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Dielectric Constant with Local Field Effects Included*

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The self-consistent field method of Cohen and Ehrenreich is used to obtain the macroscopic longitudinal dielectric constant that includes local field effects. The physical basis for the local field is discussed for nonlocalized electrons. In the limit of long wavelengths and low frequencies, it is shown that the dielectric constant can be split into an acceleration term that describes the motion of electrons from atom to atom and an atomic term that describes the motion of the electrons around each atom. It is proved that the acceleration term contains no local field correction whereas the atomic term does contain a local field correction. The local field correction is calculated explicitly for the weak binding limit and is found to be of the same order in the weak potential as the atomic term, but the coefficient is much smaller for most Fermi surfaces. This justifies, for most Fermi surfaces, the common practice of neglecting local field corrections. In the tight-binding limit, the Lorentz expression for the dielectric constant is obtained.

I. INTRODUCTION

THE use of a dielectric constant formalism to describe the behavior of a many-electron system occurs in many areas of solid-state physics. The dielectric constant has served to describe the response of a crystal to an external electric field, to study electron-electron interactions,[1] and to describe the valence screening of the core effective potential of Phillips and Kleinman[2] in the investigation of band structure.[3] In these and other treatments, the approximation has invariably been made of ignoring local field corrections to the dielectric constant. In some cases, the presence of local field corrections would merely affect numerical factors. In other cases, however, the contribution of local field corrections that were large would completely invalidate even the qualitative results. This would be true, for example, of Cohen's[4] use of the dielectric constant to determine the shape of the Fermi surface and of Biondi and Rayne's[5] treatment of optical effects. Therefore, it is of interest to examine the validity of the approximation of neglecting local field corrections to the dielectric constant. The error introduced by this approximation will be explicitly calculated and shown to be small or negligible under most circumstances.

The dielectric constant can be calculated using a many-body approach[6,7] or a self-consistent field approach.[8,9] Cohen and Ehrenreich[9] have shown that for many problems these two approaches may be regarded as rigorously equivalent within the random phase approximation. We use the self-consistent field approach. In this paper, the expression for the macroscopic longitudinal dielectric constant of a many-electron system in a periodic potential given by Cohen and Ehrenreich[9] is generalized by the inclusion of local field effects (Sec. II). In Sec. III, the effect of the local field is considered in detail. In the limit of long wavelengths and low frequencies, the dielectric constant has the following form:

$$\epsilon=\epsilon_c-4\pi N_0e^2/m_a\omega^2. \tag{1}$$

The second term is the usual acceleration term, N_0 and m_a being an appropriate carrier density and an appropriate average effective mass, respectively. In Sec. IV, it is shown that the acceleration term does not contain a local field correction. The first term ϵ_c is the analog of the ordinary atomic polarizability and does contain a local field correction, which is calculated explicitly for the weak-binding limit in Sec. V. For the typical case of copper, we find that the local field correction to the dielectric constant is only 4% of the atomic polarizability term, which in turn is small compared to another term (effective-mass correction) that is of the same order in the weak potential. In Sec. VI, we consider the tight-binding limit and recapture the Lorentz formula for the dielectric constant,

$$\epsilon-1=\frac{4\pi N_0\alpha_T}{1-\frac{4}{3}\pi N_0\alpha_T}, \tag{2}$$

where α_T is the total polarizability.

II. GENERAL FORMALISM

To calculate the macroscopic longitudinal dielectric constant, we use the self-consistent field method in which each electron interacts independently with a self-consistent electromagnetic field. In this approach, the single-particle Liouville equation,

$$i\hbar(\partial\rho/\partial t)=[H,\rho], \tag{3}$$

can be used to describe the response of any particle of the system to the self-consistent potential $V(\mathbf{r},t)$. Here ρ is the operator represented by the single-particle

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density matrix. The single-particle Hamiltonian is

$$H=H_0+V(\mathbf{r},t), \tag{4}$$

where H_0 is the kinetic energy $p^2/2m$ plus the periodic Bloch potential, and V is the self-consistent potential consisting of V_0, the applied potential, plus V_s, the screening potential. The wave functions used as a representation are the Bloch functions, $|\mathbf{k}l\rangle=\Omega^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}l}(\mathbf{r})$, which diagonalize the unperturbed Hamiltonian, $H_0|\mathbf{k}l\rangle=\mathcal{E}_{\mathbf{k}l}|\mathbf{k}l\rangle$. We expand the operator ρ in the form $\rho=\rho_0+\rho_1$, where ρ_0 is the unperturbed density-matrix operator having the property, $\rho_0|\mathbf{k}l\rangle=f_0(\mathcal{E}_{\mathbf{k}l})|\mathbf{k}l\rangle$, where $f_0(\mathcal{E}_{\mathbf{k}l})$ is the Fermi-Dirac distribution function.

We Fourier-analyze the self-consistent potential V in the form

$$V(\mathbf{r},t)=\sum_{\mathbf{q},\mathbf{K}} V(\mathbf{q},\mathbf{K},t)e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}}, \tag{5}$$

where $\mathbf{q}$ is restricted to lie in the first Brillouin zone and the $\mathbf{K}$'s are reciprocal lattice vectors. Finally, we linearize the Liouville equation to obtain

$$i\hbar(\partial\rho_1/\partial t)=[H_0,\rho_1]+[V,\rho_0]. \tag{6}$$

We now take the matrix elements of this linearized equation between the states $\langle\mathbf{k}l|$ and $|\mathbf{k}+\mathbf{q},l'\rangle$. Assume that the applied potential V_0 has harmonic time dependence and is turned on adiabatically, i.e., $V_0\sim e^{i\omega t}e^{\alpha t}$, $\alpha\rightarrow 0^+$. We make the *ansatz* that all quantities have the same time dependence as the applied potential. This *ansatz* has been rigorously justified.[10] We then obtain

$$\langle\mathbf{k}l|\rho_1|\mathbf{k}+\mathbf{q},l'\rangle =\frac{f_0(\mathcal{E}_{\mathbf{k}+\mathbf{q},l'})-f_0(\mathcal{E}_{\mathbf{k}l})}{\mathcal{E}_{\mathbf{k}+\mathbf{q},l'}-\mathcal{E}_{\mathbf{k}l}-\hbar\omega+i\hbar\alpha}\sum_{\mathbf{K}}\eta_{\mathbf{K}}V(\mathbf{q},\mathbf{K},) \tag{7}$$

where

$$\eta_{\mathbf{K}}\equiv\Delta^{-1}\int_0 d^3r\, u_{\mathbf{k}l}^*(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}u_{\mathbf{k}+\mathbf{q},l'}(\mathbf{r}).$$

