

ON MICROSCOPICAL DERIVATION OF LORENTZ-LORENZ FORMULA.

E.G.Maksimov and I.I.Mazin

P.N.Lebedev Physical Institute, B-333, Moscow, USSR

(Received 12 June, 1978, by V.M.Agranovich)

Lorentz-Lorenz formula may be derived microscopically by the analytical inversion of the dielectric matrix (DM) in the limit of tightly bound electrons. Exchange and correlation effects are to be taken into account and atomic polarisability is to be defined correctly in terms of the atomic susceptibility instead of the polarization operator. A wrong definition was the origin of usual contradictions between microscopical calculations and classical formula. The inversion of the DM diminishes dielectric constant in comparison with the diagonal element of DM but this procedure takes into account only a part of the local field effects caused by rapidly oscillating fields. Another part is connected with exchange interaction and increases the diagonal element of DM in comparison with dielectric constant without any local field effects, hence all local field effects do increase the dielectric constant.

1. It is well known that the polarizability of the system of atoms or molecules may differ very much from the sum of polarizabilities of constituent particles, even when the wave functions of electrons on different atoms do not overlap. In classical electrodynamics such a phenomenon is usually described by Lorentz-Lorentz (LL) or Clausius-Mossotti formula for dielectric constant (DC) ¹:

$$\epsilon = 1 + 4\pi n \alpha / (1 - 4\pi n \alpha / 3) \quad (1)$$

Here α is the polarizability of a single atom, n is the number of atoms in the unit volume. The difference between $\epsilon - 1$ and $4\pi n \alpha$ is due to the atom interaction in the system and is called local field effects.

The dielectric constant without local field effects may be expressed as

$$\epsilon' = 1 + 4\pi n \alpha \quad (2)$$

Comparing (1) and (2) one can see that the local field corrections always lead to the increasing of DC within the framework of the classical electrodynamics.

We should mention here that even within the framework of classical electrodynamics an applicability of LL formula is rather limited: it deals only with crystals with the tetrahedral symmetry ², does not include spatial dispersion effects and takes into account only dipolar terms in the multipole expansion. The possibility of phenomenological generalisation of LL formula was

discussed in the review article by Agranovich ³.

An interest in microscopical aspects of local field effects has grown in the last years. It may have its origin in the fact that local field effects are of the considerable importance in lattice dynamics ⁴ and high-temperature superconductivity ⁵.

2. At present many papers are available which deal with a quantum-mechanical approach to the derivation of DC for insulators and the attempts to justify LL formula microscopically ⁶⁻¹⁴. The main idea known from 1960 is that the dielectric function in crystal is to be written as a matrix in the reciprocal lattice vectors K and K' , i.e. $\epsilon(q+K, q+K', \omega)$ and non-diagonal matrix elements ($K \neq K'$) play an important part in dielectric screening.

It was shown by Adler ⁶ and Wiser ⁷ that the macroscopical DC for small momenta q $\epsilon(q, \omega)$ may be expressed in terms of inverse dielectric matrix (DM) $\epsilon^{-1}(q+K, q+K', \omega)$ as follows

$$\epsilon^{-1}(q, \omega) = [\epsilon^{-1}(q+K, q+K', \omega)]_{K=K'=0} \quad (3)$$

The usual way for the derivation of DC is obtaining in some approximation the DM $\epsilon(q+K, q+K', \omega)$ and subsequent inverting it. Recently an effective method for such an inversion has been developed using Wannier representation for electron wave functions ^{15, 16}. The main part of the above-mentioned works ⁶⁻¹² was made within a simple random

phase approximation (RPA). Moreover, the diagonal matrix element was assumed to be identical to the DC without local field correction:

$$\epsilon(q+0, q+0, \omega) = 1 + 4\pi n \alpha(\omega) \quad (2')$$

where $\alpha(\omega)$ is the atomic polarizability.

