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LOCAL FIELD EFFECTS ON THE STATIC DIELECTRIC
CONSTANT OF CRYSTALLINE SEMICONDUCTORS OR INSULATORS

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Résumé. — La correction de champ local est déterminée dans l’approximation de Hartree, à partir de deux méthodes opposées. La première consiste en une inversion analytique de la matrice diélectrique dans l’espace réciproque. Elle confirme les résultats de calculs numériques récents, montrant que la correction de champ local tend à réduire la constante diélectrique. La seconde traite ces effets dans l’espace réel en liaisons fortes, ce qui conduit à une formule de Lorentz-Lorenz. Dans cette limite il est démontré que, contrairement à ce qu’on pense habituellement, les effets de champ local tendent aussi à réduire ε. Une analyse numérique détaillée est effectuée pour les semiconducteurs covalents, montrant que cette correction augmente dans la séquence C, Si, Ge, Sn.

Abstract. — Local field effects are calculated in the R.P.A. approximation from two extreme points of view. The first consists of an analytical inversion of the dielectric matrix in reciprocal space. It confirms the results of recent numerical calculations, that local field effects tend to reduce the dielectric constant. The second treats these effects in real space in a tight-binding limit, thus leading to a Lorentz-Lorenz formula. In this limit it is shown, contrary to the usual belief, that local-field effects also tend to reduce ε. A detailed numerical analysis is performed in the case of purely covalent semiconductors, showing that the local field correction increases in the sequence C, Si, Ge, Sn.

1. Introduction. — There have been recently many theoretical calculations of local field effects on the static dielectric constant of semiconductors [1 to 9]. First principles calculations have concentrated on diamond which is by far the simplest element to consider. In this case all the recent works conclude that the local field correction reduces the dielectric constant. This is in contradiction with the early conclusion, based on the Lorentz-Lorenz formula [2], that local field effects should more or less decrease the dielectric constant.

From this point of view two extreme techniques have been used so far. The more classical one starts from non overlapping species and, using a dipolar approximation, leads to a Lorentz-Lorenz correction [2]. In this limit local field effects always tend to increase ε(0) with respect to the value deduced from the free-atom or molecule selfconsistent polarisabilities. This is in fact a calculation in real space using some sort of tight-binding limit. On the other hand all recent studies have been made in reciprocal space, where a dielectric matrix is calculated within a Hartree approximation. Inversion of this matrix then leads to the desired value of ε(0). In this way all calculations done on diamond conclude that local field effects tend to reduce the dielectric constant.

In this paper it will be shown in a simple manner that both types of results do in fact agree and that it is likely that local field effects when evaluated in a Hartree or R.P.A. approximation always tend to decrease ε(0) from its non selfconsistent value. For this, in the first part, local-field effects are determined in reciprocal space, from an analytical expansion of the inverse dielectric matrix. In the second part a real space formulation is used leading to a Lorentz-Lorenz formula. It is shown that the apparent contradiction between the two formulations is due to the fact that while the Lorentz-Lorenz correction tends to reduce the polarisability with respect to its non selfconsistent atomic value, it tends to increase it with respect to its selfconsistent one, which is the commonly adopted statement.

2. Local field effects in reciprocal space. — In this section, the dielectric constant will be calculated in reciprocal space. This requires an inversion of the q dependent dielectric matrix. Instead of doing this
numerically as many authors have done, we shall use an analytical expansion which shows easily that local field effects are likely to reduce $\varepsilon$ from its non selfconsistent value.

The first order response of a polarisable system to a static external perturbation is characterised by the dielectric matrix $\varepsilon(q, q')$ [1] which relates the $q$ Fourier component of the external potential to the $q'$ Fourier component of the total potential. Its general expression in the Hartree or R.P.A. approximation is

$$
\varepsilon(q, q') = \delta_{q,q'} + \frac{4}{V} \frac{v(q)}{\epsilon(q)} \sum_{k,k'} \times \frac{\langle k | e^{-i\alpha k} | k' \rangle}{E_{k'} - E_k} \langle k' | e^{i\alpha k'} | k \rangle.
$$

(1)