Here $\int_0$ indicates that the integration is to be performed only over a unit cell whose volume is denoted by Δ. The induced change in electron density $n(\mathbf{r})$ is given by

$$n(\mathbf{r})=\mathrm{Tr}[\delta(\mathbf{r}-\mathbf{r}_e)\rho_1]=\Omega^{-1}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{r}} \times\sum_{\mathbf{k},l,l'} u_{\mathbf{k}+\mathbf{q},l'}^*(\mathbf{r})u_{\mathbf{k}l}(\mathbf{r})\langle\mathbf{k}l|\rho_1|\mathbf{k}+\mathbf{q},l'\rangle. \tag{8}$$

We next combine Poisson's equation,

$$\nabla^2V_s=-4\pi e^2n, \tag{9}$$

with Eqs. (7) and (8) to obtain the desired result which relates the total self-consistent potential V to the screening potential V_s,

$$V_s(\mathbf{q},\mathbf{K})=-\sum\nolimits_{\mathbf{K}'} T_{\mathbf{K}\mathbf{K}'}V(\mathbf{q},\mathbf{K}'), \tag{10}$$

where

$$T_{\mathbf{K}\mathbf{K}'}=\frac{4\pi e^2}{(\mathbf{q}+\mathbf{K})^2}\sum_{\mathbf{k},l,l'}\frac{f_0(\mathcal{E}_{\mathbf{k}+\mathbf{q},l'})-f_0(\mathcal{E}_{\mathbf{k}l})}{\mathcal{E}_{\mathbf{k}+\mathbf{q},l'}-\mathcal{E}_{\mathbf{k}l}-\hbar\omega+i\hbar\alpha}\eta_{\mathbf{K}}^*\eta_{\mathbf{K}'}. \tag{11}$$

We shall look upon the quantities $T_{\mathbf{K}\mathbf{K}'}$ as the elements of a matrix $\mathbf{T}$ whose rows and columns are labeled by the reciprocal lattice vectors.

From this result, we can derive the macroscopic longitudinal dielectric constant. We suppose that the applied potential is of the form

$$V_0(\mathbf{r},t)=V_0(\mathbf{q},t)e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{12}$$

where $\mathbf{q}$ is small compared to a reciprocal lattice vector. We define a macroscopic quantity as the average of the corresponding microscopic quantity taken over a unit cell. Consider any quantity $f(\mathbf{r})$. We denote its macroscopic average by $\bar{f}(\mathbf{R})$, where the bar indicates an average taken over the unit cell whose location is given by the macroscopic position variable $\mathbf{R}$. We have

$$f(\mathbf{R})=\sum_{\mathbf{q},\mathbf{K}} f(\mathbf{q},\mathbf{K})\Delta^{-1}\int_0 d^3r\, e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}} \approx\sum_{\mathbf{q}} f(\mathbf{q},0)e^{-i\mathbf{q}\cdot\mathbf{R}}, \tag{13}$$

provided that $f(\mathbf{q},\mathbf{K})\neq 0$ for only those values of $\mathbf{q}$ which are so small that $e^{-i\mathbf{q}\cdot\mathbf{r}}$ is essentially constant over a unit cell. Comparing Eq. (13) with the Fourier transform of $\bar{f}(\mathbf{R})$, we see that

$$\bar{f}(\mathbf{q})=f(\mathbf{q},0), \tag{14}$$

and so the $\mathbf{q}$-Fourier component of any macroscopic quantity is just the $\mathbf{q}$, $\mathbf{K}=0$ component of the corresponding microscopic quantity. Further, we can easily prove (see Appendix A) that the derivative of an averaged quantity with respect to the macroscopic variable $\mathbf{R}$ (taken to be continuous on a macroscopic scale) equals the average of the derivative of that quantity, i.e.,

$$\nabla_{\mathbf{R}}\bar{f}(\mathbf{R})=\langle\nabla_{\mathbf{r}}f(\mathbf{r})\rangle_{\mathrm{av}}. \tag{15}$$

This shows how the microscopic field equations lead directly to the macroscopic field equations of Maxwell.

The macroscopic dielectric constant ϵ is defined through the relation[11]

$$\bar{V}_0(\mathbf{q})/\epsilon(\mathbf{q},\omega)=\bar{V}(\mathbf{q}). \tag{16}$$

Recalling that $V=V_0+V_s$ and $V_0(\mathbf{q},\mathbf{K})=V_0(\mathbf{q})\delta_{\mathbf{K}0}$, we obtain from Eq. (10)

$$V(\mathbf{q},0)=[(1+\mathbf{T})^{-1}]_{00}V_0(\mathbf{q}). \tag{17}$$

Here $(1+\mathbf{T})^{-1}$ denotes the inverse of a matrix whose matrix elements are explicitly known. From the defini-

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[10] M. H. Cohen and H. Ehrenreich (private communication).

[11] This definition is equivalent to the usual definition, $\bar{P}(\mathbf{q})=(4\pi)^{-1}[\epsilon(\mathbf{q},\omega)-1]\bar{E}(\mathbf{q})$.

tion of ϵ given in Eq. (16), we see that the dielectric constant is given by[12]

$$1/\epsilon=[(1+\mathbf{T})^{-1}]_{00}. \tag{18}$$

Thus far, the treatment has included local field effects and has resulted in Eq. (18). In the next section, we shall see how the neglect of local field effects modifies the dielectric constant.

III. LOCAL FIELD

The microscopic field is the total electric field due to all the charges in the system plus the applied fields. If the electrons are well localized, the microscopic field will have a singularity at the position of every electron. In this case, the local field acting on any particular electron is the electric field due to all the other electrons plus the applied fields, i.e., it is the microscopic field evaluated at the position of the electron minus the singularity caused by the electron itself. This is the definition of the local field introduced by Lorentz. However, if an electron is represented by a charge cloud that is appreciably spread out in space, then *the definition of the local field introduced by Lorentz no longer has meaning* since there is no single position of the electron at which to evaluate the microscopic field. Therefore, we shall have to extend the definition of the local field to handle this case. Obviously, our extended defintion must reduce to the Lorentz version of the local field in the case of well-localized electrons.

