van der Waals Interactions in Density-Functional Theory

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We present a framework for long-range density-functional theory which is valid for interactions between isolated fragments of matter at large separation. The van der Waals coefficients for interactions between a large number of pairs of atoms are calculated and compared to available first-principles calculations. The success in this test case shows a way of extending density-functional theory calculations with local or semilocal approximations to include van der Waals forces.

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The spectacular success of the local-density approximation (LDA) [1,2] to density-functional theory (DFT) [3] is well known. It fails, however, to describe interactions at long range, such as van der Waals interactions (vdW) [4]. The right asymptotic dependences of interaction potentials on separation are neither obtained within the LDA, nor in semilocal approximations, such as gradient corrected approximations [5–8], lately in wide use.

To restore the vdW interactions in DFT methods, we have used an approach which ties together several previous ideas where local or semilocal approximations are applied in various ways [9–12]. This approximation has proved to be successful in the simple case of two interacting atoms and seems to be a good starting point for the theory of atomic and surface physics potentials. The possibility to obtain van der Waals constants for interaction between two atoms and between an atom or a molecule and a metal surface in a general and simple way will be very useful, e.g., for obtaining accurate interaction potentials to use in simulations.

van der Waals interactions result from density fluctuations in regions separated in space. These are not properly accounted for in the LDA or in semilocal approximations. It has been shown [10,13] that for the interaction between two small but distant charge perturbations in a uniform electron gas they are described through the limiting behavior [14] of the linear response kernel K_{xc} expressing the exchange-correlation energy of a slightly nonuniform system [1],

$$E_{\mathrm{xc}} = \int d^3r_1 \int d^3r_2 K_{\mathrm{xc}}(\mathbf{r}_1,\mathbf{r}_2)\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2), \qquad (1)$$

where δn is the deviation in charge density from a uniform system. As one often wants to go beyond linear response by extrapolation of this expression, a key issue in density-functional theory has always been how to approximate the "uniform" density n_{eff} of the medium in which K_{xc} is defined, in terms of $n(\mathbf{r}_1)$ and $n(\mathbf{r}_2)$. Rapcewicz and Ashcroft (RA) [10] have suggested that one take $n_{\mathrm{eff}} = \sqrt{n(\mathbf{r}_1)n(\mathbf{r}_2)}$ and obtained in the asymptotic limit of large separation the effective long-range electron interaction ($\hbar = 1$ here and elsewhere in the article)

$$\phi_{\mathrm{RA}}(\mathbf{r}_1,\mathbf{r}_2) \to -\frac{3e^4}{4m^2}\frac{1}{\omega_p^3(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{r}_1 - \mathbf{r}_2|^6}, \qquad (2)$$

where they define the plasma frequency in terms of the effective density, $\omega_p = \sqrt{4\pi e^2 n_{\mathrm{eff}}/m}$. This contribution comes from the lowest-order perturbation-theoretic fluctuation term, representing plasmons being scattered off the potential caused by a density gradient, exchanging between points $\mathbf{r}_1$ and $\mathbf{r}_2$ in the effective medium.

If one wishes to create a density-functional theory that is valid in both the uniform gas and separate atom limits one must have a form that is viable and physically motivated in both limits. We show here that such a situation exists if we choose a different effective density to be used in K_{xc} in Eq. (1) and hence by implication in the expression for ω_p in Eq. (2). Our choice of effective density is

$$n_{\mathrm{eff}} = \left[\sqrt{n(\mathbf{r}_1)n(\mathbf{r}_2)}\left(\sqrt{n(\mathbf{r}_1)} + \sqrt{n(\mathbf{r}_2)}\right)\right]^{2/3}. \qquad (3)$$

