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Fluctuation attraction in condensed matter: A nonlocal functional approach

K. Rapcewicz and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, and Materials Science Center,  
Cornell University, Ithaca, New York 14853-2501

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By exploiting the analogy between the correlation charge surrounding an electron in an interacting electron gas and the electronic charge localized about nuclei in condensed atomic systems, we are led to a functional approach which partially preserves the nonlocality of fluctuations in an inhomogeneous system. In this way, the van der Waals and Axilrod-Teller interactions are determined solely from the fluctuation properties of the electron gas. The approach gives further insight into the local-density approximation.

At the level of electrons and nuclei, the Hamiltonian for a simple dense elemental system of volume  $\Omega$  can be written

$$\hat{H} = \hat{T}_n + \hat{T}_e + \frac{1}{2} \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2 v_c(\mathbf{r}_1 - \mathbf{r}_2) [\hat{\rho}_{ee}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 2Z_A \hat{\rho}_e^{(1)}(\mathbf{r}_1) \hat{\rho}_n^{(1)}(\mathbf{r}_2) + Z_A^2 \hat{\rho}_{nn}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)] \tag{1}$$

where  $v_c(\mathbf{r}) = e^2/r$  is the Coulomb interaction,  $Z_A$  is the atomic number, and  $\hat{T}_a$  the kinetic energies. In (1)  $\hat{\rho}_a^{(1)}$  and  $\hat{\rho}_{a,\beta}^{(1)}$  are, respectively, the one- and two-particle density operators. A ground-state trace of (1) over electron states established in a volume  $\Omega$  then defines within an adiabatic approximation a problem in nuclear coordinates; a common approximation to it in the tightly bound molecular systems considered here is

$$\hat{H}_n = \hat{T}_n + \frac{1}{2} \int_{\Omega} d^3r_1 \int_{\Omega} d^3r_2 \phi_n(\mathbf{r}_1 - \mathbf{r}_2) \hat{\rho}_{nn}^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \tag{2}$$

where  $\phi(\mathbf{r})$  is a Lennard-Jones or similar interaction. From the atomic viewpoint, the long-range part of this interaction arises from fluctuations in the electronic charge localized about all nuclei. From the statistical point of view, however, the interactions originate with fluctuations in the density  $\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle$  condensed about each nucleus. Within the adiabatic approximation, this density may also be written as  $\langle \hat{\rho}_e^{(1)}(\mathbf{r}_1) \hat{\rho}_n^{(1)}(\mathbf{r}_2) \rangle / \langle \hat{\rho}_n^{(1)}(\mathbf{r}_2) \rangle$ , which is just the conditional probability density of finding an electron at  $\mathbf{r}_1$  given a nucleus at  $\mathbf{r}_2$ . In this context the more fundamental quantity is therefore the two-particle correlation function; the electronic charge density of atomic physics can be viewed in the condensed state as response or correlation charge density. The diagrammatic representation of this interpretation is shown in Fig. 1(a)(i).

We now turn to the opposite extreme, namely, an interacting electron gas in a uniform compensating background of density  $\rho$ . The two-particle density for normal

states is then translationally invariant, i.e.,

$$\rho_{ee}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_e^2 g(\mathbf{r}_1 - \mathbf{r}_2), \tag{3}$$

and this replaces

$$\rho_{ee}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho_e^{(1)}(\mathbf{r}_1) \rho_e^{(1)}(\mathbf{r}_2) g(\mathbf{r}_1, \mathbf{r}_2), \tag{4}$$

which appears in a ground-state trace of (1) for the electronically inhomogeneous case. It follows that the equivalent to  $\langle \hat{\rho}_e^{(1)}(\mathbf{r}_1) \hat{\rho}_n^{(1)}(\mathbf{r}_2) \rangle / \langle \hat{\rho}_n^{(1)}(\mathbf{r}_2) \rangle$  is  $\rho_e g(\mathbf{r}_1 - \mathbf{r}_2)$  which possesses an exchange-correlation hole outside of which reside weak correlation maxima. Another electron, acting

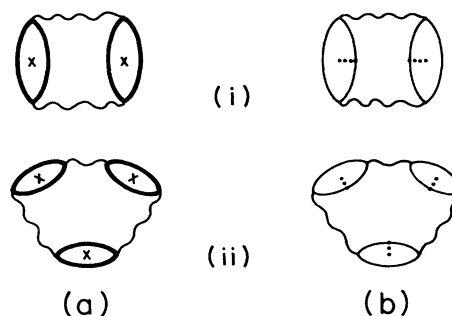


FIG. 1. Fluctuation-based interaction between (a)(i) two and (ii) three atoms; the (b)(i) two- and (ii) three-electron equivalent of (a). The wavy lines represent the bare Coulomb interaction in (a) and the dynamically screened interaction in (b). The dotted lines represent the static screened interaction.

as a test charge, sees the entire arrangement with a static *screened* interaction which decays very quickly except for weak Friedel oscillations.