Since the local field enters dielectric theory through the equation $p=\alpha E_{\text{loc}}$, where p is the dipole moment associated with the electron cloud and α is its macroscopic polarizability, we shall use this relation to guide us in constructing our definition. Thus, the generalized local field will be that quantity which determines the polarization of the electron. It will be obtained by averaging the microscopic field over the region occupied by the electron, the contribution to the average being greater from those parts of the unit cell where the electron is more easily polarized.[13] We emphasize that the local field will be different from, for example, that electric field which determines the force acting on the electron. The latter electric field must be defined to satisfy $F=qE'$, where F is the force acting on the electron having charge q. The fields E_{loc} and E' will differ in that different weighting factors are necessary in the averaging process employed in the two cases. However, for localized electrons, where both E_{loc} and E' reduce to the Lorentz local field, these quantities will be equal.

A further quantity, the macroscopic field, is obtained by simply performing a spatial average of the microscopic field over the unit cell. This unweighted average field will in general differ from the local field, which is a weighted average field. Only for a spatially uniform charge distribution, viz., a free electron, where all parts of the distribution are as easily polarized, will the weighted and unweighted average fields be the same. In the present case where we use Bloch functions, there will in general be some degree of nonuniformity of the electron cloud within the unit cell, and so the local field will differ from the macroscopic field.

To develop this in detail, we introduce the microscopic polarizability $\alpha(\mathbf{r},\mathbf{r}')$ which is expressed in terms of the polarization $P(\mathbf{r})$ by

$$P(\mathbf{r})=N_0\int d^3r'\,\alpha(\mathbf{r},\mathbf{r}')E(\mathbf{r}'), \tag{19}$$

where N_0 is the density of unit cells. The quantity $\alpha(\mathbf{r},\mathbf{r}')$ measures the ease with which the electron cloud responds to the electric field. Therefore, we shall use the polarizability as the weighting factor in determining the local field. Fourier-analyzing Eq. (19) yields[14]

$$P(\mathbf{q},\mathbf{K})=N_0\textstyle\sum_{\mathbf{K}'}\alpha(\mathbf{q},\mathbf{K},\mathbf{K}')E(\mathbf{q},\mathbf{K}'). \tag{20}$$

We see that a given Fourier component $\mathbf{q}$ (in the first Brillouin zone) of the microscopic field gives rise to polarization of the same Fourier component; moreover, it is this same $\mathbf{q}$ component of the polarizability $\alpha(\mathbf{r},\mathbf{r}')$ which determines this response of the electrons. In our case, the microscopic field contains only one Fourier component $\mathbf{q}$. Therefore, we shall write

$$\alpha(\mathbf{r},\mathbf{r}')=\sum_{\mathbf{q},\mathbf{K},\mathbf{K}'}\alpha(\mathbf{q},\mathbf{K},\mathbf{K}')e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}e^{-i\mathbf{K}\cdot\mathbf{r}}e^{+i\mathbf{K}'\cdot\mathbf{r}'} \equiv\sum_{\mathbf{q}}\alpha(\mathbf{q},\mathbf{r},\mathbf{r}'), \tag{21}$$

and use $\alpha(\mathbf{q},\mathbf{r},\mathbf{r}')$ as the appropriate weighting factor. The local field will then contain only the same Fourier component $\mathbf{q}$. We define

$$\bar{E}_{\text{loc}}(\mathbf{R})=\bar{E}_{\text{loc}}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}} \equiv\int_0 d^3r\int_0 d^3r'\,\alpha(\mathbf{q},\mathbf{r},\mathbf{r}')E(\mathbf{r}')\bigg/\int_0 d^3r\int_0 d^3r'\,\alpha(\mathbf{q},\mathbf{r},\mathbf{r}'), \tag{22}$$

where we obtain the local field $\bar{E}_{\text{loc}}(\mathbf{R})$ by weighting the microscopic field $E(\mathbf{r}')$ with $\alpha(\mathbf{q},\mathbf{r},\mathbf{r}')$ and then normalizing. Again, $\mathbf{R}$ is the macroscopic position variable locating the unit cell over which the average is taken. We emphasize the macroscopic character of the local field by placing a bar over $\bar{E}_{\text{loc}}(\mathbf{R})$. Combining the Fourier transform of Eq. (22) with Eq. (20) yields the equation

$$P(\mathbf{q})=N_0\alpha(\mathbf{q})E_{\text{loc}}(\mathbf{q}), \tag{23}$$

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[12] This equation has been obtained independently by S. L. Adler [Phys. Rev. **126**, 413 (1962)].

[13] In the Bloch scheme, each electron is spread throughout the entire crystal. Therefore, the field of an electron is no longer singular and, in fact, makes a negligible contribution to the total microscopic field and hence need not be subtracted. But, contrary to Nozières and Pines (see reference 1) and others, this does *not* imply that there is no local field correction. However, the term "local" field is clearly a misnomer for nonlocalized electrons.

[14] The Fourier transform of $\alpha(\mathbf{r},\mathbf{r}')$ is written as indicated in Eq. (21). The periodicity of the crystal, requiring that $\alpha(\mathbf{r}+\mathbf{R}_m,\,\mathbf{r}'+\mathbf{R}_m)=\alpha(\mathbf{r},\mathbf{r}')$, where $\mathbf{R}_m$ is any lattice vector, permits us to write the Fourier transform in such a form.

which shows that the weighting factor used in the definition of $\bar{E}_{\mathrm{loc}}(\mathbf{R})$ was chosen correctly. Here $\alpha(\mathbf{q}) \equiv \bar{\alpha}(\mathbf{q}) = \alpha(\mathbf{q},0,0)$, and we no longer bother to write out the bars explicitly.

We now write down the fundamental expression for the dielectric constant,

$$\epsilon(\mathbf{q},\omega) = 1 + 4\pi P(\mathbf{q})/E(\mathbf{q}), \tag{24}$$

and use Eq. (23) to introduce the local field explicitly. This gives

$$\epsilon(\mathbf{q},\omega) = 1 + 4\pi N_0 \alpha(\mathbf{q}) E_{\mathrm{loc}}(\mathbf{q})/E(\mathbf{q}). \tag{25}$$

The dependence of the dielectric constant upon the local field is now clear.