The expression for the DC obtained in these papers by the inversion of the DM from formula (3) does not coincide in fact with the LL formula even in the limit of tightly-bound electrons. Moreover, this expression, as has been emphasized by Johnson¹², contrasts sharply with LL formula and diminishes the DC relative to $\epsilon(q+0, q+0, \omega)$ (see Eq. 4.15 of this work).

$$\epsilon_{macro}(q, \omega) < \epsilon(q+0, q+0, \omega)$$

RPA neglect completely exchange and correlation effects. It was supposed by Sinha et al¹¹ and Onodera¹⁰ that the situation with the microscopic derivation of the DC can be remedied by including exchange and correlation interactions. But they believed that Eq. (2') which connects the diagonal element of the DM with the atomic polarizability, would remain faithful. We shall show that the microscopic derivation of LL formula require both the including exchange and correlation factors and the correct determination of the atomic polarizability.

3. For the subsequent discussion let us display some computations related to the DM. We may write down an equation for DM in the rigid lattice as:

$$\epsilon(x, x') = \delta(x-x') - e^2 \int dx'' \mathcal{F}(x'', x') / |x-x''| \quad (4)$$

where $\mathcal{F}(x'', x')$ is the non-reducible polarization part of polarization operator:

$$\mathcal{F}(x, x') = - \int G(x, x_2) G(x_2, x) \times \Gamma(x_1, x_2, x') d^3x_1 d^3x_2 \quad (5)$$

$\Gamma(x_1, x_2, x_3)$ is the vertex function including all exchange and correlation terms.

In RPA $\Gamma(x_1, x_2, x_3)$ is simply the product of δ -functions:

$$\Gamma^{RPA}(x_1, x_2, x_3) = \delta(x_1-x_2) \delta(x_1-x_3) \quad (6)$$

Using Wannier representation we may perform Fourier transformation

$$\epsilon(q+k, q+k') = \delta_{kk'} - V(q+k) \sum_{\alpha\beta\gamma\delta} A_{\alpha\beta}^n(q+k) \mathcal{F}_{\alpha\beta\gamma\delta}^{nn'} A_{\gamma\delta}^{*n'}(q+k') \quad (7)$$

$$A_{\alpha\beta}^n(q+k) \mathcal{F}_{\alpha\beta\gamma\delta}^{nn'} A_{\gamma\delta}^{*n'}(q+k')$$

where we have introduced the following notations:

$$A_{\alpha\beta}^n = \int \rho_{\alpha}^*(z) e^{-i(q+k)z} \rho_{\beta}(z+R_n) d^3z \quad (8)$$

$$V(q+k) = 4\pi e^2 / |q+k|^2 \quad (9)$$

$\rho_{\alpha}(z+R_n)$ is the Wannier function of an electron in the zone α , centered in the cell with the coordinate R_n . $\mathcal{F}_{\alpha\beta\gamma\delta}(q, \omega)$ is the matrix element of the polarization operator with respect to Wannier functions.

The inversion of (7) gives:

$$\epsilon^{-1}(q+k, q+k', \omega) = \delta_{kk'} + V(q+k) \sum_{\alpha\beta\gamma\delta} A_{\alpha\beta}^n(q+k) \mathcal{S}_{\alpha\beta\gamma\delta}^{-1}(q, \omega) A_{\gamma\delta}^{*n'}(q+k') \quad (10)$$

where the matrix $\hat{\mathcal{S}}$ is defined by

$$\hat{\mathcal{S}} = \hat{\mathcal{F}}^{-1} - \hat{V} \quad (11)$$

the matrix \hat{V} is given by

$$V_{\alpha\beta\gamma\delta}^{nn'}(q) = - \sum_{\kappa} A_{\alpha\beta}^n(q+k) V_{\kappa}(q+k) A_{\gamma\delta}^{*n'}(q+k) \quad (12)$$

Since we are interested in the LL limit (we call the limit of non-overlapping atomic wave functions the "LL limit" because LL formula must exist just in this limit), we may suppose that $A_{\alpha\beta}^n = A_{\alpha\beta} \delta_{nn'}$. Therefore we can write the following relation 17:

$$\lim_{q \rightarrow 0} V_{\alpha\beta\gamma\delta}(q) = e^2 \int d^3z_1 d^3z_2 \times \rho_{\alpha}^*(z_1) \rho_{\beta}^*(z_2) \rho_{\gamma}(z_1) \rho_{\delta}(z_2) / (|z_1-z_2| + 8\pi f_{\alpha\beta} f_{\gamma\delta} / 3) \quad (13)$$