The question of dispersion interactions arising from *fluctuations* in this otherwise static *response* charge can now be raised as it was for the atomic case. Indeed, the standard argument<sup>1</sup> together with dimensional analysis leads to the expectation<sup>2</sup> of an attractive pair interaction  $\sim -\hbar\omega_p(r_s/r)^6$  in the absence of damping (see below). This accounts for the diagram in Fig. 1(b)(i); note the evident similarity to Fig. 1(a)(i). Given this similarity, we turn now to an approach to density-functional theory which attempts to include the major manifestations of these fluctuations. Common to most applications of density-functional theories is a local-density approximation (LDA) in which the functional for the inhomogeneous system is obtained by replacing the uniform density in the homogeneous electron-gas energy density by the spatially varying density at a chosen local point (a strict LDA) or some function of it (a weighted density counter-

part). A tacit assumption is that important nonlocal fluctuation effects inherent in the original problem can be restored merely by allowing the density to take on an appropriate spatial dependence. Though often satisfactory for ground-state and cohesive properties, it is known that the LDA, when applied to atomic systems, does not correctly reproduce effective long-range interactions.<sup>3</sup> We shall show that there is an approach that *is* capable of including such fluctuations, which links to the viewpoint advanced above, and which, when applied to atom pairs, does recover the van der Waals interaction.

The lowest order fluctuational term shown in Fig. 1(b)(i) leads to a static van der Waals *attraction* between electrons.<sup>2,4</sup> Its physical significance is greater than its formal order in perturbation theory might imply<sup>5</sup> because the internal screened Coulomb lines are dynamical<sup>2</sup> and therefore *incompletely* screened in the high-frequency, small momentum limit. The form of the effective attraction between electrons<sup>6</sup> at  $\mathbf{r}_1$  and  $\mathbf{r}_2$  is

$$\begin{aligned} \phi(\mathbf{r}_1 - \mathbf{r}_2) = & -\frac{i\hbar}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int \frac{d^3q_1}{(2\pi)^3} \int \frac{d^3q_2}{(2\pi)^3} \exp[-i(\mathbf{q}_1 - \mathbf{q}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)] \frac{1}{\hbar^2} S(\mathbf{q}_2 - \mathbf{q}_1, 0, \mathbf{q}_1, \omega, -\mathbf{q}_2, -\omega) \\ & \times \frac{v_c(\mathbf{q}_1)}{\epsilon(\mathbf{q}_1, \omega)} \frac{v_c(\mathbf{q}_2 - \mathbf{q}_1)}{\epsilon(\mathbf{q}_2 - \mathbf{q}_1, 0)} \frac{1}{\hbar^2} S(\mathbf{q}_1 - \mathbf{q}_2, 0, -\mathbf{q}_1, -\omega, \mathbf{q}_2, \omega) \\ & \times \frac{v_c(\mathbf{q}_2)}{\epsilon(\mathbf{q}_2, -\omega)} \frac{v_c(\mathbf{q}_1 - \mathbf{q}_2)}{\epsilon(\mathbf{q}_1 - \mathbf{q}_2, 0)}, \end{aligned} \quad (5)$$

where  $S(\mathbf{q}_1, \omega_1, \mathbf{q}_2, \omega_2, \mathbf{q}_3, \omega_3)$  is the three-point function of the electron gas. The inclusion of the Lindhard dielectric function  $\epsilon(q, \omega)$  approximately incorporates screening effects.

In approaching this diagram in the inhomogeneous case, static screening arguments lead us to expect that the fluctuations of interest will be largely confined to a local screening length for an electron at  $\mathbf{r}_1$  (or  $\mathbf{r}_2$ ). If the density varies over a distance large compared to such screening lengths, it is reasonable to assume that static screening and associated fluctuations occur at the *local density* of the electron at  $\mathbf{r}_1$  (or  $\mathbf{r}_2$ ). These fluctuations occur at high frequencies where the random-phase approximation screened interaction arises from the exchange of plasmons. This exchange, however, can be viewed as taking place in an equivalent *homogeneous* electron system of density  $\rho_{\text{eff}}$  which is determined by noting that the emphasis here is on the energetics, and especially the ground-state energy of (1). Thus, because the form taken by the requisite  $\langle \hat{\rho}_{ee}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rangle$  is given by (4) and because the pair distribution functions are close to unity except at small relative separations, it follows from (3) that the effective density should be chosen as  $\rho_{\text{eff}} = [\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)]^{1/2}$ . Consequently, the required *average* plasmon frequency is

$$\omega_p(\mathbf{r}_1, \mathbf{r}_2) = [\omega_p(\mathbf{r}_1)\omega_p(\mathbf{r}_2)]^{1/2},$$

where  $\omega_p(\mathbf{r}) = [4\pi\rho^{(1)}(\mathbf{r})e^2/m]^{1/2}$  is the local plasmon

frequency.

