VAN DER WAALS INTERACTIONS IN DENSITY FUNCTIONAL THEORY

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INTRODUCTION

The history of van der Waals or dispersion forces dates a long way back [1, 2]. The recent book *Van der Waals and Molecular Sciences* [1] gives a detailed account of van der Waals's own contributions and life-long interest in the field. It is interesting to note that this truly quantum-mechanical problem [3, 4, 5] has been addressed by theorists long before the birth of quantum mechanics. The force between atoms, molecules, clusters, complexes, surfaces, and other fragments of matter is dominated by the weak but long-ranged van der Waals interactions at large separations. This is the region that has been primarily addressed. Calculations of the interaction potential between neutral species were first done for molecules [6, 7], leading to the well known asymptotic R^{-6} form of London [5]. The asymptotic z^{-3} form of the interaction potential between a neutral atom and a surface was first identified by Lennard-Jones [8], with subsequent refined treatments of the atom and surface polarizabilities [9, 10]. For the interaction between solid bodies, general formulas have been derived [11], which for flat surfaces a long distance d apart give an interaction energy that varies as d^{-2} [12]. For very large distances, where the limited magnitude of the velocity of light matters, retardation effects are important [13]. Such relativistic effects are physically interesting but beyond the scope of the present work.

In electron systems the attractive van der Waals interaction is always present. Its significance relative to other types of interactions is particularly large for neutral

non-polar systems, where it, in fact, is the only source of attraction. Examples [14] of physical phenomena that are governed by van der Waals attraction are adhesion and cohesion of less densely packed matter, for example, liquid crystals, layered compounds, polymers, and biomolecular surfaces. The van der Waals interaction is relevant both for microscopic and macroscopic objects. Interactions between atoms and molecules are interesting per se. In addition, in studies of more complex systems, such as molecular solids, liquids, polymers, biomacromolecules, and membranes [15], sometimes called soft matter, a prerequisite is an understanding of such binary interactions. For instance, studies of van der Waals molecules and complexes are sometimes motivated by getting van der Waals interaction potentials as a bridge between microscopic and macroscopic properties [16]. The van der Waals interaction also plays a key role in such modern experimental tools as scanning-force microscopy [17].

Basic experimental data has been scarce in the past, but is now burgeoning. We give a few examples from different areas: The interplay between experiment and theory on dimers of atoms, molecules, and molecular complexes is expanding [18, 16]. The van der Waals force between a ground-state atom and a dielectric wall has recently been obtained in a direct-force measurement [19]. In studies of the forces between macromolecules in liquids, and in particular in water solution, the interplay between the attractive van der Waals forces and the repulsive, basically electrostatic, hydration forces is an area of recent study and progress [20]. A most detailed experimental characterization of the van der Waals potential in the full distance range has been obtained in surface physics, e.g., from the diffractive scattering of beams of light molecules off metal surfaces [21, 22]. There is a hope that the generally limited experimental data should increase substantially in the near future.

On the theoretical side, the magnitude of the van der Waals interaction is very small compared to other contributions to the total energy of a typical system. At the same time, the correlations responsible for the van der Waals effects are subtle ones. These aspects make it difficult to calculate van der Waals interaction energies. A proper and accurate theoretical treatment quickly gets quite demanding with growing size or complexity of the system. To some extent this is reflected in the fact that accurate published calculations on explicit atomic, molecular, or larger objects are relatively few. This scarcity is particularly pronounced when seen alongside of the great number of physical, chemical, and biological systems for which the ubiquitous van der Waals interaction is essential. A simple scheme for calculating the van der Waals interactions, to be used for real systems, would be very desirable.

Density functional theory (DFT) has proved to be an extremely useful tool for many types of calculations. The only approximation needed in a DFT scheme is the one for the exchange and correlation energy. An effect of common local and semilocal approximations for this quantity is that van der Waals interactions are lost. The commonly used local-density (LDA) and generalized-gradient approximations (GGA) have been successful beyond expectation for densely-packed systems [23, 24]. Although DFT embraces the notion of van der Waals interactions in principle, actual usable approximations that make use of this capability have been non-existent.

In this review we describe a practical density functional theory for the calculation of van der Waals interactions. Although its derivation makes approximations that are crude by the most rigorous standards, the resulting density functional scheme is shown by comparison with ab initio calculations to give useful results in a wide variety of circumstances. Because it can be easily used on systems that are way too large or complex to be subjected to the corresponding ab initio calculations, it should have enormous predictive power.

VAN DER WAALS INTERACTIONS IN DENSITY FUNCTIONAL THEORY

Our starting point is the well known *adiabatic-connection formula* for the exchange-correlation energy as defined in DFT [25, 26, 27],*

$$E_{\rm xc}[n] = \frac{e^2}{2}\int\int d^3r\, d^3r'\, n(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}n_{\rm xc}(\mathbf{r},\mathbf{r}')\,. \tag{1}$$

The exchange-correlation hole, $n_{\rm xc}$, is expressed as

$$n_{\rm xc}(\mathbf{r},\mathbf{r}'-\mathbf{r}) = n(\mathbf{r}')\int_0^1 d\lambda\,[g_n(\mathbf{r},\mathbf{r}';\lambda)-1]\,, \tag{2}$$

where λ is a coupling constant multiplying the e^2 in the interparticle Coulomb interaction, and g_n is the pair-correlation function. The latter should be calculated in the presence of a λ-dependent external potential that maintains the density $n(\mathbf{r})$ at its physical value.