We also use the total fragment density instead of δn in the isolated fragment limit, following other works in the field [6,7,10]. We then get the effective long-range electron interaction

$$\phi(\mathbf{r}_1,\mathbf{r}_2) \to -\frac{3e^4}{2m^2} \times \frac{1}{\omega_p(\mathbf{r}_1)\omega_p(\mathbf{r}_2)[\omega_p(\mathbf{r}_1) + \omega_p(\mathbf{r}_2)]|\mathbf{r}_1 - \mathbf{r}_2|^6}, \qquad (4)$$

where $\omega_p(\mathbf{r}_i) = \sqrt{4\pi e^2 n(\mathbf{r}_i)/m}$ is the local plasma frequency at the position of electron i. It is suggestive that with the identification $\omega_A = \omega_p(\mathbf{r}_1)$, $\omega_B = \omega_p(\mathbf{r}_2)$, the expression above is identical in form to the London expression for the vdW interaction between two atoms A and B at separation R, for the case where only one excitation frequency $\omega_{A/B}$ needs to be considered for each atom [15,16],

$$E_{\mathrm{vdW}}^{\mathrm{London}} = -\frac{3e^4}{2m^2}\frac{Z_A Z_B}{\omega_A\omega_B(\omega_A + \omega_B)}\frac{1}{R^6}. \qquad (5)$$

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Even more important is the observation that when Eq. (4) is integrated over $\mathbf{r}_1$ and $\mathbf{r}_2$ to obtain the correlation energy between two widely separated pieces of matter with volumes V_1 and V_2, one finds that one can express the long-range interaction as

$$E_{\mathrm{xc}}^{l\text{-}r} = -\frac{3}{\pi}\int_0^\infty du \int_{V_1} d^3 r_1 \int_{V_2} d^3 r_2 \, \frac{\chi_1(iu)\chi_2(iu)}{|\mathbf{r}_1 - \mathbf{r}_2|^6} \,, \tag{6}$$

where the coordinate r_i is restricted to the volume V_i. Here $\chi(\omega)$ is the electric susceptibility or polarization response P of a uniform electron gas at density $n(\mathbf{r})$ to a spatially constant applied electric field,

$$\chi(\omega) = \frac{1}{4\pi}\left[1 - \frac{1}{\epsilon(\omega)}\right] = \frac{1}{4\pi}\,\frac{\omega_p^2}{-\omega^2 + \omega_p^2} \,, \tag{7}$$

where $\epsilon(\omega)$ is the electron gas dielectric function at zero wave vector, $\epsilon(\omega) = 1 - \omega_p^2/\omega^2$. For two atoms widely separated by a distance R, Eq. (6) gives $E = -C_6/R^6$, where

$$C_6 = -\frac{3}{\pi}\int_0^\infty du \, \alpha_1(iu)\alpha_2(iu) \tag{8}$$

and

$$\alpha_i(\omega) = \int d^3 r \, \chi_i(\omega) \,. \tag{9}$$

Equation (8) is the standard expression [16] for C_6 in terms of the atomic polarizabilities α_i. The essence of the approximation is that the atomic polarizabilities are calculated in a local approximation, where the response function χ, giving the polarization per unit volume of a uniform electron gas, is integrated over the atom.

A number of types of local approximations have been suggested [11,12] for different response functions in order to obtain the van der Waals interaction. Here we introduce one [Eq. (9)] which is also not only highly physically motivated, but which we show to give reasonable results for wide classes of atomic systems. The fact that we have found a theory that not only does this, but also gives the correct kernel for small deviations from the uniform electron gas limit, holds promise that in the future a density-functional theory at intermediate ranges can be developed.