In the limit of high frequencies and small momenta, the three-point function<sup>6</sup> reduces to

$$S(\mathbf{q}_1 - \mathbf{q}_2, 0, -\mathbf{q}_1, -\omega, \mathbf{q}_2, \omega; \mathbf{r}) = -i \frac{k_F(\mathbf{r})}{\pi^2} \frac{\mathbf{q}_1 \cdot \mathbf{q}_2}{\omega^2}, \quad (6)$$

where  $k_F(\mathbf{r}) = [3\pi^2\rho^{(1)}(\mathbf{r})]^{1/3}$  is the local Fermi wave vector; correspondingly, the dielectric function is given by the plasmon pole approximation<sup>7</sup> with plasmon frequency  $\omega_p(\mathbf{r}_1, \mathbf{r}_2)$ . In addition, the static screened Coulomb interaction is given within the Thomas-Fermi approximation by  $k_{\text{TF}}(\mathbf{r}) = [4e^2k_F(\mathbf{r})/\pi a_0]^{1/2}$ . With these *separately local* approximations, the effective interaction obtained from (5), and now appropriate to the inhomogeneous context, is

$$\begin{aligned} \phi[\mathbf{r}_1 - \mathbf{r}_2, \rho^{(1)}(\mathbf{r}_1), \rho^{(1)}(\mathbf{r}_2)] \\ = -\frac{3}{4} \hbar \left( \frac{e^2}{m} \right)^2 \frac{1}{[\omega_p(\mathbf{r}_1, \mathbf{r}_2)]^3 |\mathbf{r}_1 - \mathbf{r}_2|^6}. \end{aligned} \quad (7)$$

A more detailed calculation<sup>4</sup> introduces a weak logarithmic correction to (7) whose effect in the asymptotic region is, however, marginal.

The approximations leading to (7) can be applied more generally to higher center interactions. Figure 1(b)(ii), for example, shows the three-body equivalent of Fig. 1(b)(i). For electrons at  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$ , the asymptotic form of this interaction is

$$U_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -\frac{C_{123}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)[3 \cos(\theta_1)\cos(\theta_2)\cos(\theta_3) + 1]}{\mathbf{r}_{12}^3 \mathbf{r}_{13}^3 \mathbf{r}_{23}^3}, \quad (8)$$

where the  $\theta_i$  are the interior angles of the triangle formed by the three vectors  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$  with sides  $r_{ij}$ , and

$$C_{123}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{3}{2} \hbar \left( \frac{e^2}{m} \right)^3 \frac{1}{\omega_p(\mathbf{r}_1, \mathbf{r}_2) \omega_p(\mathbf{r}_2, \mathbf{r}_3) \omega_p(\mathbf{r}_3, \mathbf{r}_1)} \times \frac{[\omega_p(\mathbf{r}_1, \mathbf{r}_2) + \omega_p(\mathbf{r}_2, \mathbf{r}_3) + \omega_p(\mathbf{r}_3, \mathbf{r}_1)]}{[\omega_p(\mathbf{r}_1, \mathbf{r}_2) + \omega_p(\mathbf{r}_2, \mathbf{r}_3)][\omega_p(\mathbf{r}_2, \mathbf{r}_3) + \omega_p(\mathbf{r}_3, \mathbf{r}_1)]} \frac{1}{[\omega_p(\mathbf{r}_1, \mathbf{r}_2) + \omega_p(\mathbf{r}_3, \mathbf{r}_1)]}. \quad (9)$$

This interaction is immediately recognized as taking the Axilrod-Teller<sup>8</sup> form.

Comparison of (7) and of (8) and (9), with the standard perturbative expression for interatomic interactions,<sup>1,9</sup> reveals a striking identity. In the fluctuational sense, each electron and its attendant screening cloud behaves as an “atom” with a single excitation frequency, namely the appropriate  $\omega_p$ . This reinforces the analogy made between the correlation charge about an electron and the electronic charge condensed about a nucleus, and it leads us to conjecture that this identification will generalize to all multielectron interactions. These results and the identifications made with atomic physics are also valid in the homogeneous limit.

