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NOTES ON THE STATIC DIELECTRIC RESPONSE FUNCTION IN THE DENSITY FUNCTIONAL THEORY

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We discuss several aspects of the dielectric response theory application to the density functional theory. This field has been an unceasing source of confusion during several decades. The most frequent reasons for this confusion are (a) uncritical transfer of the results, especially regarding so-called local field corrections, obtained in many-body perturbation theory onto density functional theory, and (b) mixing up the statements true for the exact density functional theory with those applicable to the local density approximation only. In these notes we try to draw an appropriate lines between those theories. We also discuss a newly introduced (X. Gonze, Ph. Ghosez and R. W. Godby, *Phys. Rev. Lett.*, 74, 4035, 1995) "polarization + density functional" and show that within a given (e.g., local density) approximation to the exchange-correlation energy the Gonze *et al.* approach is exactly equivalent to the conventional one.

Keywords: Periodic boundary conditions; Kohn Sham theorem; polarization; density functional theory

Even now, 30 years after the discovery of the density functional theory (DFT)[1] there is still considerable confusion about applicability of DFT to static dielectric response[2]. On the one hand, there is seemingly no room for questioning the validity of the DFT in this respect: The Hohenberg-Kohn theorem, which is the basis of DFT, is a mathematical theorem, rigorously proven, that states that the total energy of the ground state of a many-electron system is a unique functional of its electronic density, and the density-density response function, defined as

$$\chi(\mathbf{r}, \mathbf{r}') = \delta^2 E / \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}'),$$

is also a unique functional of the electronic density. Surprisingly, this simple theorem is not readily digested by everybody. The reasons for confusion are several: First, one commonly confuses the exact DFT with its local, approximate version (LDA). As we shall discuss below, mixing up these two notions is much more dangerous when dealing with dielectric response than with the total energy itself. Second, to have this theorem satisfied, one has to take into account properly exchange-correlations to the dielectric susceptibility – and be aware that those corrections are functionally different in DFT, and, say in the many-body perturbation theory or in the Fermi-liquid theory (needless to say that all observable quantity are the same in any of these theories). Third, the notorious failure of LDA-DFT to produce the correct band gap (well understood by now, thanks to seminal works of Levy and Perdew[4] and Sham and Schlüter[5]) combined with the conventional wisdom that the dielectric gap determines the response, forces ingenuous researchers to question the formal applicability of the DFT to response functions calculations. Finally, in the last decades accurate LDA-DFT calculations of the dielectric constant of semiconductors have been performed[6], which were usually in error by 10–15%. Incredible success of the LDA calculations of structural properties (a few percent) made people infer indirectly that similar accuracy is attainable in other ground-state properties calculations. When it turned out to be not true, a suspicion rose that something may be principally wrong with the approach (in reality, of course, 10–15% accuracy is excellent for such a simple approximation as LDA). In particular, the Hohenberg-Kohn theorem itself has been questioned[2]. The goal of the current notes is not to produce a new physical result but to help, especially newcomers in the field, to avoid confusion and misleading of incorrect claims spread around in the literature.

One of the sources of confusion is the fact that exchange-correlation local field (XCLF) corrections are formally different in all three theoretical approaches to the dielectric response of many-electron systems. The most traditional one is the many-body perturbation theory, sometimes referred to as Green function theory. In this theory one-electron excitations are poles of the Green function, $G^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ determined by the Dyson eq. (3),

$$G^{-1}(\mathbf{r}, \mathbf{r}', \omega) = G_0^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \Sigma(\mathbf{r}, \mathbf{r}', \omega)$$

where Σ is the self-energy operator, and $G^{-1}(\mathbf{r}, \mathbf{r}', \omega)$ is the Green function of free electrons. An alternative form for the Dyson equation is

$$H_0(\mathbf{r})\psi_n(\mathbf{r}, E_n) + \int \Sigma(\mathbf{r}, \mathbf{r}', E_n)\psi_n(\mathbf{r}', E_n) = E_n\psi_n(\mathbf{r}, E_n), \qquad (1)$$