If we wish to neglect local field corrections, we merely replace $E_{\mathrm{loc}}(\mathbf{q})$ by $E(\mathbf{q})$ and then obtain

$$\epsilon(\mathbf{q},\omega) \approx 1 + 4\pi N_0 \alpha(\mathbf{q},\omega), \tag{26}$$

where the ω dependence of α is made explicit. Using Eq. (20) and the Fourier transforms of the well-known equations[15]

$$\nabla \cdot \mathbf{P} = en, \tag{27}$$

$$\nabla^2 V_s = -4\pi e^2 n, \tag{28}$$

and

$$e\mathbf{E} = \nabla V, \tag{29}$$

we find that $4\pi N_0 \alpha(\mathbf{q},\omega) = T_{00}$. Thus, we see that had we ignored the local field corrections, we would have obtained

$$\epsilon = 1 + T_{00}, \tag{30}$$

in place of the considerably more complicated Eq. (18).

IV PROOF THAT THE ACCELERATION TERM HAS NO LOCAL FIELD CORRECTIONS

We shall now examine the complete dielectric constant that contains local field effects in the limit of long wavelengths and low frequencies. Take ω to be less than any band gap $\omega_{ll'}(\mathbf{k})$ and let $\mathbf{q} \to 0$. This corresponds to the semiclassical case. In this limit, the present formalism enables us to split $T_{\mathbf{KK}'}$ conveniently into two terms, each of which has a simple physical interpretation:

$$T_{\mathbf{KK}'} = T_{\mathbf{KK}'}(\text{acceleration}) + T_{\mathbf{KK}'}(\text{atomic}), \tag{31}$$

$$T_{\mathbf{KK}'}(\text{acceleration}) = \frac{-e^2q^2}{\pi^2(\mathbf{q}+\mathbf{K})^2(\hbar\omega)^2} \sum_l \int d^3k \times f_0(\mathcal{E}_{\mathbf{k}l}) \frac{\partial^2 \mathcal{E}_{\mathbf{k}l}}{\partial k^2} \eta_{\mathbf{K}}^* \eta_{\mathbf{K}'}, \tag{32}$$

$$T_{\mathbf{KK}'}(\text{atomic}) = \frac{2e^2q}{\pi^2(\mathbf{q}+\mathbf{K})^2} {\sum_{ll'}}' \mathcal{P} \int d^3k \times f_0(\mathcal{E}_{\mathbf{k}l}) \frac{\omega_{l'l}\eta_{\mathbf{K}}^*\eta_{\mathbf{K}'}}{\omega_{l'l}^2 - \omega^2}, \tag{33}$$

where $\mathcal{P}$ indicates that the principal part of the integral is to be taken and the prime on the summation means that the terms $l' = l$ are to be excluded. The acceleration term describes the motion of the electrons from atom to atom in the presence of the applied field. It is similar in form to the acceleration term for free electrons with the free-electron mass replaced by an average effective mass. The atomic term describes the motion of the electrons around each atom and contains the contribution to the dielectric constant from polarization effects. The acceleration term should thus exhibit no local field corrections whereas there should be a local field correction to the atomic term. It will be seen that this is precisely what occurs.

We can easily show that for $\mathbf{q} \to 0$, the imaginary part of $T_{\mathbf{KK}'}$ vanishes and all the matrix elements of the acceleration term are of higher order in $\mathbf{q}$ than the corresponding matrix elements of the atomic term except for $\mathbf{K} = \mathbf{K}' = 0$. Therefore, in the long-wavelength limit, we may neglect all acceleration terms except T_{00}. By using standard expressions for the inverse of a matrix, we may rewrite Eq. (18) as

$$\epsilon = 1 + T_{00} + {\sum_{\mathbf{K}}}' T_{0\mathbf{K}} [(\mathbf{1}+\mathbf{T})^{0\mathbf{K}}/(\mathbf{1}+\mathbf{T})^{00}], \tag{34}$$

where the superscript denotes the cofactor of the matrix element and the prime means that the $\mathbf{K}=0$ term is excluded from the summation. By comparing this expression with the form of the dielectric constant in the absence of local field effects, Eq. (30), we see that the last term of Eq. (34) contains all the local field corrections. The important feature of this last term is that it does *not* contain T_{00} and hence contains only atomic terms and no acceleration terms, Thus, we see that in the limit $\mathbf{q} \to 0$, there are no local field corrections to the acceleration term.

V. WEAK-BINDING LIMIT

We now calculate explicitly the local field corrections in the weak-binding limit. We proceed by expanding the periodic Bloch potential,

$$V_{\mathrm{Bloch}} = \sum_{\mathbf{K}} V_{\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}, \tag{35}$$

and treating the $V_{\mathbf{K}}$ as expansion parameters in ordinary second-order perturbation theory. We could obtain $E_{\mathrm{loc}}(\mathbf{q})/E(\mathbf{q})$ directly from the Fourier transform of Eq. (22) and we would find that $E_{\mathrm{loc}}(\mathbf{q}) = E(\mathbf{q})[1+O(V_{\mathbf{K}}^2)]$. However, it is easier to turn to Eq. (34) and merely evaluate the last term. We easily find that, to lowest order in $V_{\mathbf{K}}$, all diagonal matrix elements of $\mathbf{1}+\mathbf{T}$ are independent of $V_{\mathbf{K}}$ and all off-diagonal matrix elements

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[15] We will always use e as a positive quantity; thus, the electronic charge is $-e$.

are proportional to $V_{\mathbf{K}}$. Then, by writing out the matrix $\mathbf{1}+\mathbf{T}$, it is easy to see that, to lowest order in $V_{\mathbf{K}}$,

$$(\mathbf{1}+\mathbf{T})^{0\mathbf{K}}=\frac{-T_{0\mathbf{K}}}{(1+T_{\mathbf{KK}})}\prod_{\mathbf{K}'}{}'(1+T_{\mathbf{K}'\mathbf{K}''}) \tag{36}$$

and

$$(\mathbf{1}+\mathbf{T})^{00}=\prod_{\mathbf{K}'}{}'(1+T_{\mathbf{K}'\mathbf{K}'}), \tag{37}$$

where the prime denotes that the $\mathbf{K}'=0$ factor is excluded from the product. Thus, in the weak-binding limit to second order in $V_{\mathbf{K}}$, Eq. (34) becomes

$$\epsilon=1+T_{00}-\sum_{\mathbf{K}}{}'\frac{T_{0\mathbf{K}}T_{\mathbf{K}0}}{1+T_{\mathbf{KK}}} \tag{38}$$