We test (7) by determining the effective interaction between two identical atoms separated by a distance  $\mathbf{R}$  and each with electron density  $\rho_a^{(1)}(\mathbf{r})$  centered on its nucleus. From (5), this is

$$\Phi(\mathbf{R}) = \int d^3r_1 \int d^3r_2 \phi[\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}, \rho_a^{(1)}(\mathbf{r}_1), \rho_a^{(1)}(\mathbf{r}_2)] \times \rho_a^{(1)}(\mathbf{r}_1) \rho_a^{(1)}(\mathbf{r}_2) \quad (10)$$

and in the large  $\mathbf{R}$  limit, we find from (7) and (10) the dipole-dipole attraction

$$\Phi(\mathbf{R}) = -\frac{C_{dd}}{R^6}, \quad (11)$$

which gives the required power-law dependency;  $C_{dd}$  is the dispersion coefficient (in a.u., with energy in rydbergs).

In the derivation of (7), we have assumed that plasmons can be exchanged between  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ; however, if the local wave vector introduced by Langreth and Mehl<sup>10</sup> (namely,  $q(\mathbf{r}) = |\nabla \log[k_{TF}(\mathbf{r})]|$  a quantity characterizing the rate of density variations) is actually larger than the local plasmon cutoff  $q_c(r) = k_{TF}(r)/\sqrt{3}$  at either  $\mathbf{r}_1$  or  $\mathbf{r}_2$ , then the plasmons will be Landau damped and no fluctuating multipole interaction can occur. Therefore the cutoff  $\Theta(q_c(\mathbf{r}_1) - q(\mathbf{r}_1))\Theta(q_c(\mathbf{r}_2) - q(\mathbf{r}_2))$  implicit in (11) is also included in the calculation of the dispersion coefficient  $C_{dd}$  listed in Table I and compared there with the experimental  $C_{dd}$  for noble-gas atoms<sup>11</sup> [spherically averaged double-zeta wave functions<sup>12</sup> are used for the required atomic electron densities  $\rho_a^{(1)}(\mathbf{r})$ ]. The agreement is seen to be reasonably good; also, it is equally good for unlike atoms [e.g., Ne-Kr,  $C_{dd}(\text{theor}) = 61.6$  while  $C_{dd}(\text{expt}) = 54.5$  a.u.].

The Axilrod-Teller triple-dipole interaction between atoms is obtained using the same arguments, but starting with (8) and (9). Table I also compares the theoretically determined Axilrod-Teller dispersion coefficient  $C_{ddd}$  with the literature values.<sup>11</sup> The level of agreement again highlights the difficulty of strictly local approaches<sup>3</sup>

which generally fail to reproduce the correct power-law dependence of the three-particle interactions.<sup>13</sup> Thus the determination of both the van der Waals and Axilrod-Teller interactions from *fluctuation properties* of the electron gas appears to stand in some contrast to the predictions of the standard LDA approaches.

The search for alternate functionals or improvements to existing functionals has been hitherto carried out largely within homogeneous systems; it has resulted in a continuous improvement of the *average* treatment of fluctuations occurring in homogeneous systems, although it is well known that it neglects effects of a long-range character such as interactions between fluctuations occurring in regions of different density. In terms of a *momentum-space* expansion for the ground-state energy density at  $\mathbf{r}$ , the LDA treats every diagram in perturbation theory on an equal footing, as if the physical process were occurring in an electron gas whose *uniform* density is set at the value  $\rho^{(1)}(\mathbf{r})$ . Thus fluctuations separated in space and occurring at different densities can be included in such an approximation, but only insofar as the density in these two regions can be taken to be  $\rho^{(1)}(\mathbf{r})$ . To go beyond this it is necessary to be sensitive to the role of each diagram in the inhomogeneous context.

To assist in the understanding of this role, we define a diagram to be irreducible with respect to the interaction if it cannot be divided into subdiagrams by cutting only *bare* interaction lines. As an example, consider the expansion for the polarization propagator; a diagram in this expansion that cannot be so divided is one that involves the interchange of particles between the external vertices and therefore possesses an exchange character; see, e.g., Fig. 2(a). Diagrams that *can* be divided into subdiagrams are of the following two types: (i) correlation diagrams in which the external vertices are found in different subdiagrams—the particles interact with one another at a distance [see, e.g., Fig. 2(b)]; and (ii) those in which the two external vertices are found within a single subdiagram, and which may therefore be termed *reducible* exchange diagrams, see, e.g., Fig. 2(c). The key physical

TABLE I. Dispersion energy coefficients,  $C_{dd}$  and  $C_{ddd}$ , in a.u., for the noble-gas atoms. The first entry is the calculated value. In parentheses are the literature values based on atomic data (e.g., Ref. 11).