Systems where van der Waals forces are important can to a good approximation be divided into subsystems a and b [28]. The Hamiltonian may then be written

$$H = H_a + H_b + V_{ab}\,, \tag{3}$$

where V_{ab} is the Coulomb-interaction operator. We will consider subsystems separated by a vector $\mathbf{R}$, sufficiently large for this to be valid, but still not large enough for retardation effects to be significant ($R \ll c/\omega$, where ω is a characteristic excitation frequency for the fragments).

Using perturbation theory to second order in the interaction V_{ab}, the adiabatic-connection expression Eq. (1) for the exchange-correlation interaction energy can be cast [29, 30] into the form [31]

$$\Delta E_{\rm xc}(\mathbf{R}) = E_{\rm xc}^{\infty} - \int\int\int\int d^3r_1 d^3r_2 d^3r_3 d^3r_4\, V(\mathbf{R}+\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{R}+\mathbf{r}_3-\mathbf{r}_4)\times \int_0^\infty \frac{du}{2\pi}\,\Pi_a(\mathbf{r}_1,\mathbf{r}_3;iu)\Pi_b(\mathbf{r}_2,\mathbf{r}_4;iu)\,, \tag{4}$$

where Π_i is the linear response function giving the density change induced in the subsystem i by an applied potential $v_{\rm applied}$ oscillating with frequency ω:

$$\delta n_i(\mathbf{r},\omega) = \int d^3r'\,\Pi_i(\mathbf{r},\mathbf{r}';\omega)\,v_{\rm applied}(\mathbf{r}',\omega)\,. \tag{5}$$

Since the van der Waals expressions for different model systems can be obtained from the DFT exchange-correlation energy expression, we conclude that the van der Waals interaction is included within DFT [30]. Thus the inability of currently used calculational schemes to account for it is merely a shortcoming of the local and semi-local approximations used for exchange-correlation.

Absence of van der Waals Interactions in Local and Semi-local DFT Schemes

The local-density approximation (LDA) and the various generalized-gradient approximations (GGA's) for the exchange-correlation energy have enabled the success of

*The equations in the text are in Gaussian units, but with $\hbar = 1$. The tables and figures measure energy in Rydberg units and lengths in units of the Bohr radius.

DFT [23, 24]. However, when using LDA and GGA in DFT schemes, the van der Waals interaction is not present. The power-law decay of interaction energies at large separations caused by van der Waals interactions is replaced by an exponential decay. In the light of the locality imposed on the treatment of exchange and correlation within those schemes it is not very surprising that the van der Waals interaction, being non-local correlation, is lost. In the LDA, in particular, the treatment of an electron system as being 'pointwise homogeneous' removes all effects of interactions taking place between points of different density—they are instead treated as if occurring at the same density. In GGA's, the gradient of the electron density is supposed to bring such effects back into the models, but since the exchange and correlation holes are cut off in these schemes, long-ranged effects still are lost.

OUR APPROACH

A number of authors [30, 32, 33, 29, 34, 35, 36] have addressed the problem of restoring the van der Waals interaction in DFT methods. We have developed an approach to this problem that we will describe and prove to be useful by giving physical results for various model systems. It is reassuring that both Refs. [35] and [36] have reached similar conclusions. The latter approach is described in the article by Dobson and Dinte [37] in this volume.

In the original works on DFT [38, 39] the exchange-correlation energy to second order in the density inhomogeneity is expressed using an exchange-correlation kernel, $K_{\rm xc}(\mathbf{r}-\mathbf{r}', n)$,

$$E_{\rm xc}[n] = \int d^3r\, n(\mathbf{r})\epsilon_{\rm xc}\left(n(\mathbf{r})\right) - \tfrac{1}{2}\int\int d^3r d^3r'\, K_{\rm xc}(\mathbf{r}-\mathbf{r}'; n)\left[n(\mathbf{r})-n(\mathbf{r}')\right]^2 . \qquad (6)$$

We focus on the non-local interaction between two distant perturbations of the charge in an otherwise uniform electron gas and thereby define a non-local exchange-correlation kernel,

$$E_{\rm xc}^{\rm non-local} = \int\int d^3r_1 d^3r_2\, K_{\rm xc}^{\rm non-local}(\mathbf{r}_1, \mathbf{r}_2)\delta n(\mathbf{r}_1)\delta n(\mathbf{r}_2)\,, \qquad (7)$$

where $\delta n(\mathbf{r})$ is the deviation from the background density at point $\mathbf{r}$. The long-range part of $K_{\rm xc}^{\rm non-local}$ has been calculated by Langreth and Vosko (LV)† [41], Rapcewicz and Ashcroft (RA) [33] and others. RA argue that since the screened interaction is present in this term and therefore screens the interaction between the electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$, the important fluctuations take place within a screening length of the electron. In the slowly-varying electron gas, where the density varies over distances large compared with the screening length, these fluctuations might be assumed to occur at the local densities at $\mathbf{r}_1$ and $\mathbf{r}_2$. The screened interaction is here mediated by plasmon-exchange between $\mathbf{r}_1$ and $\mathbf{r}_2$, an exchange that RA view as occurring in a medium with the effective electron density, $n_{\rm eff} = \sqrt{n(\mathbf{r_1})n(\mathbf{r_2})}$.