where H_0 is the one-electron Hamiltonian, $\psi_n(\mathbf{r}, E_n)$ is the Green function amplitude and E_n is the corresponding pole. E_n are in general complex. In the random phase approximation the dielectric susceptibility of the system can be written in terms of the bare polarization operator as

$$\chi^{GF}_{RPA}(1,2) = [1 - V_C(1-3)\Pi^{GF}_0(3,4)]^{-1}\Pi^{GF}_0(4,2),$$

where we introduced superscript GF for the Green functions theory, and integration over the space coordinates is implicitly implied. Here 1, 2, etc. are short for $\mathbf{r}_1, \mathbf{r}_2$, etc. Π_0 is the bare polarization operator. Symbolically one can write this equation as

$$\chi^{GF}_{RPA} = \frac{\Pi^{GF}_0}{1 - V_C\Pi^{GF}_0}, \tag{2}$$

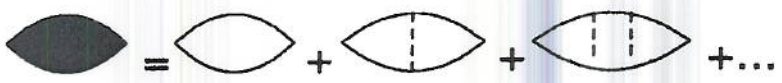
and we shall use such notation throughout the paper, when unambiguous. Going beyond RPA demands replacing Π^{GF}_0 by renormalized (full irreducible) polarization operator Π^{GF}. The XCLF, as introduced by Hubbard in 1958[7], assumes that Π^{GF} can be approximately written as

$$\Pi^{GF} \approx \Pi^{GF}_0/(1 - I\,\Pi^{GF}_0), \tag{3}$$

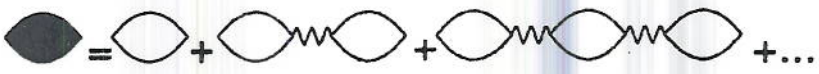
where exchange-correlation interaction $I(\mathbf{r}, \mathbf{r}')$ is negative (as well as Π^{GF}_0), and thus the total susceptibility is enhanced compared to RPA:

$$\chi \approx \frac{\Pi^{GF}_0}{1 - (V_C + I)\Pi^{GF}_0} = \frac{\chi^{GF}_{RPA}}{1 - I\chi^{GF}_{RPA}}. \tag{4}$$

An important fact is that the difference between Π^{GF} and Π^{GF}_0 comes first of all from exchange processes, namely



In semiconductors, the exchange interaction remains long-ranged. In other words, when this series is approximated by eq. 3,



the corresponding effective interaction I (wavy line) diverges in reciprocal space as $1/q^2$. As we shall see below, it is not the case in LDA.

Formula (4) looks very similar to the expression for the susceptibility in the Fermi-liquid theory

$$\chi = \frac{\chi^{\mathrm{FL}}_{\mathrm{RPA}}}{1 - f\chi^{\mathrm{FL}}_{\mathrm{RPA}}}. \tag{5}$$

However, while the left-hand sides of eqs. 4 and 5 are the same, $\chi^{\mathrm{FL}}_{\mathrm{RPA}}$ differs from $\chi^{\mathrm{GF}}_{\mathrm{RPA}}$, as it usually defined in the many-body theory, in the sense that it is calculated with exact one-electron excitation spectrum, given by the poles of the full Green function (1), while $\chi^{\mathrm{GF}}_{\mathrm{RPA}}$ assumes bare Green functions. For instance, in the theory of the homogeneous electron gas $\chi^{\mathrm{GF}}_{\mathrm{RPA}}$ is just the Lindhardt susceptibility. However, in practical calculations for semiconductors, for instance in the GW approximation, it is common to call "RPA" susceptibility the quantity calculated with fully renormalized one-electron spectrum, that is, $\chi^{\mathrm{FL}}_{\mathrm{RPA}}$. Correspondingly, effective interaction $f(\mathbf{r},\mathbf{r}')$, the effective Landau interaction, is the analog of Coulomb + Hubbard interaction in the Hubbard approximation.