So far we have essentially a zero wave vector theory, which needs a cutoff. In the limit of two small distant disturbances in an electron gas, this cutoff occurs physically because the long-range interaction is propagated by plasmons, which become highly damped for $q \sim \omega_p/v_F = k_{FT}/\sqrt{3}$, where they meet the electron-hole continuum. In a full finite q theory such as done in this limit by Langreth and Vosko [9], this cutoff occurs smoothly and naturally, with their function Z_c falling off rapidly when q becomes of this order. RA implemented the cutoff in a real space form, using the Langreth-Mehl (LM) [6] expression $q = |\nabla n|/6n$ as a measure of the local wave vector, and cutting off the integrals when this became equal to ω_p/v_F, where $v_F = k_F/m = (3\pi^2 n)^{1/3}/m$ is the local Fermi velocity. In the limit of widely separated atoms a cutoff to our zero q theory is also necessary. Physically this can be seen by considering our expression (9) for the atomic polarizabilities. In the spirit of local approximations, it is reasonable to suppose as we have done that the interior portions of the atom polarize in roughly the same way as a uniform electron gas at the same local density. However, this is not true in the outer tails of the wave function, where the length scale l_d for density change is much shorter than the electron gas screening length l_s. In this case it should be a much better approximation to suppose that these parts of the atom do not respond at all to an applied field. The crossover should come when the length l_d measuring the fractional rate of change (with respect to distance) of the local Fermi wave vector k_F is of the order of the electron gas screening length. We use $l_d = 1/q$ with q determined by the LM formula above, and the local value of v_F/ω_p for l_s. In this manner we obtain a cutoff criterion that is exactly the same as that introduced by RA. Thus, although the mechanisms are different, the cutoff is the same for the limit both of separated atoms and of distant disturbances in an electron gas.

We have calculated the frequency-dependent polarizability for a number of atoms using Eq. (9) and found good agreement with available first-principles calculations (see Tables I and II).

When integration over the complex frequency in Eq. (6) is carried out, and the χ_i are expressed using the atomic charge densities, the long-range interaction between the two separated fragments of matter becomes

TABLE I. Atomic polarizabilities $\alpha(iu)$ (in atomic units). Results from Eq. (9) in left columns and first-principles results from Ref. [17] in right columns. (u in Ry units.)

u	Ne		Na$^+$		Ar		K$^+$		Kr	
0	2.83	2.97	1.15	1.08	14.17	12.15	6.55	5.60	22.27	17.55
1	2.09	2.29	1.01	0.94	5.80	7.22	3.91	4.45	7.56	9.78
2	1.42	1.55	0.81	0.81	3.10	3.64	2.36	2.77	3.71	4.59
4	0.67	0.74	0.47	0.54	1.35	1.28	1.08	1.15	1.69	1.48
6	0.40	0.47	0.34	0.34	0.81	0.61	0.61	0.54	0.94	0.61
8	0.27	0.27	0.27	0.27	0.47	0.27	0.40	0.34	0.67	0.27
10	0.20	0.20	0.20	0.20	0.34	0.13	0.27	0.20	0.47	0.13

TABLE II. Atomic polarizabilities $\alpha(iu)$ (in atomic units). Results from Eq. (9) in left columns and first-principles results from Ref. [18] in right columns. (u in Ry units.)

u	H		He	
0.01	4.84	4.50	2.07	1.38
0.53	2.79	3.20	1.65	1.28
1.07	1.41	1.76	1.12	1.06
1.79	0.72	0.88	0.71	0.77
2.21	0.52	0.63	0.57	0.63
3.19	0.29	0.34	0.37	0.42
4.32	0.17	0.19	0.24	0.27
6.30	0.08	0.10	0.14	0.15
8.56	0.05	0.05	0.08	0.09
10.21	0.03	0.04	0.06	0.07

$$E_{\mathrm{xc}}^{l\text{-}r} = \frac{6e}{4(4\pi)^{3/2} m^{1/2}} \int_{V_1} d^3 r_1 \times \int_{V_2} d^3 r_2 \, \frac{\sqrt{n_1(\mathbf{r}_1) n_2(\mathbf{r}_2)}}{\sqrt{n_1(\mathbf{r}_1)} + \sqrt{n_2(\mathbf{r}_2)}} \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6}, \qquad (10)$$

where $n(\mathbf{r}_i)$ is the charge density of fragment i. The vdW constants C_6 for the interaction between a large number of different atoms and also for hydrogen molecules, calculated using this expression, are displayed in Fig. 1. Numerical values of the coefficients are also presented in Figs. 2 and 3 and in Table III. The cutoff discussed above has been applied to the integrals in Eq. (10), and in determining the cutoff we have accounted for spin polarization when present. The atomic charge densities have been extracted from available Roothaan-Hartree-Fock wave functions with Slater basis sets [19–21].