† The $1/R^6$ long-range part of $K_{\rm xc}(R)$ is controlled by the non-analyticity in the variable q^2 at small q in its Fourier transform, $K_{\rm xc}(q) = K_{\rm xc}(0) + (\pi e^2/16k_{\rm F}^4)Z(q)q^2$; this is Eq. (4) of LV with the factor of 2 error, previously pointed out [40], corrected. At small q, one can show analytically from LV's expressions that $Z(Q) \to Z(0) - (3\pi^2/8)Q$, where Q is the dimensionless form of q defined by LV. Fourier transformation back to real space gives $\phi(R) \equiv 2K_{\rm xc}(R) \to -(3e^2/4m^2\omega_p^3)(1/R)^6$ in agreement with Eq. (9) in the present chapter. It was not made clear in LV that Eq. (8) was an analytic fit to the small q numerical points, and not the analytic limiting form.

The concept of an effective medium is very useful, because it can be used in attempts to extend (6) beyond its rigorous range of validity. In our case we would like a choice for the effective density, $n_{\rm eff}$, that gives the correct form for the energy in both the uniform and separated fragment limits. With the application to the interaction between atoms and molecules in mind, we introduce the replacement for the RA effective density by

$$n_{\rm eff} = \frac{1}{2^{2/3}} \left[\sqrt{n(\mathbf{r}_1) n(\mathbf{r}_2)} \left(\sqrt{n(\mathbf{r}_1)} + \sqrt{n(\mathbf{r}_2)} \right) \right]^{2/3} . \tag{8}$$

Following the analysis of RA, the long-range interaction between two electrons in an electron gas in the high-density, small-momentum limit then is

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = -\frac{3e^4}{2m^2} \frac{1}{\omega_p(n(\mathbf{r}_1))\ \omega_p(n(\mathbf{r}_2))\ [\,\omega_p(n(\mathbf{r}_1)) + \omega_p(n(\mathbf{r}_2))\,]\ |\mathbf{r}_1 - \mathbf{r}_2|^6} , \tag{9}$$

with $\omega_p^2(n) = 4\pi n e^2/m$.

The interaction between two separated fragments of matter is obtained by integrating the electron-electron interaction over the electron densities of the two bodies. Finally, 'undoing' the frequency integral over the imaginary frequency iu yields the long-range interaction

$$E_{\rm xc}^{\rm non-local} = -\frac{3}{\pi} \int_{V_1} d^3 r_1 \int_{V_2} d^3 r_2 \int_0^\infty du\, \frac{\chi_1(iu; n(\mathbf{r}_1)) \chi_2(iu; n(\mathbf{r}_2))}{|\mathbf{r}_1 - \mathbf{r}_2|^6} \tag{10}$$

between the two macroscopic fragments. Here the dielectric susceptibility is given by

$$\chi(\omega; n(\mathbf{r})) = \frac{1}{4\pi} \left[1 - \frac{1}{\epsilon(\omega; n(\mathbf{r}))} \right] , \tag{11}$$

where $\epsilon(\omega; n)$ is the exact dielectric function at zero wave vector and frequency ω for a uniform electron gas of density n:

$$\epsilon(\omega; n) = 1 - \frac{\omega_p^2(n)}{\omega^2} . \tag{12}$$

Since the χ's are functions of the local density in each of the fragments, Eq. (10) defines that part of the full density functional that obtains when the fragments are disjoint. Eq. (10) is of course close to what one gets exactly [30] from Eq. (1). The approximations are (i) the introduction of finite volumes V_1 and V_2 defined by the cut-off below, (ii) the approximate expression (11), and the introduction of the local density. The approximations (ii) and (iii) are common in the collective descriptions of atoms [42], while (i) is an important innovation introduced by RA [33].

The nature of these approximations deserves some further discussion. A comparison between Eqs. (4) and (10) shows that insofar as these total-energy expressions are concerned, we are assuming that the local polarization in a fragment is given by

$$\mathbf{P}(\mathbf{r}, \omega) = \chi(\omega; n(\mathbf{r}))\, \mathbf{E}_{\rm applied}(\mathbf{r}, \omega) . \tag{13}$$

This is a doubly local approximation within the fragment. First, it is local in the sense that χ is taken to be the electron gas value at the local density; it is thus a local-density approximation for the dielectric response. Second, it is local in that the electrodynamics is assumed local; this is a separate approximation. Normally one would define local

electrodynamics to mean a local relationship between $\mathbf{P}$ and the *total* electric field $\mathbf{E}$:

$$4\pi\mathbf{P}(\mathbf{r},\omega) = [\epsilon(\omega; n(\mathbf{r})) - 1]\,\mathbf{E}(\mathbf{r},\omega)\,. \tag{14}$$

On a macroscopic scale, such a relationship is normally true. However, because fields from the induced polarization can act at macroscopically large distances, the applied field and the polarization do not bear a local relationship to each other. The relationship $\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}_{\rm applied}(\mathbf{r},\omega)/\epsilon(\omega; n(\mathbf{r}))$ implied by the comparison of (13) and (14) should be expected to be inadequate for inhomogeneous systems of macroscopic size. The exception is the case when the polarization is weak (e.g., due to large ω), in which case the approximation (13) or (10) provides the leading term in an expansion in the size of the dielectric response. Therefore, in the case where one or both of the fragments is macroscopic, one generally needs to treat the electrodynamics exactly, and use (14) instead of (13). This is done simply by substituting into (4) the $\Pi(\mathbf{r},\mathbf{r}',\omega)$ implied by (14), instead of using (10). For a planar surface case the implementation of this procedure is simple. Our application of the better electrodynamics to atoms and molecules is still pending,[‡] although the present results in this case are so good that one could hardly hope for improvement thereby.

