that the result of the present paper about the asymptotic validity of the Clausius-Mosotti relation holds exactly also within the above-mentioned model, eliminating the need of any artificial regularization procedure.

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