where $f_{\alpha\beta}$ are the matrix elements of the atomic dipole

$$f_{\alpha\beta} = e \int \rho_{\alpha}^*(z) z \rho_{\beta}(z) d^3z$$

Using the usual relation

$$\hat{\mathcal{F}}^{-1} = \hat{\mathcal{F}}_{RPA}^{-1} + V_{xc} \quad (14)$$

we see from Eqs. (11) and (13) that the matrix $\hat{\mathcal{S}}$ is given by

$$\hat{\mathcal{S}} = \hat{\mathcal{F}}_{RPA}^{-1} + V_{xc} - V_H - 8\pi f_{\alpha\beta} f_{\gamma\delta} / 3 \quad (15)$$

where V_{xc} is the operator of the exchange and correlation interaction. We have called the first term in (13) V_H because it represents simply Hartree interaction between electrons located in the same cell.

In the LL limit we may say that the first three terms in (14) are connected only with the properties of electrons in the same atom and may be expressed in terms of the atomic susceptibility function

$$\hat{\mathcal{F}}_{RPA}^{-1} + V_{xc} - V_H = \chi_{at}^{-1} \quad (16)$$

It is well known¹⁸ that the atomic susceptibility matrix $\chi_{\alpha\beta\gamma\delta}$ and the inverse matrix $\chi_{\alpha\beta\gamma\delta}^{-1}$ may be diagonalized with respect to transition indices $\mu = (\alpha, \beta)$ and $\mu' = (\gamma, \delta)$

$$\chi_{\mu\mu'}^{-1}(\omega) = \chi_{\mu}^{-1}(\omega) \delta_{\mu\mu'} \quad (17)$$

In such a representation the matrix has this very simple form:

$$S_{\mu\mu'} = \chi_{\mu}^{-1} \delta_{\mu\mu'} - 8\pi f_{\mu}^* f_{\mu'} / 3 \quad (18)$$

Then this matrix may be inverted very easily

$$S_{\mu\mu'}^{-1} = \chi_{\mu} \delta_{\mu\mu'} + \frac{8\pi \chi_{\mu} f_{\mu} f_{\mu'} \chi_{\mu'} / 3}{1 - 8\pi \sum_{\mu} \chi_{\mu} |f_{\mu}|^2 / 3} \quad (19)$$

Using Eq. (19) in Eq. (10) and taking into account the limit

$$\lim_{\omega \rightarrow 0} A_{\alpha\beta}(\omega) = f_{\alpha\beta} \quad (20)$$

we obtain for the diagonal matrix element of the inverse DM the following expression:

$$\lim_{\omega \rightarrow 0} \epsilon^{-1}(\omega, \omega, \omega) = 1 + \frac{4\pi n \sum_s \chi_s(\omega) |f_s|^2}{1 - 8\pi n \sum_s \chi_s |f_s|^2 / 3} \quad (21)$$

Using Eq. (3) for DC we obtain finally

$$\epsilon(\omega) = 1 - \frac{4\pi n \sum_s \chi_s(\omega) |f_s|^2}{1 - 4\pi n \sum_s \chi_s(\omega) |f_s|^2 / 3} \quad (22)$$

which is exactly the LL formula because the correct determination of the atomic polarizability is

$$d = - \sum_s \chi_s |f_s|^2 \quad (23)$$

4. It was seen that the correct microscopic derivation of the LL formula required only one assumption, namely Eq. (16). It means that the exchange and correlation interactions between electrons on different atoms must be ignored. It is not necessary to make any additional assumption about the specific form of these interactions.

Some difficulties with the LL formula in the preceding microscopic calculations 10-12,17 arose due to incorrect determination of the atomic polarizability in terms of the polarization operator $\mathcal{F}_{\mu\mu}$. Moreover as one can see

from Eqs. (16) and (23), the DC without local field corrections which is defined by Eq. (2) is not equal to the diagonal element of DM as was supposed in previous works 10,11. It is not strange therefore diminishing DC in comparison with the diagonal matrix element of $\epsilon(\omega, \omega, \omega)$ as a result of the inversion procedure, as has been noted by Johnson 12 and Lannoo 14.