Our theory is crude in the sense that the results in some cases are sensitive to the cutoff. Nevertheless, our results are good over wide classes of atoms. Our work also explains why RA's results for several rare gas atoms are as good as they are. Unlike the previous work our theory provides a physically correct form for the density-functional in the separated fragment limit. We believe it will provide the framework in which future finite wave vector theories will have to be discussed.

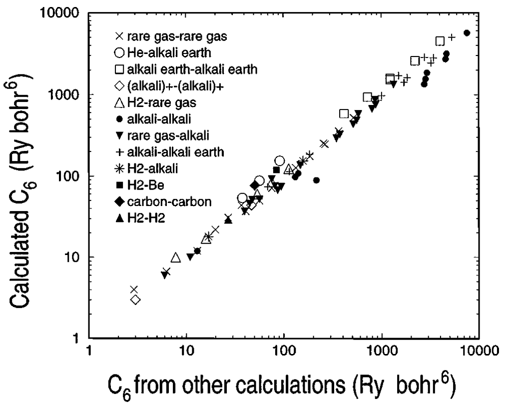

FIG. 1. van der Waals coefficients C_6 (in Ry atomic units) calculated from Eq. (9), plotted against corresponding values from first-principles calculations.

	He	Ne	Ar	Kr	Xe	H_2
He	4 (3)	7 (6)	22 (20)	31 (27)	44 (37)	10 (8)
Ne		12 (12)	37 (41)	50 (57)	71 (76)	17 (16)
Ar			126 (134)	175 (187)	253 (258)	60 (54)
Kr				245 (266)	356 (368)	84 (76)
Xe					520 (522)	123 (114)
H	6 (6)	10 (11)	37 (40)	52 (57)	76 (82)	18 (17)
Li	46 (82)	67 (88)	292 (350)	434 (518)	669 (808)	154 (159)
Na	51 (48)	74 (95)	325 (378)	486 (562)	750 (876)	
K	92 (76)	136 (150)	580 (584)	862 (866)	1327 (1338)	

FIG. 2. Values of C_6 coefficients plotted in Fig. 1. In parentheses the corresponding values from Refs. [22] and [25] (H_2) are given (in Ry atomic units).

	H	Li	Na	K
H	12 (13)	97 (133)	108 (142)	189 (218)
Li		1335 (2780)	1543 (2900)	2719 (4640)
Na			1849 (3020)	3159 (4800)
K				5640 (7800)
Be	74 (69)	852 (934)	973 (1010)	1705 (1510)
Mg	114 (116)	1404 (1708)	1612 (1840)	2842 (2779)
Ca	185 (186)	2440 (3229)	2818 (3445)	5002 (5326)

FIG. 3. Values of C_6 coefficients plotted in Fig. 1. In parentheses the corresponding values from Refs. [22] (alkali–alkali) and [24] (alkali–alkali earth) are given (in Ry atomic units).

TABLE III. Values of C_6 coefficients plotted in Fig. 1 (in Ry atomic units).

	Eq. (10)	Other calculations
Na^+-Na^+	3	3[a]
K^+-K^+	44	47[a]
C-C	77	51[b]
He-Be	38	26[c]
He-Mg	57	44[c]
He-Ca	92	64[c]
H_2-He	10	7.8[d]
H_2-Ne	17	16[d]
H_2-Ar	60	54[d]
H_2-Kr	84	76[d]
H_2-Xe	123	114[d]
H_2-H	18	17[d]
H_2-Li	154	159[d]
H_2-Be	119	85[d]
H_2-H_2	29	27[e]

[a] Reference [17].
[b] Reference [23].
[c] Reference [24].
[d] Reference [25].
[e] Reference [26].

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