Evaluation of the matrix elements is straightforward and leads to

$$\begin{aligned}\epsilon(0,\omega)=1&-\frac{4\pi N_0e^2}{m\omega^2}+\frac{2e^2\hbar^4}{\pi^2m^2}\frac{1}{(\hbar\omega)^2}\sum_{\mathbf{K}}{}'|V_{\mathbf{K}}|^2(K^\mu)^2J_3^{\mathbf{K}}\\&+\frac{2e^2\hbar^4}{\pi^2m^2}\sum_{\mathbf{K}}{}'|V_{\mathbf{K}}|^2(K^\mu)^2I_3^{\mathbf{K}}\\&-\left(\frac{2e^2\hbar^2}{\pi^2m}\right)^2\sum_{\mathbf{K}}{}'\frac{|V_{\mathbf{K}}|^2(K^\mu/K)^2(I_1^{\mathbf{K}})^2}{1+(2e^2I_{-1}^{\mathbf{K}}/\pi^2K^2)},\end{aligned} \tag{39}$$

where K^μ is the projection of $\mathbf{K}$ in the direction of propagation of the wave $\mathbf{q}$, N_0 is the electron density, and the integrals $I_n^{\mathbf{K}}$ and $J_n^{\mathbf{K}}$ are defined as follows:

$$I_n^{\mathbf{K}}\equiv\int d^3k\,f_0(\mathbf{k})(\Delta\mathcal{E}_{\mathbf{K}})^{-n}[(\Delta\mathcal{E}_{\mathbf{K}})^2-(\hbar\omega)^2]^{-1}, \tag{40}$$

and

$$J_n^{\mathbf{K}}\equiv\int d^3k\,f_0(\mathbf{k})(\Delta\mathcal{E}_{\mathbf{K}})^{-n}, \tag{41}$$

where

$$\Delta\mathcal{E}_{\mathbf{K}}\equiv\frac{\hbar^2(\mathbf{k}+\mathbf{K})^2}{2m}-\frac{\hbar^2k^2}{2m}.$$

In Eq. (39), the first two terms represent the free-electron result, the third term is the effective mass correction, the fourth term is the atomic polarizability, and the last is the local field correction to the atomic polarizability term. To estimate the relative magnitudes of the various terms, we may actually perform the integrals using the physical constants of copper and a typical infrared wavelength of 12 000 Å. In this case, $\hbar\omega\ll\Delta\mathcal{E}_{\mathbf{K}}$ for all $\mathbf{K}$, implying that $I_n^{\mathbf{K}}\approx J_{n+2}^{\mathbf{K}}$ and so the last two terms are independent of wavelength. The effective mass correction is almost 50 times as large as the atomic polarizability, and the local field correction is only 4% of the atomic polarizability. Examination of the integrals occurring in the last two terms of Eq. (39) shows that the local field corrections may be neglected for almost all Fermi surfaces. However, peculiar cases must be looked into on an individual basis, a matter which can easily be done.

VI. TIGHT-BINDING LIMIT

While the expression for the dielectric constant given by Eq. (18) is completely general, it is cumbersome to use it in the tight-binding limit. There are two reasons for this. First, we have used Bloch functions as a basis in our expression for the dielectric constant. These functions are not convenient to describe the localized electrons which characterize the tight-binding limit. Second, the matrix $(\mathbf{1}+\mathbf{T})^{-1}$ is in the $\mathbf{K}$, $\mathbf{K}'$ representation. Evaluation of the matrix in the present case requires making two complicated transformations.[16] Only then is one able to reproduce the Lorentz expression for the local field correction to the dielectric constant.

It is simpler and physically clearer to derive the Lorentz result using an approach that is more in keeping with the spirit of Lorentz' work. We shall use Wannier functions, $|lm\rangle=\psi_l(\mathbf{r}-\mathbf{R}_m)$, which are related to the periodic part of the Bloch functions by

$$\psi_l(\mathbf{r}-\mathbf{R}_m)=N^{-1}\Delta^{-1/2}\sum\nolimits_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_m)}u_{\mathbf{k}l}(\mathbf{r}) \tag{42}$$

and

$$u_{\mathbf{k}l}(\mathbf{r})=\Delta^{-1/2}\sum\nolimits_m e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_m)}\psi_l(\mathbf{r}-\mathbf{R}_m), \tag{43}$$

and which satisfy the orthogonality relation

$$\int d^3r\,\psi_l^*(\mathbf{r}-\mathbf{R}_m)\psi_{l'}(\mathbf{r}-\mathbf{R}_{m'})=\delta_{ll'}\delta_{mm'}. \tag{44}$$

Again, Δ is the volume of a unit cell and N is the number of unit cells in the crystal. In the tight-binding limit, the Wannier function $\psi_l(\mathbf{r}-\mathbf{R}_m)$ is centered in the mth unit cell, labeled by the lattice vector $\mathbf{R}_m$, and is similar to an atomic function. Because of this localization property, these functions, rather than Bloch functions, are appropriate to the problem. As before, we shall deal with an applied potential of the form

$$V_0(\mathbf{r},t)=V_0(\mathbf{q},t)e^{-i\mathbf{q}\cdot\mathbf{r}}. \tag{45}$$

Then, the total microscopic potential $V(\mathbf{r})$, as well as all other quantities, will contain $e^{-i\mathbf{q}\cdot\mathbf{r}}$ multiplied by a $\mathbf{q}$-dependent periodic function representing the influence of the lattice. We can write all such quantities in the convenient Wannier-like form[17]

$$V(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\sum\nolimits_m v(\mathbf{r}-\mathbf{R}_m)e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_m)}, \tag{46}$$

where the time dependence is not explicitly stated. Because the $v(\mathbf{r}-\mathbf{R}_m)$ arise from the response of the electrons to V_0, in the tight-binding limit each of the $v(\mathbf{r}-\mathbf{R}_m)$ is centered in its respective unit cell m.

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[16] S. L. Adler, see reference 12.

[17] Any $\mathbf{q}$-dependent function $F_{\mathbf{q}}(\mathbf{r})$ can be written in the form of Eq. (46) if it has the following properties: $F_{\mathbf{q}}(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\times$periodic function and $F_{\mathbf{q}+\mathbf{K}}(\mathbf{r})=F_{\mathbf{q}}(\mathbf{r})$. Both conditions are satisfied by $V(\mathbf{r})$.