Here $\delta$ is the Kronecker symbol, $V$ the volume of the system, $\upsilon(q) = 4\pi q^2 \chi_k^2$ and $| k \rangle$ and $| k' \rangle$ are respectively valence and conduction band states of energies $E_k$ and $E_{k'}$. In a crystalline solid, from translational symmetry, one can show that this matrix factorizes, each block being of general form $E(q + G, q + G')$ where $G$ and $G'$ are reciprocal lattice vectors. The non selfconsistent dielectric constant will be defined as:

$$
ev_{\text{NC}} = \lim_{q \to 0} \varepsilon(q, q)
$$

(2)

while its selfconsistent value (including local field effects) is given by:

$$
ev = \lim_{q \to 0} \frac{1}{\varepsilon^{-1}(q, q)}
$$

(3)

$\varepsilon^{-1}$ being the inverse dielectric matrix.

Now, it is easily seen that a term like $\lim_{q \to 0} \varepsilon(q, q + G)$ diverges as $1/q$ while, in contrast $\lim_{q \to 0} \varepsilon(q + G, q)$ tends to zero as $q$. The correct method to estimate $\varepsilon$ is to use the following inversion formula

$$
ev = \varepsilon(0,0) - \sum_{G,G'} S(G,G') \varepsilon^{-1}(G',0)
$$

(4)

where both types of terms cancel out (the prime on the sum indicate that $G \neq 0$, $G' \neq 0$). Here $S(G,G')$ is the part of the dielectric matrix restricted to non zero $G$ and $G'$.

To analyse expression (4) in more detail let us consider systems where all valence states can be derived from a given set of orthonormal atomic or bonding orbitals, or even from both of them. This is now a quite commonly used approximation and describes very well the situation in many covalent and ionic solids [10 to 14]. In this case expression (1) can generally be written, retaining only intraatomic or intrabond terms:

$$
ev(q, q') = \delta_{q,q'} + \frac{4}{V} \frac{v(q)}{\Delta(q, q')} \sum_{\alpha,i} \langle \alpha_i | e^{-i(q-q') \alpha} | \alpha_i \rangle - \sum_{\alpha,i} \langle \alpha_i | e^{-i(q-q') \alpha} | \alpha_i \rangle - \sum_{\alpha,i} \langle \alpha_i | e^{i(q-q') \alpha} | \alpha_i \rangle.
$$

(5)

Here $\Delta(q, q')$ has the meaning of an average gap which should be some function of $q$ and $q'$ but is necessarily greater than the true gap. In (5) the summation is made over the atomic or bonding states $\alpha$, corresponding to the $i$th atom or bond. We have also used the fact that

$$
\sum_{k} \langle k | 0 | k \rangle = \sum_{\alpha,i} \langle \alpha_i | 0 | \alpha_i \rangle
$$

(6)

Turning now to $\varepsilon(q + G, q + G')$ one can first easily show that for cubic systems (5) leads to

$$
ev(0, 0) = 1 + \frac{16\pi}{3V \Delta(0, 0)} \sum_{\alpha,i} \langle \alpha_i | (r - r_{\alpha})^2 | \alpha_i \rangle
$$

(7)

where $r_{\alpha}$ is the average value of $r$ in state $\alpha_i$.

In the same way $\varepsilon(0, G)$ and $\varepsilon(G, 0)$ can be written:

$$
\varepsilon(0, G) = \lim_{q \to 0} -\frac{16\pi q}{Vq^2 \Delta(q, G)} \sum_{\alpha,i} \langle \alpha_i | e^{iG \alpha} (r - r_{\alpha}) | \alpha_i \rangle
$$

$$
\varepsilon(G, 0) = \lim_{q \to 0} +\frac{16\pi q}{VG^2 \Delta(G, q)} \sum_{\alpha,i} \langle \alpha_i | e^{-iG \alpha} (r - r_{\alpha}) | \alpha_i \rangle.
$$

(8)

It is clear that if the atomic or bonding states $| \alpha_i \rangle$ have an extension of the order of the Wigner and Seitz cell the product $\varepsilon(0, G) \varepsilon(G', 0)$ will decrease very rapidly with $| G |$.