The second approximation above, that of a local-density type of approximation for the electrodynamic-response functions, is a venerable one. In the context of van der Waals interactions, an early work [32] from the mid-1970's proposed an approximation of the form

$$4\pi\mathbf{P}(\mathbf{r},\omega) = \int d^3r'\,[\epsilon(\mathbf{r}-\mathbf{r}',\omega; n_{\rm eff}) - \delta(\mathbf{r}-\mathbf{r}')]\,\mathbf{E}(\mathbf{r}',\omega). \tag{15}$$

and showed that a van der Waals interaction would result. Here $\epsilon(\mathbf{r}-\mathbf{r}',\omega; n_{\rm eff})$ is the fully non-local electron gas dielectric function at density $n_{\rm eff}$. Thus the electrodynamics is non-local as it should be, but the actual response function is taken to be given by a local-density type of approximation. Ref. [32] actually proposed a specific approximation for the effective-medium density $n_{\rm eff}(\mathbf{r},\mathbf{r}')$, while here, for more generality, we leave it unspecified. Here the choice would presumably be less critical than in Eq. (7) where the specification was required to be sensible even over macroscopic distances.

Later, a number of proposals in a context somewhat different from density functional theory, were put forth [44, 45, 46, 47], which in some sense could be regarded as approximations to (15), more like (14). To determine the actual detailed behavior of the fields as a function of frequency and position, this type of approximation has severe limitations [48]. Exact non-local theories should be used for systems simple enough to permit their application. One should therefore be reminded not to over-interpret our results and use them for more than total-energy calculations. A final point in this regard is that the earlier attempts at this type of approximation did not have the benefit of a density-functional motivated cut-off scheme, which has been proven by experience to be effective [49, 50, 33]. The cut-off, which we have found to be crucial for getting good results, presumably mimics some of the non-local aspects. This is discussed in detail in the next section.

[‡] The procedure requires solving $\nabla\cdot[\epsilon(\omega; n(\mathbf{r}))\mathbf{E}(\mathbf{r})] = 0$, with $\nabla\times\mathbf{E}(\mathbf{r}) = 0$, for each frequency in the presence of an external field (and with $\epsilon(\omega; n(\mathbf{r}))$ replaced with unity in the region specified by the cut-off criterion). This is no problem for spherical atoms, and in general certainly much simpler in the approximation (14), than in the more general situation when ϵ is non-local. Hopefully, when these tests are done, the approximation (13) will prove sufficient in atoms and molecules, because otherwise the potential attractiveness for the use of our functional for the largest systems could be diminished. For an illuminating pedagogical discussion of dielectric screening in the context of atoms and molecules in more general approximation schemes, see Ref. [43].

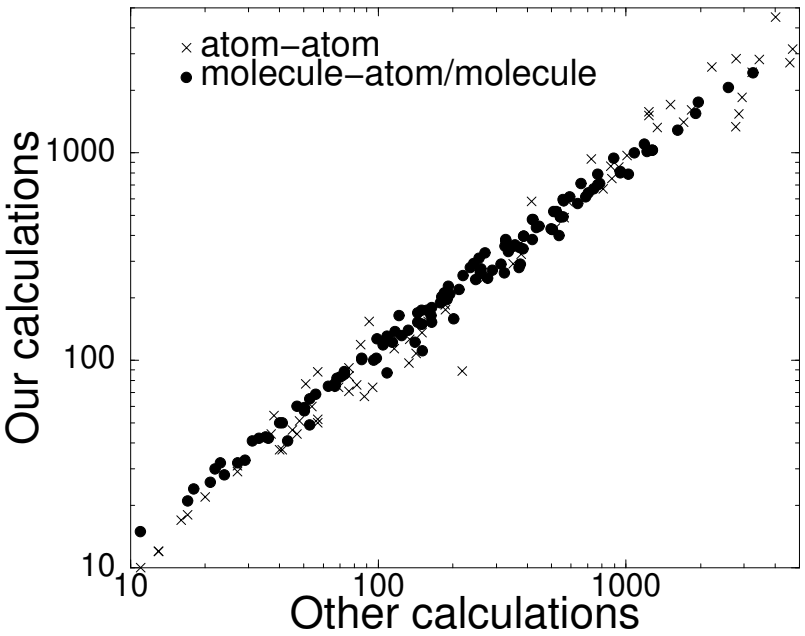

Figure 1. Our results for the van der Waals coefficients for atom–atom, atom–molecule and molecule–molecule interactions, compared with first-principles results.

APPLICATION TO MODEL SYSTEMS

There are three distinct classes of systems that require three successively more sophisticated levels of approximation. These are (i) interaction between two microscopic bodies, (ii) interaction between one microscopic and one macroscopic body, and (iii) interaction between two macroscopic bodies. Each has a simplest prototype problem, which we discuss. For (i), it is the interaction between two atoms or molecules; for (ii), it is the interaction between an atom or molecule and a planar surface; and for (iii), it is two parallel surfaces. The transition between (i) and (ii) requires an improved treatment of the electrodynamics as discussed earlier. The transition between (ii) and (iii) is an even larger step, because second-order perturbation theory in the inter-electron Coulomb interaction [Eq. (4)] fails to give the asymptotic form of the interaction correctly. We treat the prototypes for these three cases in the three sub-sections below.