We now introduce the approximations that characterize the extreme tight-binding limit. First, we ignore any $\mathbf{k}$ dependence of the energy, $\mathcal{E}_l(\mathbf{k})=\mathcal{E}_l$. Then, the Wannier functions diagonalize the unperturbed Hamiltonian (which is not true in general),

$$H_0|lm\rangle=\mathcal{E}_l|lm\rangle. \tag{47}$$

Second, we neglect overlap of the wave functions. We now proceed exactly as in Sec. II, starting with the linearized Liouville equation, Eq. (6), and taking matrix elements between the Wannier states $\langle lm|$ and $|l'm\rangle$, (not $|l'm'\rangle$ because we are neglecting overlap). This leads to

$$\langle lm|\rho_1|l'm\rangle=F_{l'l}\langle lm|V|l'm\rangle, \tag{48}$$

where

$$F_{l'l}\equiv(f_{l'}-f_l)/(\mathcal{E}_{l'}-\mathcal{E}_l-\hbar\omega+i\hbar\alpha),\quad \alpha\rightarrow 0^+,$$

since we again assume that the applied potential has harmonic time dependence and is turned on adiabatically. The matrix element of V in Eq. (48) is integrated only over cell m. Within cell m, we can split V into two parts,

$$V(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}V_{\text{ext}}{}^m(\mathbf{r})+e^{-i\mathbf{q}\cdot\mathbf{r}}V_{\text{int}}{}^m(\mathbf{r}), \tag{49}$$

where

$$V_{\text{ext}}{}^m(\mathbf{r})=\sum_{i\neq m}{}' v(\mathbf{r}-\mathbf{R}_i)e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_i)}, \tag{50}$$

and

$$V_{\text{int}}{}^m(\mathbf{r})=v(\mathbf{r}-\mathbf{R}_m)e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_m)}. \tag{51}$$

The interpretation of these two terms is clear. We use the subscript "int" to denote that part of the microscopic potential in cell m resulting from the polarization within cell m itself, and the subscript "ext" denotes both the potential arising from the rest of the medium and the applied potential. We can rewrite the matrix element of V by recalling that $v(\mathbf{r}-\mathbf{R}_i)$ is centered in cell i and hence is relatively flat in cell m and that we are dealing with $\mathbf{q}$ small compared to a reciprocal lattice vector. Therefore $V_{\text{ext}}{}^m$ is a slowly varying function throughout cell m and we may expand

$$V_{\text{ext}}{}^m(\mathbf{r})\approx V_{\text{ext}}{}^m(\mathbf{R}_m)+(\mathbf{r}-\mathbf{R}_m)\cdot\nabla_{\mathbf{R}_m}V_{\text{ext}}{}^m(\mathbf{R}_m). \tag{52}$$

This gives

$$\begin{aligned}\langle lm|V|l'm\rangle&\\ =e^{-i\mathbf{q}\cdot\mathbf{R}_m}&[\mathbf{X}_{ll'}\cdot\nabla_{\mathbf{R}_m}V_{\text{ext}}{}^m(\mathbf{R}_m)+\langle lm|V_{\text{int}}{}^m|l'm\rangle],\\ &\qquad l'\neq l,\end{aligned} \tag{53}$$

where

$$\mathbf{X}_{ll'}\equiv\langle lm|\mathbf{r}-\mathbf{R}_m|l'm\rangle.$$

The induced change in electron density $n(\mathbf{r})$ is given by

$$\begin{aligned}n(\mathbf{r})&=\mathrm{Tr}[\delta(\mathbf{r}-\mathbf{r}_e)\rho_1]\\ &=\sum_{l,l',m}\psi_{l'}{}^*(\mathbf{r}-\mathbf{R}_m)\psi_l(\mathbf{r}-\mathbf{R}_m)\langle lm|\rho_1|l'm\rangle.\end{aligned} \tag{54}$$

Using Eqs. (48) and (53), we obtain

$$\begin{aligned}n(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}&\sum_{l,l',m}\psi_{l'}{}^*(\mathbf{r}-\mathbf{R}_m)\psi_l(\mathbf{r}-\mathbf{R}_m)e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_m)}F_{l'l}\\ &\times[\mathbf{X}_{ll'}\cdot\nabla_{\mathbf{R}_m}V_{\text{ext}}{}^m(\mathbf{R}_m)+\langle lm|V_{\text{int}}{}^m|l'm\rangle].\end{aligned} \tag{55}$$

We now average over a unit cell, say cell m, to get

$$\begin{aligned}\bar{n}^m=e^{-i\mathbf{q}\cdot\mathbf{R}_m}i\Delta&\sum_{l'l}\mathbf{q}\cdot\mathbf{X}_{l'l}F_{l'l}\\ &\times[\mathbf{X}_{ll'}\cdot\nabla_{\mathbf{R}_m}V_{\text{ext}}{}^m(\mathbf{R}_m)+\langle lm|V_{\text{int}}{}^m|l'm\rangle],\end{aligned} \tag{56}$$

where the bar means average taken over the indicated unit cell. To obtain Eq. (56), we again expanded $e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_m)}$ and retained terms to lowest order in $\mathbf{q}$ (semiclassical case).

The next step is to introduce the local field in a way similar to Lorentz. As with the potential, we shall split the microscopic field into two parts (but here it is convenient to incorporate the factor $e^{-i\mathbf{q}\cdot\mathbf{r}}$ into the parts of E),

$$E(\mathbf{r})=E_{\text{ext}}{}^m(\mathbf{r})+E_{\text{int}}{}^m(\mathbf{r}). \tag{57}$$

We note that $E_{\text{ext}}{}^m$ is just the local field of Lorentz, i.e., the field in cell m caused both by the polarization of all unit cells other than cell m and by the applied field. From Eq. (52), we have

$$eE_{\text{ext}}{}^m(\mathbf{r})=e^{-i\mathbf{q}\cdot\mathbf{r}}\nabla_{\mathbf{R}_m}V_{\text{ext}}{}^m(\mathbf{R}_m). \tag{58}$$

Thus, we see that the local field is essentially constant over a unit cell and we can equivalently use a macroscopic local field. Therefore, we define

$$\bar{E}_{\text{loc}}{}^m=\bar{E}_{\text{ext}}{}^m. \tag{59}$$

Then, the macroscopic average field is given by

$$\bar{E}^m=\bar{E}_{\text{ext}}{}^m+\bar{E}_{\text{int}}{}^m=\bar{E}_{\text{loc}}{}^m+\bar{E}_{\text{int}}{}^m. \tag{60}$$