Let us now examine a general element $\varepsilon(G, G')$ of the dielectric matrix, for $G$ and $G' \neq 0$. When $G \neq G'$, for the same reasons as before, $\varepsilon(G, G')$ will decrease rapidly. If $G = G'$ it will rapidly tend to unity. We shall
consider the case where all \( s(G, G') \) with \( G \neq G' \) are sufficiently small so that the inversion of \( s(G, G') \) can be made in power series of these elements. To the first significative order one then finds from (4)

\[
\varepsilon \approx \varepsilon(0, 0) - \frac{1}{12} \sum_\delta \frac{|\varepsilon(0, 0) - 1|^2}{1 + \frac{3}{|G|^2} \langle \varphi^2 \rangle \varepsilon(0, 0) - 1} \exp \left( - \frac{|G|^2 \langle \varphi^2 \rangle}{3} \right). \tag{10}
\]

The corresponding results are given in table I (\( \Delta \varepsilon_1/\varepsilon \)). They are of the usual order of magnitude reported in the literature [4 to 9]. To compare with the very detailed study by Brener [9], one can choose a case where \( \varepsilon(0, 0) = 3 \) which corresponds to one of his numerical values. The correction thus becomes equal to \( \Delta \varepsilon_1 = -0.2 \) which compares very well with his value for local field corrections. Our value for Si, i.e. 12.5 \( \% \) also compares very well with the result of ref. [7], i.e. 11 \( \% \).

The first corrective term to (9) can also be evaluated. It leads for \( \varepsilon \) to the following expression

\[
\varepsilon \approx \varepsilon(0, 0) - \sum_\delta \frac{\varepsilon(0, G)}{\varepsilon(G, G)} \left\{ \varepsilon(G, 0) - \sum_{G' \neq G} \frac{\varepsilon(G, G') \varepsilon(G', 0)}{\varepsilon(G', G')} \right\}. \tag{11}
\]

The corresponding correction is found to be negligible, of the order of 1 \( \% \) of \( \Delta \varepsilon_1 \).

3. **Local field effects in real space.** — We shall now determine the dielectric response directly in real space. This can be done simply only in a tight binding limit and we shall rederive the well known Lorentz-Lorenz formula which will be considered in detail for a simple system.

An externally applied static electric field \( \mathbf{E} \) induces in the system a change in electron density \( \delta \rho(r) \) which can be expressed as:

\[
\delta \rho(r) = 4 \text{Re} \sum_{k'k} \frac{\langle k' | W | k \rangle}{E_k - E_{k'}} \psi_k^*(r) \psi_k(r) \tag{12}
\]
\( \psi_{k}, \psi_{k'} \) being respectively valence and conduction band states of energies \( E_{k} \) and \( E_{k'} \); \( W(r) \) is the total potential, i.e. the sum of the bare perturbative potential \( U_b(r) = -E_0 \cdot r \) and the selfconsistent potential \( \delta U(r) \) given by:

\[
\delta U(r) = \int \frac{\delta \rho(r') \, \mathrm{d} \tau'}{|r - r'|}.
\]

To determine \( \epsilon \), one must evaluate the polarization \( \mathbf{P} \) defined as

\[
\mathbf{P} = -\frac{1}{V} \int \delta \rho(r) \, r \, \mathrm{d} \tau = \mathbf{\mathbf{\bar{e}}} \cdot \mathbf{E}.
\]

This defines the susceptibility tensor \( \mathbf{\chi} \) to which \( \mathbf{E} \) is related by:

\[
\mathbf{\mathbf{\bar{e}}} = 1 + 4 \pi \mathbf{\mathbf{\chi}}.
\]

From (12) this leads to

\[
\mathbf{P} = \frac{4}{V} \operatorname{Re} \sum_{k,k'} \frac{\langle k | r | k' \rangle \langle k' | W | k \rangle}{E_{k'} - E_{k}}.
\]

To go on further it is necessary to assume that both valence and conduction states of interest in (16) can be expressed from independent basis sets \( | \alpha_i \rangle \) and \( | \beta_j \rangle \) built from atomic or bond wave functions (i and j are the atomic or bond indices). Then \( \mathbf{P} \) is given by:

\[
\mathbf{P} = \frac{4}{V} \Delta \sum_{\alpha_i, \beta_j} \langle \alpha_i | r | \beta_j \rangle \langle \beta_j | W | \alpha_i \rangle.
\]