Two Atoms or Molecules

Our expression (9) for the electron-electron interaction can be identified with the London expression [2, 4] for the van der Waals interaction between two atoms, each having only one important frequency for electron excitations,

$$E_{\rm vdW}^{\rm London} = -\frac{3e^4}{2m^2}\frac{Z_a Z_b}{\omega_a\omega_b(\omega_a+\omega_b)}\frac{1}{R^6}\,. \tag{16}$$

Moreover, Eq. (10) applied to two atoms at large separation R becomes

$$E_{\rm xc}^{\rm non-local}(R) = -\frac{1}{R^6}\frac{3}{\pi}\int_0^\infty du\,\alpha_1(iu)\alpha_2(iu) = -\frac{C_6}{R^6}\,, \tag{17}$$

which is the standard expression for the van der Waals interaction in terms of atomic polarizabilities [51, 2] (C_6 is the atom–atom van der Waals coefficient). The essence of

Table 1. Some representative results for atom–atom van der Waals coefficients C_6 (Ry atomic units).

	our C_6	C_6 from other calculations	Reference
He–He	4.0	2.9, 3.6, 2.9[a]	[52], [53], [54]
Ne–Ne	12	13, 14, 13[a]	[52], [53], [54]
Ar–Ar	126	134, 132, 130[a]	[52], [53], [54]
Kr–Kr	245	266, 262, 262[a]	[52], [53], [54]
Xe–Xe	520	522	[52]
Ar–Xe	253	258	[52]
Ne–Ar	37	41	[52]
Mg–Mg	1513	1237	[55]
Mg–Ca	2592	2224	[55]
H–H	12	13, 13	[52], [55]
H–K	189	218, 209	[52], [55]
Na–Na	1849	3020, 2944, 3080	[52], [56], [55]
H–Ne	10	11	[52]
Li–He	46	45	[52]
K–Ne	136	150	[52]
Na–Kr	486	562	[52]
K–Xe	1327	1338	[52]

[a] experiment

the approximation is that the exact $\alpha(\omega)$ is replaced by the local approximation

$$\alpha(\omega) = \int_{V_i} d^3r\, \chi(\omega; n(\mathbf{r}))\,, \tag{18}$$

where χ is given by Eq. (11).

When integration over the complex frequency in Eq. (17) 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

$$E_{\rm xc}^{\rm non-local} = \frac{6e}{4(4\pi)^{3/2}m^{1/2}} \int_{V_1} d^3r_1 \int_{V_2} d^3r_2 \, \frac{\sqrt{n_1(\mathbf{r}_1)n_2(\mathbf{r}_2)}}{\sqrt{n_1(\mathbf{r}_1)} + \sqrt{n_2(\mathbf{r}_2)}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6}\,, \tag{19}$$

where $n(\mathbf{r}_i)$ is the charge density of fragment i, and the integration is carried out over volumes determined by the cut-off described below.

The replacement of the exact polarizibility by a local approximation, as described above, is reasonable in the interior of a charge distribution. In the outer regions, however, the length scale l_d for density variations gets much shorter than the screening length l_s of the electron gas, causing the approximation to overestimate the response. To cure this we cut off the response in regions where $l_d < l_s$, assuming on good grounds that the true response is small and thus much more accurately approximated by zero than by the local approximation. This argument is, however, not correct at very high frequencies, and imposing the cut-off causes a failure of our approximation to $\alpha(\omega)$ to satisfy the limiting high-frequency form or f-sum rule. The size of this deviation varies considerably among the dozen atoms we have tested it on, but is normally not large (median fractional error $\sim$0.2), since the cut-off occurs well outside the bulk of the atomic electrons.

The electron gas screening length l_s must be inversely proportional to the Thomas-Fermi wave vector $k_{\rm TF}$, given by $k_{\rm TF}^2 = 4me^2(3n/\pi)^{1/3}$. For total-energy calculations the analysis of Ref. [41] suggests that the choice $l_s = (k_{\rm TF}/\sqrt{3})^{-1} = v_F/\omega_p$ is most appropriate, where v_F is the Fermi velocity. It is thus a quantity that is easily evaluated

Table 2. Atomic polarizabilities $\alpha(iu)$ (Ry atomic units). Results from Eq. (18) in left columns and ab initio results from Ref. [53] in right columns. Reprinted from Ref. [34].

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

from electron densities. It is not quite as obvious how l_d should be defined. This parameter can be identified with the ξ used by Langreth and Mehl [49, 50] to define a wave vector $q = \xi^{-1}$ when going beyond the LDA. We use the expression for q that they arrive at, $q = |\nabla n|/6n$. The cut-off criterion (that the approximation for the response should be set to zero whenever $l_d < l_s$) is fulfilled by multiplying the response function by a step function in real space, which makes sure that no contribution from such regions is included. In practice this means that the integration in Eqs. (19) is carried out only in regions V_1 and V_2 where

$$\left|\frac{\nabla n(\mathbf{r})}{6n(\mathbf{r})}\right| < \sqrt{4me^2}\left(\frac{n(\mathbf{r})}{9\pi}\right)^{1/6}, \tag{20}$$

where individual molecular electron densities $n(\mathbf{r})$ are used. This is precisely the same cut-off criterion as the one derived by RA [33] for van der Waals interactions between fluctuations in the bulk, using somewhat different arguments. We believe that the scaling of the above cut-off with size and nuclear charge for neutral atoms and molecules is correct. The precise numerical definitions of the length scales and hence the overall constant on one side of the inequality (20) are, of course, arbitrary to a limited extent. It is true that the imposition of this cut-off is crucial for obtaining accurate results, and that the predictions are sensitive to the choice made. Therefore one could probably obtain a more accurate functional if the constant in Eq. (20) were optimized by fitting to the experimental database which we have now collected. Nevertheless, in all our calculations (except for sensitivity tests and the case discussed in the next paragraph), we have kept the RA cut-off of Eq. (20), as discussed above.