The most common way to calculate the dielectric function is related to the density functional theory. To refresh readers' memory, let us recall the basic equation of this theory:

$$H_{\mathrm{DFT}}(\mathbf{r})\varphi_n(\mathbf{r}) \equiv H_0(\mathbf{r})\varphi_n(\mathbf{r}) + V_{\mathrm{KS}}\varphi_n(\mathbf{r}') = \varepsilon_n\varphi_n(\mathbf{r}),$$

where the wave functions φ and the (real) eigenvalues ε are for a fictitious system of non-interacting fermions with the same density as the electronic system in question. The above equation is a tool to find this spectrum, and the Kohn-Sham potential V_{KS} is defined as

$$V_{\mathrm{KS}}(\mathbf{r}) = \frac{\delta E_{\mathrm{int}}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}.$$

E_{int} is a unique functional of the total density, and the total energy of the electronic system is, by definition, $\Sigma_{\varepsilon<\mu}\langle\varphi_i|-\frac{\nabla^2}{2m}|\varphi_i\rangle + E_{\mathrm{int}}[\rho(\mathbf{r})]$, where μ is the chemical potential. Since the dielectric susceptibility can be defined entirely in terms of the total energy and total density,

$$\chi(\mathbf{r},\mathbf{r}') = -\frac{\delta E_{\mathrm{tot}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}, \tag{6}$$

it is also a unique density functional. Unlike the Green functions theory, DFT allows a formally exact expression for χ, which follows directly from eq. 6 and looks similar to the *approximate* eq. 4 in the Green functions theory:

$$\chi = \frac{\chi_{\mathrm{RPA}}^{\mathrm{DFT}}}{1 - I_{xc}\chi_{\mathrm{RPA}}^{\mathrm{DFT}}}, \tag{7}$$

where now by definition

$$I_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} = \frac{\delta V_{xc}[\rho](\mathbf{r})}{\delta\rho(\mathbf{r}')}.$$

There is principal difference between I_{xc} behavior in LDA and exact DFT: In the former, $I_{xc}(\mathbf{r}, \mathbf{r}') \propto \delta(\mathbf{r} - \mathbf{r}')$, while in the latter $I_{xc}(\mathbf{r}, \mathbf{r}')$ may be of arbitrary long range. A good example (which was communicated to the authors by O. Gunnarsson) is exact DFT for an insulator: adding one electron to arbitrary large insulator induces a uniform shift of the exchange-correlation potential for the whole system (so-called "density-derivative discontinuity"[4, 5], thus making $I_{xc}(\mathbf{r}, \mathbf{r}')$ of infinite range. Since the density-derivative discontinuity is always non-zero (because of the exchange-correlation part of kinetic energy, see Ref. [4], that means that in the exact DFT $I_{xc}(\mathbf{q})$ diverges at $q \to 0$ as $\delta(q)$. Nevertheless, the magnitude of the divergency may be arbitrary small. In fact, it appears that the DFT expression (7), if the spacial dependence is properly dealt with, yields good results (with 10–15% accuracy) even in LDA[6]. Again, it is instructive to compare the long-distance behavior of I_{xc} in GF theory, in LDA and in the exact DFT: in GF theory I_{xc} diverges, in insulators, at $q \to 0$ as $1/q^2$; this statement is not necesserily true in exact DFT, where the most divergent term is just a δ-function and nothing can be said rigorously about the next terms. Finally, in LDA I_{xc} remains constant at $q \to 0$[1].

The spatial dependence is rather important. Proper treatment of the spacial dependence includes Umklapp processes,

$$1/\varepsilon(q) = [\varepsilon_{\mathbf{q}+G,\mathbf{q}+G'}]_{00}^{-1} \tag{8}$$

$$\varepsilon_{\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}'}^{-1} = \delta_{GG'} + V_C \cdot \Pi_0^{\mathrm{DFT}} \cdot [\delta_{GG'} - (V_C + I_{xc})\Pi]^{-1}$$

[1] One can hear occasionally statements that I_{xc}^{DFT} should diverge as $1/q^2$ at small q's; we are not aware of any proof of this statement which would not indirectly use an unproven parallel with I_{xc}^{GF}.