In order to clear up these question we consider for simplicity the one-oscillator model 12. In this approximation we can write down the static DM in the LL limit

$$\epsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0) = 1 - V(\mathbf{q} + \mathbf{K}) A^*(\mathbf{q} + \mathbf{K}) \mathcal{F}(0) A(\mathbf{q} + \mathbf{K}') \quad (24)$$

Here $\mathcal{F}(0)$ is the polarization operator including exchange and correlation corrections. It may be written in the one-oscillator model as follows

$$\mathcal{F}(0) = \frac{\mathcal{F}_{RPA}(0)}{1 + V_{KC}(0) \mathcal{F}_{RPA}(0)} \quad (25)$$

Then the static microscopic DC may be written inverting the matrix (24)

$$\epsilon(\mathbf{q}, 0) = 1 - V(\mathbf{q}) A^*(\mathbf{q}) \mathcal{F}'(0) A(\mathbf{q}) \quad (26)$$

where $\mathcal{F}'(0)$ is the reducible polarization operator

$$\mathcal{F}' = \mathcal{F}(0) / [1 - \sum_{\mathbf{K}} A^*(\mathbf{q} + \mathbf{K}) V(\mathbf{q} + \mathbf{K}) A(\mathbf{q} + \mathbf{K}) \mathcal{F}(0)] \quad (27)$$

The sum in the denominator in Eq. (27) does not include the term with $\mathbf{K} = 0$.

It is clear from Eqs. (26), and (27) that the inversion procedure is no more than accounting Umklapp processes (or rapidly oscillating fields) with all momenta $\mathbf{q}' = \mathbf{q} + \mathbf{K}$. It is well known that in RPA there exists an inequality

$$\mathcal{F}_{RPA}(0) < 0 \quad (28)$$

It is easy to check that in RPA such condition does exist

$$\epsilon(\mathbf{q}, 0) < \epsilon(\mathbf{q} + 0, \mathbf{q} + 0, 0) \quad (29)$$

The correct polarization operator is very likely also to obey inequality (28). Then inequality (29) will remain faithful. Some interesting questions might arise for systems with negative DC 19 but we shall not touch upon this matter now.

It is easy to rewrite Eq. (25) in the usual LL form adding and subtracting the term $A^*(\mathbf{q}) \mathcal{F}(0) A(\mathbf{q})$ in the denominator and using Eq. (13).

Acknowledgements - the authors are grateful to Prs. L.V. Keldysh and D.A. Kirzhnits for fruitful discussions. Pr. V.L. Ginsburg and the participants of his seminar are also great acknowledged.

REFERENCES

1. SLATER J.C., Insulators, Semiconductors, Metals. McGraw-Hill, N.Y., 1967.
2. BORN M. & HUANG K., Dynamical Theory of Cristal Lattice, N.Y., 1954.
3. ARGANOVICH V.M. Usp. Fiz. Nauk 112, N 1, 143 (1974).
4. SINHA S.K., in: Proc. of Int. Conf. on Latt.Dyn., Flammarion, Paris (to be published).
5. The Problem of High Temperature Superconductivity, ed. Ginsburg V.L. & Kirshnits D.A., Moscow, 1977 (in Russian).
6. ADLER S., Phys. Rev., 126, 413 (1962).
7. WISER N., Phys. Rev., 119, 62 (1963).
8. GANDELMAN G. & ERMACHENKO V., Zh. Teor. Fiz., 45, 522 (1963).
9. VAN VECHTEN J.A. & MARTIN R.M., Phys. Rev. Let., 26, 1324 (1971).
10. ONODERA Y., Prog. Theor. Phys., 49, 37 (1973).
11. SINHA S.K., GUPTA R.P., PRICE P.L., Phys. Rev., B9, 2564 (1974).
12. JOHNSON D.L., Phys. Rev., B9, 4475 (1974).
13. HANKE W., SHAM L.J., Phys. Rev., B12, 4501 (1975).
14. LANOO M., J. de Phys., 38, 473 (1977).
15. SHAM L.J., in "Dynamical Properties of Solides", ed. by Horton C.K. & Maradudin A.A., North-Holland, Amst., 1974.
16. HANKE W. & BILTZ H., in Proc. Int. Symp. Neutron Inel. Scatt., Vien, 1972.
17. GIAQUINTA P.V., PARRINELLO M., TOSATTI E., TOSI M.P., J. Phys. C9, 2031 (1976).
18. RIBARSKY M.W. Phys. Rev., A12, 1739 (1975).
19. KIRZHNITS D.A. Usp. Fiz. Nauk, 119, 357 (1976).