The method described above, similarly to the local-density approximation for close-packed matter, is based on the total electronic density. For the latter systems, it is well known that the LDA results can be improved by a theory based on the electronic *spin* density [26] for atoms with spin polarization. For our case, it is particular easy to implement a spin-dependent theory in the case of 100% spin polarization, by adjusting the expression for v_F in l_s for the fact that there are twice as many electron states inside the Fermi-sphere for an unpolarized electron gas as for a polarized one. Then v_F is replaced by $2^{1/3}v_F$ in the cut-off criterion, and (20) is replaced by

$$\left|\frac{\nabla n(\mathbf{r})}{6n(\mathbf{r})}\right| < \sqrt{2me^2}\left(\frac{2n(\mathbf{r})}{9\pi}\right)^{1/6}. \tag{21}$$

For the purposes of calculating the van der Waals coefficient, an atom with one electron outside a closed shell can be considered approximately 100% spin-polarized, because the $\alpha(\omega)$ is dominated by the contribution from the outer shell. Since all the atoms with

Table 3. Some representative results for molecule–molecule van der Waals coefficients C_6 (Ry atomic units).

	our C_6	C_6 other calculations	Reference
HCl–HCl	277	211, 261[a]	[18], [18]
O_2–O_2	137	117.0	[60]
O_2–H_2O	123	106	[60]
H_2O–H_2O	102	97.6, 66.7, 91[a]	[61], [18], [18]
H_2O–CO	139	131.8	[62]
NH_3–H_2O	152	133.4	[62]
NH_3–CO	201	180.4, 207	[62], [63]
CO–CO	189	178, 126, 163[a]	[61], [18], [18]
CO_2–CO_2	265	322, 283, 246, 317[a]	[61], [63], [18], [18]
CH_4–CH_4	268	225, 259[a]	[18], [18]
CH_3OH–CH_3OH	442	362, 444	[18], [18]
C_3H_7OH–C_3H_7OH	1747	1671, 1955	[18], [18]
C_2H_6–NH_3	396	386	[61]
C_2H_2–H_2O	228	191	[64]
C_2H_2–C_3H_7OH	947	890	[64]
C_6H_6–C_2H_2	1102	1186	[64]
C_6H_6–CH_7OH	2057	2586	[64]

[a] experiment

odd electron number which we considered fell into this category, we applied the 100% spin-polarized cut-off (21) to these cases, thus improving the predictions over those from the non-polarized theory. The more general case is more complicated, however, and has not yet been implemented. In particular, all the molecular calculations were made with the form of the theory involving only the total density rather than the spin density, and hence used the cut-off (20).

In Fig. 1 our calculated van der Waals coefficients C_6 for interactions between a large number of atoms and molecules are compared to various first-principles results. Some representative results for atoms are shown numerically in Table 1. Even the values of $\alpha(\omega)$ for imaginary ω are in fair agreement with ab initio calculations, as illustrated in Table 2. Finally we show some representative molecule–molecule calculations in Table 3. We have made calculations for almost all systems that have been considered in first-principles calculations in the literature, and these are all shown in Fig. 1, although not in the tables. The calculations for atom–atom interactions have been made using Hartree-Fock atomic wave functions [34, 57] as input for the electron densities, while we have calculated electron densities for the molecules [58] using DFT-based commercial software [59]. The van der Waals coefficients obtained for the molecules are almost unbelievably consistent with the "better" calculations, and nurture our belief that the method should have good predictive power, when applied to systems too large for such better calculations, which are discussed in the paragraph below, to be feasible.

Systems of stable molecules are termed van der Waals complexes [15]. The last ten years have seen an explosion of calculations and experiments on van der Waals complexes, thanks to a rapid development of theoretical and experimental methods for investigating such systems. Another significant reason is an increasing interest in systems like molecular solids and liquids, polymers, and membranes. The van der Waals interaction we consider here arises from a correlation between fluctuating dipoles. More generally there might also be interactions between a permanent dipole on one molecule and the induced dipole on a second, but this case is not the focus here. This interaction potential is often anisotropic. In the calculations done so far only the isotropic van der Waals coefficient has been considered. Many systems, though,