where $V_C(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')=4\pi e^2\delta_{GG'}/|\mathbf{q}+\mathbf{G}|^2$, and I_{xc} is the Fourier transform of $I_{xc}(\mathbf{r},\mathbf{r}')$, and the tensor dot-products are taken in the right-hand side. All terms here which originate from $G, G' \neq 0$ are called "local field corrections". An elegant approach which is mathematically equivalent with eqs. 8, and is often called "the Sternheimer equation", avoids using polarization operators explicitly, but instead deals directly with the change of the density (see, e.g. Ref. [8], Eqs. 12–16:)

$$\delta\rho(\mathbf{q}+\mathbf{G}) = 4 \sum_{\mathbf{k},n\in occ} \langle \psi_{n\mathbf{k}} | e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}} P_c | \delta\psi_{n\mathbf{k}+\mathbf{q}} \rangle \tag{9}$$

$$(\varepsilon_{n\mathbf{k}} - H_{\mathrm{DFT}}) | \delta\psi_{n\mathbf{k}+\mathbf{q}} \rangle = P_c \delta H_{\mathrm{DFT}} | \psi_{n\mathbf{k}} \rangle,$$

where P_c is the projector operator on the conduction (unoccupied) bands. These equations, are formally equivalent to eqs. 8 and thus are exact within the DFT. Furthermore, if one uses the same (approximate) exchange-correlation energy functional, for example LDA, both sets of eqs. (8) and (9) should yield the same result.

Much of confusion was raised by the fact that the Hohenberg-Kohn theorem applies to the *total* electron density. That is, upon applying a long wave ($q \to 0$) perturbation, the total energy depends not only on the *periodic* part of the density change, $\Sigma_{G\neq 0}\delta\rho(\mathbf{q}+\mathbf{G})$, but also on the long wave part, $\delta\rho(\mathbf{q}+0)$. Despite this fact, neither eq. 8 nor eq. 9 demand supercell calculations with periodicity $1/q$. The reason is that the original, unperturbed system, which is periodic, bears all information (in linear regime) about the properties of the system, perturbed by any external field (as long as it weak enough), including long-range perturbation. It was claimed recently by Gonze *et al.*[2] that eqs. 9 are incomplete *because they do not treat the long-wave part of the density properly*. This is of course a fallacy. Interestingly, trying to overcome non-existent incorrectness of eqs. 9, Gonze *et al.* derived another equation, but failed to realized that it was mathematically equivalent to eqs. 9. This is worth elaborating.

Gonze *et al.* suggested in Ref. [2] to use a functional of two functions: the periodic electron density, $\rho_{\mathrm{per}} = \Sigma_{G\neq 0}\rho(\mathbf{q}+\mathbf{G})e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}$, and macroscopic polarization $\mathbf{P}(\mathbf{q})$. The latter is uniquely related to the macroscopic density perturbation, $\rho_{\mathrm{mac}} = \rho(\mathbf{q})e^{i\mathbf{q}\mathbf{r}} \approx i(\mathbf{q}\mathbf{r})\rho(\mathbf{q})$ for $q \to 0$, so $\mathbf{P}$ and ρ_p together uniquely define the total density and therefore the total energy. Obviously, one has full freedom to chose with which variables to work, periodic density plus macroscopic density, or periodic density plus macroscopic polarization. Having chosen the second scheme, Gonze *et al.* derived equations

where instead of the change of the total exchange correlation potential in δH_{DFT} they used only periodic part of this potential. Their final expression corresponded to substitution of $P_c \delta V_{xc}^{\mathrm{tot}} |\psi_{nk}\rangle$ in eqs. 9 by

$$P_c \delta V_{xc}^{\mathrm{per}} |\psi_{nk}\rangle + \left[\frac{\delta^2 E_{xc}}{\delta \mathbf{P}^2} \delta \mathbf{P} + \sum_{\mathbf{G} \neq 0} \frac{\delta^2 E_{xc}}{\delta \mathbf{P} \delta \rho_G(\mathbf{r})} \delta \rho_{\mathbf{G}}(\mathbf{r}) \right] P_c \mathbf{r} |\psi_{nk}\rangle. \qquad (10)$$