The quantity $\bar{E}_{\text{int}}{}^m$ is the macroscopic field at cell m caused by the polarization of that cell itself. Hence, letting $-e\phi_{\text{int}}{}^m(\mathbf{r})\equiv e^{-i\mathbf{q}\cdot\mathbf{r}}V_{\text{int}}{}^m(\mathbf{r})$, we have

$$\begin{aligned}\bar{E}_{\text{int}}{}^m&=-\Delta^{-1}\int_{0,m}d^3r\,\nabla_\mu\phi_{\text{int}}{}^m(\mathbf{r})\\ &=-\Delta^{-1}\int_{A,m}dA_\mu\,\phi_{\text{int}}{}^m(\mathbf{r}),\end{aligned} \tag{61}$$

where μ denotes the projection in the direction of propagation of the wave $\mathbf{q}$. The second form of Eq. (61) has the advantage of requiring values of the integrand only at the surface of the unit cell. There, one is justified in using the dipole approximation for tightly bound electrons, and we can write

$$\phi_{\text{int}}{}^m(\mathbf{r})=\mathbf{p}\cdot\mathbf{r}/r^3, \tag{62}$$

where $\mathbf{p}$ is the dipole moment of the atom in cell m. The integral is then easily performed for cells of cubic symmetry and we get

$$\bar{E}_{\text{int}}{}^m=-\tfrac{4}{3}\pi\bar{P}^m. \tag{63}$$

Combining Eqs. (63) and (57) gives Lorentz' relationship between the local field and the macroscopic field in cases of cubic symmetry,

$$\bar{E}_{\mathrm{loc}}{}^{m}=\bar{E}^{m}+\tfrac{4}{3}\pi\bar{P}^{m}. \tag{64}$$

We now return to the induced electron density, Eq. (56), and, exactly as in Sec. III, we relate $\bar{n}^m$ to $\bar{P}^m$ and $V_{\mathrm{ext}}{}^m$ to $\bar{E}_{\mathrm{ext}}{}^m=\bar{E}_{\mathrm{loc}}{}^m$.
This gives the relationship

$$\bar{P}^{m}=N_0\alpha\bar{E}_{\mathrm{loc}}{}^{m}-N_0e^2\sum_{l'l}{}' F_{l'l}X_{l'l}{}^{\mu}e^{-i\mathbf{q}\cdot\mathbf{R}_m}$$
$$\times\langle lm|-e^{-1}V_{\mathrm{int}}{}^{m}|l'm\rangle\equiv N_0(\alpha-\alpha_{\mathrm{sp}})\bar{E}_{\mathrm{loc}}{}^{m}, \tag{65}$$

where

$$\alpha\equiv(e^2/m^2)\sum_{l'l}{}' F_{l'l}|P_{l'l}{}^{\mu}|^2\omega_{l'l}{}^{-2}. \tag{66}$$

We have introduced

$$P_{l'l}{}^{\mu}\equiv\langle l'm|-i\hbar\nabla_{\mu}|lm\rangle,$$

noted that $F_{ll}=0$, and used the well-known result

$$\mathbf{P}_{l'l}=im\omega_{l'l}\mathbf{X}_{l'l}. \tag{67}$$

The quantity $\alpha-\alpha_{\mathrm{sp}}$ is shown in Appendix B to be just the atomic polarizability of an isolated atom in an applied field. The quantity α_{sp} is the contribution to the polarizability that arises from the field caused by the self-consistent response of the electrons. We may call α_{sp} the self-polarization part of the polarizability.

Equations (64) and (65), together with the definition of the dielectric constant,

$$\bar{P}^{m}=(4\pi)^{-1}(\epsilon-1)\bar{E}^{m}, \tag{68}$$

are sufficient to obtain the desired result,

$$\epsilon-1=\frac{4\pi N_0(\alpha-\alpha_{\mathrm{sp}})}{1-\frac{4}{3}\pi N_0(\alpha-\alpha_{\mathrm{sp}})}. \tag{69}$$

Thus, the tight-binding limit in the semiclassical approximation does indeed lead to the Lorentz expression for the dielectric constant.

VII. CONCLUSIONS

In the semiclassical limit, the expression for the dielectric constant has been conveniently split into an acceleration term and an atomic term. The acceleration term has been shown to contain no local field corrections. Therefore, whenever the acceleration term dominates the dielectric constant, neglect of local field corrections is rigorously correct. Moreover, in the weak binding limit, the local field correction is of the same order in the weak potential as the atomic polarizability term, but the coefficient is much smaller (usually less than 5%) for most Fermi surfaces. However, peculiar cases must be examined individually. Therefore, in the core effective potential of Phillips and Kleinman, for example, when one wants to use the dielectric constant to write down the self-consistent Hartree potential,[3] neglect of local corrections usually introduces only a small error. It is also felt that the definition and physical interpretation of the local field given in Sec. III is generally useful in making qualitative estimates of the effect of local field corrections for various situations.

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APPENDIX A

Consider the quantity $f(\mathbf{r})$. We want to show that

$$\nabla_{\mathbf{R}}\bar{f}(\mathbf{R})=\langle\nabla_{\mathbf{r}}f(\mathbf{r})\rangle_{\mathrm{av}}, \tag{A1}$$

where the bar indicates an average taken over a unit cell. We use $\mathbf{R}$ to denote the macroscopic position variable locating the unit cell over which the average is taken. We start by Fourier-analyzing $f(\mathbf{r})$, yielding

$$f(\mathbf{r})=\sum_{\mathbf{q},\mathbf{K}}f(\mathbf{q},\mathbf{K})e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}}, \tag{A2}$$

and we again assume $f(\mathbf{q},\mathbf{K})=0$ unless $\mathbf{q}$ is so small that $e^{-i\mathbf{q}\cdot\mathbf{r}}$ is almost constant over a unit cell. If we first take the derivative of Eq. (A2) and then average, we get

$$\langle\nabla_{\mathbf{r}}f(\mathbf{r})\rangle_{\mathrm{av}}=\sum_{\mathbf{q},\mathbf{K}}-i(\mathbf{q}+\mathbf{K})f(\mathbf{q},\mathbf{K})\Delta^{-1}\int_0 d^3r\, e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}}$$
$$\approx\sum_{\mathbf{q}}-i\mathbf{q}f(\mathbf{q},0)e^{-i\mathbf{q}\cdot\mathbf{R}}. \tag{A3}$$