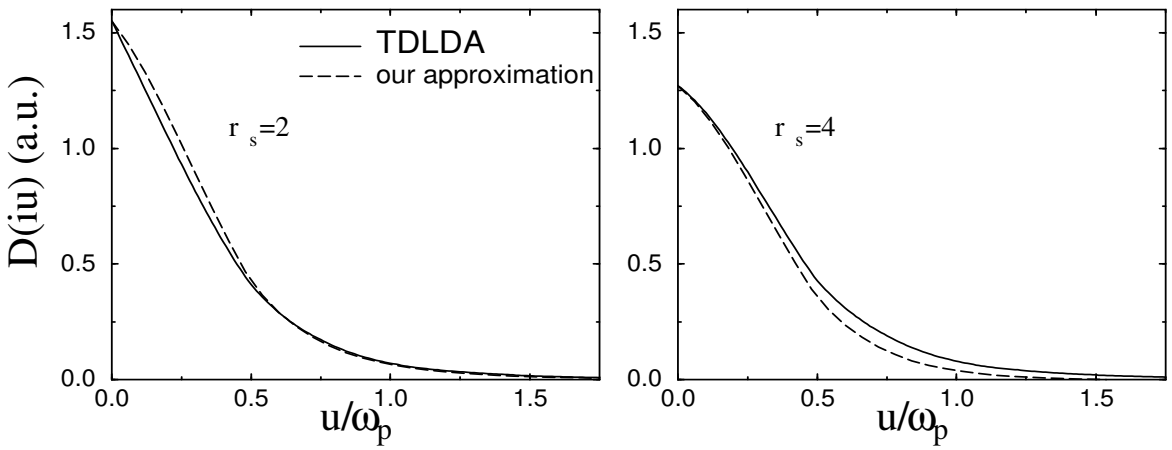

Figure 2. Our approximation for $D(iu) = [\epsilon_b(iu)(\epsilon_b(iu) - 1)/(\epsilon_b(iu) + 1)^2]\, d(iu)$ compared with time-dependent LDA calculations [67]. Reprinted from Ref. [35].

have a low anisotropy, typically about 8% [65]. There are various types of results with which we compare our results for the van der Waals coefficients: From second-order perturbation theory the C_6-coefficient for the interaction between two molecules is obtained as a coupling between their respective polarizabilities taken at imaginary frequencies [66]; Using ab initio methods such as time-dependent coupled Hartree-Fock or many-body perturbation theory, molecular polarizabilities can be obtained with very good accuracy, but this method is applicable only to small molecules, because of an unfavorable scaling of computational effort with system size; finally, C_6-coefficients are sometimes calculated as sums of atom–atom interactions for large molecules.

With increasing complexity of the van der Waals complexes, the possibilities for describing them accurately using first-principles quantum-chemical methods decrease rapidly. This fact puts our approach in a favorable position. It is characteristic for the DFT approach that the price for simplicity is a less detailed insight. The relatively good accuracy (see Table 2) of the atomic polarizabilities calculated from Eq. (18) opens up possibilities for an increased insight, however.

Atom or Molecule Outside a Surface

In the approach applied to two microscopic fragments, the electric field that is caused by the polarization of the medium is taken to be a local function of the applied field. As discussed earlier, this is bound to be an inadequate approximation when one or both of the bodies is macroscopic. Therefore, although still using the same local approximation for response functions, we now treat the electrodynamics within the approximation (14) exactly, rather than approximately according to Eq. (13). For an atom or molecule outside a planar surface, this is implemented simply by using the $\Pi(\mathbf{r}, \mathbf{r}', \omega)$ implied by Eq. (14) directly in Eq. (4). Then, following Zaremba and Kohn [31], one obtains the standard expressions:

$$E_{\mathrm{vdW}} = -\frac{C_3}{(z - Z_0)^3}\,, \tag{22}$$

where the van der Waals coefficient, C_3, and the displacement, Z_0, of the van der Waals plane from the jellium edge are given by

$$C_3 = \frac{1}{4\pi}\int_0^\infty du\, \alpha(iu)\, \frac{\epsilon_b(iu) - 1}{\epsilon_b(iu) + 1} \tag{23}$$

Table 4. The van der Waals coefficient C_3 and the van der Waals plane position Z_0 (Ry atomic units) for He, Be and H_2 outside jellium. In the second and fourth column results from other calculations are given. The van der Waals plane obtained using polarizabilities as in Ref. [67], Z_0^*, is also given. After Ref. [35].

	r_s	C_3	$C_3^{\rm ref}$	Z_0	$Z_0^{\rm ref}$	Z_0^*
He:	2	0.13	0.10[a]	0.83	0.74[b]	0.77
	3	0.086	0.064[a]	0.67	0.64[b]	0.61
	4	0.062	0.045[a]	0.56	0.59[b]	0.53
Be:	2	1.4	1.5[c]	1.2	1.1[c]	
	4	0.96	0.97[c]	0.8	0.79[c]	
H_2:	2	0.36	0.32[a]	0.97	0.85[b]	0.88
	3	0.26	0.22[a]	0.76	0.71[b]	0.68
	4	0.20	0.16[a]	0.63	0.64[b]	0.57

[a] Ref. [31], [b] Ref. [67], [c] Ref. [69]

and

$$Z_0 = \frac{1}{4\pi C_3}\int_0^\infty du\,\alpha(iu)\,\frac{\epsilon_b(iu)-1}{\epsilon_b(iu)+1}\frac{\epsilon_b(iu)}{\epsilon_b(iu)+1}\,d(iu)\,, \tag{24}$$

where $\alpha(\omega)$ is the atomic or molecular polarizibility as defined previously, and $\epsilon_b(\omega)$ is the dielectric function deep in the bulk. The quantity $d(\omega)$ is the usual perpendicular surface response function defined by Feibelman [48]. It is proportional to the surface dipole moment per unit area induced by a normal electric field. The normalization is chosen [48] so that $\mathrm{Re}\,d(\omega)$ is the centroid of the induced charge measured relative to the jellium edge, which we take as the origin. We might note that the simplified form of our functional based on (13) rather than (14) gives [68] expressions whose integrands agree with those in (23) and (24) only for the regions where $\epsilon_b - 1$ is small, e.g., large imaginary frequencies. The values thereby obtained for C_3 and Z_0 are therefore not as accurate as those reported here.