Here \( \Delta \) is the average energy gap. The unknown quantities in (17) are the terms \( \langle \beta_j | W | \alpha_i \rangle \) which must be determined in a self-consistent way. To do this let us write, using the definition of \( W \) together with (12) and (13)

\[
\langle \beta_j | W | \alpha_i \rangle = \langle \beta_j | U_b | \alpha_i \rangle - \frac{4}{\Delta} \operatorname{Re} \sum_{\alpha_i', \beta_j', \alpha_i, \beta_j} \langle \beta_j' | W | \alpha_i' \rangle \langle \alpha_i' | \beta_j' \rangle \langle \beta_j | W | \alpha_i \rangle.
\]

The sum over \( \beta' \) and \( \alpha' \) in (18) being carried out over conduction band and valence band states respectively and

\[
\langle \alpha_i' | \beta_j' | \alpha_i \beta_j \rangle = \iint \psi_{\alpha_i}^*(r) \psi_{\beta_j}^*(r) \psi_{\alpha_i'}^*(r') \psi_{\beta_j'}(r') \, \mathrm{d} \tau \, \mathrm{d} \tau'.
\]

To see clearly what happens let us now examine the simple case of a crystalline array of identical molecules for which the polarization is essentially due to a transition from the bonding ground state to an antibonding excited state. Ignoring intermolecular terms and remembering that in the long wavelength limit all \( \langle \beta_i | W | \alpha_i \rangle \) are equal one obtains:

\[
\langle \beta | W | \alpha \rangle = \frac{\langle \beta | U_b | \alpha \rangle}{1 + \frac{4}{\Delta} \sum_{i} \langle \alpha_{i} | \beta_{0} | \alpha_{i} \beta_{i} \rangle}
\]

where the index \( i \) has been dropped for the matrix elements. With this expression the dielectric tensor has only one non zero component \( \varepsilon_{xx} \) if \( x \) is the direction parallel to the axis of the molecules. With this, one obtains:

\[
\varepsilon_{xx} = 1 + \frac{4 \pi N \alpha_{\text{NSC}}}{1 + \frac{4}{\Delta} \sum_{i} \langle \alpha_{i} | \beta_{0} | \alpha_{i} \beta_{i} \rangle}
\]

Here \( \alpha_{\text{NSC}} \) is the non selfconsistent free molecule polarisability and \( N \) is the number of molecules per unit volume. To recover the classical form of the Lorentz-Lorenz formula, one must evaluate the lattice sum occurring in (21) using a dipole approximation
for terms \( i \neq 0 \). For a system with cubic symmetry this denominator \( D \) can be written

\[
D = 1 + \frac{4}{\Delta} \left\langle \alpha_0 \beta_0 | \alpha_0 \beta_0 \right\rangle - \frac{16 \pi}{3} \frac{N}{\Delta} \left| \left\langle x | x | \beta \right\rangle \right|^2 . \tag{22}
\]

This clearly allows us to rewrite (21) under the form:

\[
\varepsilon_{xx} = 1 + \frac{4 \pi N \alpha_{SC}}{1 - \frac{4 \pi}{3} N \alpha_{SC}} \alpha_{SC} = \frac{\alpha_{NSC}}{1 + \frac{4}{\Delta} \left\langle \alpha_0 \beta_0 | \alpha_0 \beta_0 \right\rangle} . \tag{23}
\]

This is the classical Lorentz-Lorenz formula [2] which proves that the total polarisability is increased with respect to its free molecule value \( \alpha_{SC} \). However notice that in (23) this free molecule value \( \alpha_{SC} \) is the selfconsistent one and is different from \( \alpha_{NSC} \). Thus (23) does not prove that \( \varepsilon \) is increased with respect to its non selfconsistent value \( 1 + 4 \pi N \alpha_{NSC} \). This clearly depends on the sign of the total sum \( \sum_i \left\langle \alpha_0 \beta_0 | \alpha_i \beta_i \right\rangle \) which we shall prove to be always positive.