On the other hand, if we first average Eq. (A2), we get

$$\bar{f}(\mathbf{R})=\sum_{\mathbf{q},\mathbf{K}}f(\mathbf{q},\mathbf{K})\Delta^{-1}\int_0 d^3r\, e^{-i(\mathbf{q}+\mathbf{K})\cdot\mathbf{r}}$$
$$\approx\sum_{\mathbf{q}}f(\mathbf{q},0)e^{-i\mathbf{q}\cdot\mathbf{R}}. \tag{A4}$$

Taking the derivative of Eq. (A4) with respect to the macroscopic variable $\mathbf{R}$ yields Eq. (A3) directly. This proves Eq. (A1), as desired. In this proof we have actually carried out the averaging process, i.e., we evaluated both sides of Eq. (A1) and showed that they are equal. The usual method of proof is merely to transform one side of Eq. (A1) into the other without actually evaluating.

APPENDIX B

We wish to show that the expression $\alpha-\alpha_{\mathrm{sp}}$, defined in Eqs. (58) and (66), is indeed the atomic polarizability, with α_{sp} being the contribution due to self-polarization effects. Consider an isolated atom in an applied field. Then, the Wannier functions become atomic functions and

$$V(\mathbf{r})=V_0e^{-i\mathbf{q}\cdot\mathbf{r}}+V_{\mathrm{int}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{B1}$$

where $V_0e^{-i\mathbf{q}\cdot\mathbf{r}}$ is the applied potential and $V_{\text{int}}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}$ is the screening potential. Proceeding as before, we get

$$\langle l|\rho_1|l'\rangle=F_{l'l}\langle l|V|l'\rangle$$
$$\approx F_{l'l}e^{-i\mathbf{q}\cdot\mathbf{R}}[-i\mathbf{q}\cdot\mathbf{X}_{ll'}V_0+\langle l|V_{\text{int}}|l'\rangle], \quad \text{(B2)}$$

and

$$n(\mathbf{r})=\sum_{l'l}\psi_{l'}^*(\mathbf{r})\psi_l(\mathbf{r})\langle l|\rho_1|l'\rangle$$
$$=e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{l'l}\psi_{l'}^*(\mathbf{r})\psi_l(\mathbf{r})$$
$$\times e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R})}F_{l'l}[-i\mathbf{q}\cdot\mathbf{X}_{ll'}V_0+\langle l|V_{\text{int}}|l'\rangle]. \quad \text{(B3)}$$

Next, we average $n(\mathbf{r})$ to obtain

$$\bar{n}\approx e^{-i\mathbf{q}\cdot\mathbf{R}}i\Delta^{-1}\sum_{l'l}F_{l'l}\mathbf{q}\cdot\mathbf{X}_{ll'}$$
$$\times[-i\mathbf{q}\cdot\mathbf{X}_{ll'}V_0+\langle l|V_{\text{int}}|l'\rangle], \quad \text{(B4)}$$

where the bar here denotes an average taken over the region occupied by the atom, whose location is given by the macroscopic position variable $\mathbf{R}$. Finally, relating $\bar{n}$ to $\bar{P}$ and V_0 to $\bar{E}_0$ gives

$$p=\bar{P}\Delta=(e^2/m^2)\sum_{l'l}F_{l'l}|P_{l'l}^{\mu}|^2\omega_{l'l}^{-2}\bar{E}_0$$
$$-e^2\sum_{l'l}F_{l'l}X_{l'l}^{\mu}e^{-i\mathbf{q}\cdot\mathbf{R}}\langle l|-e^{-1}V_{\text{int}}|l'\rangle, \quad \text{(B5)}$$

where p is the dipole moment of the atom. Use was again made of Eq. (67).

By definition, the ratio of the dipole moment to the macroscopic applied field is just the polarizability. The first term in Eq. (B5) arises directly from the applied field, showing that

$$\alpha=(e^2/m^2)\sum_{l'l}F_{l'l}|P_{l'l}^{\mu}|^2\omega_{l'l}^{-2}. \quad \text{(B6)}$$

The second term arises from the field caused by the self-consistent response of the electrons, showing it to be a self-polarization effect. In our linear treatment, the matrix element of V_{int} must be proportional to $\bar{E}_0$ giving the desired result,

$$\alpha_{\text{sp}}\bar{E}_0=e^2\sum_{l'l}F_{l'l}X_{l'l}^{\mu}e^{-i\mathbf{q}\cdot\mathbf{R}}\langle l|-e^{-1}V_{\text{int}}|l'\rangle. \quad \text{(B7)}$$

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Optical Properties of the Silver and Cuprous Halides

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The exciton spectrum of AgI, CuI, CuBr, and CuCl is discussed and various peaks attributed to several coexisting crystal modifications. The shift of the peaks with alloy concentration in the pseudobinary systems formed with these compounds is reported and interpreted. The absorption and reflection spectra of these materials and their alloys for energies between the energy gap and 10 eV is reported and the structure attributed to transitions between regions of the valence band lying below the highest maximum and parts of the conduction band higher than the lowest minimum. These spectra are compared with the corresponding spectra of other zincblende- and wurtzite-like materials.

I. INTRODUCTION

THE silver and cuprous halides are members of a family of semiconductors which has received much attention: the semiconductors with four valence electrons per atom. Among these semiconductors are the elementary semiconductors of the fourth group of the periodic table (diamond, Si, Ge, and gray tin) which crystallize in the diamond lattice. The next members of the family are the so-called III-V semiconductors whose unit cell has one atom of the third group and one of the fifth group. Most of these semiconductors crystallize in the zincblende lattice at normal conditions, but a few (among those of high band gap and high melting point) crystallize in the wurtzite (AlN, GaN, and InN) and other more complicated structures (BAs, BN). The next members in the direction of increasing polarity are the II-VI compounds which crystallize ordinarily in the zincblende or the wurtzite structures. Some of these compounds may exist at room temperature in both forms, one of them metastable.

The intrinsic reflection and transmission spectra of all these semiconductors with zincblende structure exhibit a striking systematic similarity.[1–4] The lowest-energy direct absorption edge, due to transitions at $k=0$, shows a splitting which can be correlated with the spin-orbit splitting of the constituent atoms. The next absorption edge has been attributed to direct transitions at a point in the [111] direction of k space: This edge has a splitting which is approximately two-

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