In fact, Gonze *et al.* claimed that previous LDA calculations of the dielectric response in semiconductors were incorrect, because they had used eqs. 9 instead of eq. 10. One can easily show, however, that the two sets of equations are formally equivalent: From the definition of I_{xc} it follows that $(\delta^2 E_{xc}/\delta \mathbf{P}^2)\delta \mathbf{P} = \mathbf{q} I_{xc}(\mathbf{q}, \mathbf{q}) \delta \rho(\mathbf{q})$, and $[\delta^2 E_{xc}/\delta \mathbf{P} \delta \rho(\mathbf{q} + \mathbf{G})] \delta \rho(\mathbf{q} + \mathbf{G}) = \mathbf{q} I_{xc} \times (\mathbf{q}, \mathbf{q} + \mathbf{G}) \delta \rho(\mathbf{q} + \mathbf{G})$. One can now notice that the part of the eqs. 9 which depends on the macroscopic component of the exchange-correlation potential, $\delta V_{xc}^{\mathrm{mac}}$, is nothing else but

$$P_c \delta V_{xc}^{\mathrm{mac}}(\mathbf{r}) |\psi_{nk}\rangle = P_c \sum_{\mathbf{G}} \mathbf{e}^{i\mathbf{q}\mathbf{r}} \mathbf{I}_{xc}(\mathbf{q}, \mathbf{q} + \mathbf{G}) \delta \rho(\mathbf{q} + \mathbf{G}) |\psi_{nk}\rangle,$$

which is the same as the second term in eq. 10. Not surprisingly, polarization + density functional of Gonze *et al.* appears to be equivalent to the original Hohenberg-Kohn functional. An unfortunate consequence of this fact is that the hope that density-polarization functional of Gonze *et al.* can remedy the above-mention deficiency of LDA, namely the local character of the interaction $I_{xc}(\mathbf{r}, \mathbf{r}')$, is futile. New, more advanced approximations to the density functional are needed to improve the results. It is possible, although not guaranteed, that these approximations will be easier to deal with in the density-polarization formulation than in the total-density formulation. Promising routes are the generalized density approximation, much advanced lately, and truly non-local functionals like the weighted-density approximation. In this regard, a recent study by Dal Corso *et al.*[9], where a sizable improvement over LDA was found for the dielectric constant of silicon, provided that calculations are done at the same (experimental) lattice parameter.

References

[1] Hohenberg, P. and Kohn, W. (1964). *Phys. Rev.*, **136**, B864; Kohn, W. and Sham, L. J. (1965). *Phys. Rev.*, **140**, A1133.
[2] Gonze, X., Ghosez, Ph. and Godby, R. W. (1995). *Phys. Rev. Lett.*, **74**, 4035 [mtrlth/9501006].
[3] Abrikosov, A. A., Gorkov, L. P. and Dzyaloshinski, I. E. Methods of quantum field theory in statistical physics (Dover, New York, 1975).

[4] Levy, M. and Perdew, J. P. (1983). *Phys. Rev. Lett.*, **51**, 1884.
[5] Sham, L. J. and Schlüter, D. (1983). *Phys. Rev. Lett.*, **51**, 1888.
[6] Baroni, S. and Resta, R. (1986). *Phys. Rev.*, B33, 7017; Gianozzi, P., de Gironcoli, S., Pavone, P. and Baroni, S. (1991). *Phys. Rev.*, B43, 7233, and other.
[7] Hubbard, J. (1958). *Proc. R. Soc. A*, **243**, 336.
[8] Gianozzi, P., de Gironcoli, S., Pavone, P. and Baroni, S. (1991). *Phys. Rev.*, B43, 7233.
[9] Dal Corso, A., Baroni, S. and Resta, R. (1994). *Phys. Rev.*, B49, 5323.