For this we shall not use a dipolar expansion but instead work in reciprocal space where such lattice sums are evaluated most easily. One can show that:

\[
\sum_i \left\langle \alpha_0 \beta_0 | \alpha_i \beta_i \right\rangle = \frac{4 \pi}{\Omega} \sum_k \frac{\rho_k \rho_{-k}}{K^2} \tag{24}
\]

where \( K \) are reciprocal lattice vectors and \( \rho(r) \) is given by:

\[
\rho(r) = \psi_{sc}(r) \psi_{bc}(r) .
\]

As \( \rho(r) \) is real, the sum in (24) involves \( |\rho_K|^2 \) and is thus essentially positive. This shows that \( D \) is always greater than 1 and thus that local field effects, at least in this simple case, tend to reduce \( \varepsilon \) with respect to its non selfconsistent value. This is in agreement with the conclusion of section 2 and does not contradict the classical statement, it is in fact also decreased with respect to its non selfconsistent value. The contradiction is thus apparent, and this shows that some care must be taken when applying the Lorentz-Lorenz formula to actual systems.

4. Conclusion. — Local field effects in semiconductors or insulators have been calculated using two different methods. First, the dielectric matrix in reciprocal space has been inverted in an analytical expansion which is found to converge fairly rapidly in most cases. This leads to a simple direct confirmation of recent results showing that the dielectric constant is reduced with respect to its non selfconsistent value. Second local field corrections in the long wavelength limit have been evaluated in real space. In this limit one recovers a Lorentz-Lorenz formula. A careful examination shows that while \( \varepsilon \) is increased with respect to the value obtained from the selfconsistent free molecule or atom polarisability (which is the classical statement), it is in fact also decreased with respect to its non selfconsistent value. The contradiction is thus apparent, and this shows that some care must be taken when applying the Lorentz-Lorenz formula to actual systems.

Appendix. — To obtain \( \varepsilon \) in covalent systems one applies the external electric field \( E \) along a \( <111> \) direction. Within a bonding-antibonding description [10 to 14], there are now two types of matrix elements which occur in (18). The first one corresponds to the bonds oriented along the field direction (one per unit cell), the second one to the bonds along \( (111) \) directions (three equivalent per unit cell). Equation (18) then reduces to:

\[
\langle \beta^0 | W | \alpha^0 \rangle = \langle \beta^0 | U_b | \alpha^0 \rangle - \frac{4}{\Delta} \{ \langle \beta^0 | W | \alpha^0 \rangle \beta_0 + 3 \langle \beta^1 | W | \alpha^1 \rangle I_1 \}
\]

\[
\langle \beta^1 | W | \alpha^1 \rangle = \langle \beta^1 | U_b | \alpha^1 \rangle - \frac{4}{\Delta} \{ \langle \beta^0 | W | \alpha^0 \rangle I_1 + \langle \beta^1 | W | \alpha^1 \rangle (I_0 + 2 I_1) \} . \tag{A.1}
\]

Here the exponent 0 concerns the bond along the \( <111> \) direction the exponent 1 the three bonds along \( (111) \) directions. \( I_0 \) and \( I_1 \) are lattice sums.

\[
I_0 = \sum_i \langle \alpha_0 \beta_0 | \alpha_i \beta_i \rangle , \quad I_1 = \sum_i \langle \alpha_0 \beta_0 | \alpha_i \beta_i \rangle . \tag{A.2}
\]

Using the fact that \( U_b = - E \xi \) where \( \xi \) is the component of \( r \) along the \( <111> \) direction it is easy to show that

\[
\langle \beta^0 | W | \alpha^0 \rangle = \frac{\langle \beta^0 | U_b | \alpha^0 \rangle}{1 + \frac{4}{\Delta} (I_0 - I_1)}
\]
so that $E$ is found to be equal to:

$$
e = 1 + \frac{64 \pi \frac{\Omega}{3A} |\langle \beta^0 | \xi | \alpha^0 \rangle|^2}{1 + \frac{4}{A} (I_0 - I_1)} \quad \text{(A.3)}$$

To compare with the results of the previous section we choose $|\langle \beta^0 | \xi | \alpha^0 \rangle|^2$ such that, if $I_0$ and $I_1$ vanish one finds $\varepsilon$ equal to the same value $\varepsilon(0, 0)$ given in table I. In this way (A.3) can be written

$$
e = 1 + \frac{\varepsilon(0, 0) - 1}{1 + \frac{4}{A} (I_0 - I_1)} \quad \text{(A.4)}$$

The lattice sums $I_0$ and $I_1$ can be evaluated in reciprocal space as in (23), the convergence being quite rapid. The numerical results are given in table I ($\Delta \varepsilon_2/\varepsilon$).

References