	$C_{dd}$	$C_{ddd}$
Xe	595 (537)	12771 (10570)
Kr	286 (261)	3847 (3157)
Ar	143 (131)	1362 (1051)
Ne	13.3 (12.6)	26.5 (23.7)
He	4.2 (2.91)	6.5 (2.94)

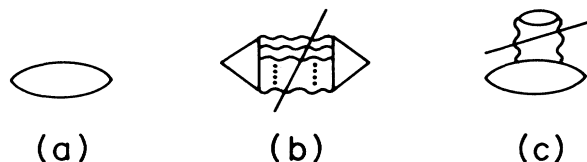


FIG. 2. Diagrams contributing to the polarization propagator; (a) interaction-irreducible exchange diagram, (b) correlation diagram, (c) interaction-reducible exchange diagram. The wavy lines represent *bare* interactions.

point is that the long-range nature of the bare interaction means that the interaction irreducible subdiagrams in the correlation diagram, Fig. 2(b), *can* be at different densities. In consequence it appears that in the treatment of fluctuations by the LDA and its variants, the correlation diagrams are the ones most seriously misrepresented.

The concept of interaction irreducibility enables us to *selectively* make the local approximation on just the interaction reducible diagrams which correspond to the multipole sequence in the real-space expansion of quantities of interest (energy, polarization propagator, etc.). In this case the effective density  $\rho_{\text{eff}}$  obtained in a manner as suggested above determines an appropriate plasmon fre-

quency for each dynamic screened interaction line. The effects of spatial variations of the density which have their greatest impact on processes involving the exchange of plasmons can be incorporated by including the Landau damping of the plasmons using, e.g., the prescription of Langreth and Mehl.<sup>10</sup> As demonstrated, this approach provides an approximate means of treating the nonlocal effects of fluctuations in an inhomogeneous system.

If fluctuating multipole interactions in inhomogeneous systems are to be correctly described by a nonlocal density functional approach, it is essential to draw a qualitative distinction between physical processes that are essentially local and those whose character derives from fluctuations in spatially separated regions of *different* density. The approach we have presented incorporates this distinction, leads to the correct long-range fluctuating dipole interactions between atoms, and can be simply extended to a spin dependent version.<sup>14</sup> Dimensionality is also important: The two-dimensional fluctuation-based attraction appears to go as  $-r_s^3/r^{9/2}$  at long range because of the crucially different plasmon dispersion relation.

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<sup>1</sup>Y. Barash and V. Ginzburg, Usp. Fiz. Nauk. **143**, 345 (1984) [Sov. Phys. Usp. **27**, 467 (1984)].

<sup>2</sup>A. Maggs and N. W. Ashcroft, Phys. Rev. Lett. **59**, 113 (1987).

<sup>3</sup>R. Gordon and Y. Kim, J. Chem. Phys. **56**, 3122 (1972); E. Lieb and W. Thirring, Phys. Rev. A **34**, 40 (1986).

<sup>4</sup>D. Langreth and S. Vosko, Phys. Rev. Lett. **59**, 497 (1987).

<sup>5</sup>M. Rasolt and D. Geldart, Phys. Rev. Lett. **35**, 234 (1975).

<sup>6</sup>R. Goldstein, A. Parola, and A. Smith, J. Chem. Phys. **91**, 1842 (1989); see also N. W. Ashcroft, Philos. Trans. R. Soc. London, Ser. A **334**, 407 (1991).

<sup>7</sup>A. Fetter and J. Walecka, *Quantum Theory of Many-Particle*

*Systems* (McGraw-Hill, New York, 1971).

<sup>8</sup>B. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

<sup>9</sup>A. Dalgarno and A. Davison, Adv. At. Mol. Opt. Phys. **2**, 1 (1966).

<sup>10</sup>D. Langreth and M. Mehl, Phys. Rev. Lett. **47**, 446 (1981); see also D. Langreth, Adv. Quantum Chem. **21**, 175 (1990).

<sup>11</sup>R. Bell and A. Kingston, Proc. Phys. Soc. London **88**, 901 (1966).

<sup>12</sup>E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

<sup>13</sup>Y. Kim, Phys. Rev. A **11**, 796 (1975).

<sup>14</sup>K. Rapcewicz and N. W. Ashcroft (unpublished).