Since our original approach gives good results for dimers, we continue to approximate $\alpha(\omega)$ according to Eqs. (18) and (11). Within our approximation (14), it is trivial to calculate the polarization P_z induced by a perpendicular applied field from a charge sheet at infinity. One finds [35]

$$P_z(z,\omega) = \frac{1}{4\pi}\frac{\epsilon(\omega;n(z))-1}{\epsilon_b(\omega)+1}\frac{2\epsilon_b(\omega)}{\epsilon(\omega;n(z))}\,E_z^{\rm applied}(\omega)\,, \tag{25}$$

from which $d(\omega)$ is obtained as

$$d(\omega) = \frac{1}{P_z(-\infty,\omega)}\int dz\, z\left(-\frac{dP_z(z,\omega)}{dz}\right)\,. \tag{26}$$

As discussed above for the atom–atom case, the replacement of the true response function by a local approximation cannot be justified in the tails of electron distributions. Following the same line here, we should multiply the surface response (25) by a step function. For a flat surface we would then multiply the right hand side of Eq. (25) by a factor $\Theta(z_c - z)$. Doing this, however, and taking the static limit shows z_c to equal $d(0)$. Since static image planes $d(0)$ are rather easy to calculate within time independent DFT, we thus choose to replace the cut-off parameter z_c by $d(0)$.

Our approximation for $d(\omega)$ compares favorably with time-dependent LDA calculations [67] for jellium (Fig.2), for the imaginary ω values important for the energy.

Table 5. Results for some of our homo-nuclear atom–atom van der Waals interactions (unmarked) compared with results we obtain (marked by *) by using first-principles static polarizabilities $\alpha(0)^*$ to define the cut-off radii, r_c^*. C_6^{ref} is from first-principles calculations. (Ry atomic units).

	$\alpha(0)$	$\alpha(0)^*$	r_c	r_c^*	C_6	C_6^*	C_6^{ref}
He	2.1	1.4[a]	1.8	1.7	4	2.6	2.9[b], 3.6[f], 2.9[g]
Ne	2.9	2.8[d], 3.0[f]	2.1	2.1	12.0	12.4	12[b]
Ar	14	11[d], 12[f]	3.5	3.2	126	108	134[b], 132[f], 130[g]
Kr	22	18[f]	4.1	3.8	245	194	266[b]
Be	62	40[d], 37[c]	5.7	4.8	582	326	416[c]
Mg	119	70[d]	7.1	6.0	1513	907	1237[c]
Ca	242	154[c]	9.0	7.6	4500	2810	4010[c]

[a] Ref. [72], [b] Ref. [52], [c] Ref. [55], [d] Ref. [73], [e] Ref. [56], [f] Ref. [53], [g] Ref. [54] (exp't.)

Thus it is not surprising that our results for the van der Waals plane for jellium, given in Table 4, are in good agreement with more accurate calculations. This comparison is hindered by the fact that the two calculations used different atomic α's; the differing values of C_3 are of course due entirely to this difference. To eliminate this effect for the purpose of testing the surface aspects of our approximation scheme alone, we have calculated the van der Waals plane position using the same atomic polarizabilities as those used in the reference calculations. These results are displayed in the final column of Table 4. Note that the jellium model is used only for the purpose of comparison. To give a realistic account of the surface response, improved models are needed, as discussed later.

As in the atomic case high-frequency sum rules fail to be satisfied exactly [35]. This is due to the small fraction of the electrons in the tail that are not counted. For example, for an $r_s = 2$ jellium surface the value of $d(\infty)$ is not zero as it should be, but rather -0.1 a.u., with still larger deviations for lower electronic densities. Similarly the stress sum rule [70, 71] is not fulfilled, although for $r_s = 2$ the deviation was completely negligible. In the expression (24) these deviations introduce only a minor error, however, because the integral over $\omega = iu$ is heavily weighted at small values of u.

We have also tried the RA type of cut-off (20) used in the atom–molecule case. It gives values for the van der Waals planes that are somewhat too large. We do not understand yet, why cut-off (20) is better for atoms and molecules than for surfaces. Possibly it relates to the use of the approximation (13) for the first case and (14) for the second. If this is so, the answer will have to await the implementation of (14) in the atomic case. Perhaps, on the other hand, the cut-off for the atomic case should be fixed by the value of $\alpha(0)$ from first-principles calculations. As illustrated by Table 5, the values for the van der Waals coefficient C_6 come out with a reduced but still interesting agreement with the more accurate numbers. A comparison with both the more accurate electrodynamic treatment *and* an $\alpha(0)$ based cut-off would be desirable.

While waiting for good answers to these questions, we feel that one can use the approximations in their present form without unacceptably large errors to calculate the van der Waals coefficients and planes for various combinations of simple metals and rather complex molecules. One should thereby obtain useful results in cases where better ab initio calculations are unavailable and too expensive to perform.

From Eqs. (23) – (25) it is clear that the van der Waals coefficient C_3 depends only on the bulk electron density, while the position of the van der Waals plane Z_0 depends in addition on the induced surface charge density. The interactions of an atom with

Table 6. The van der Waals reference plane positions Z_0 (atomic units) for H_2 outside the low-indexed Al faces. Values used for d(0) are also given. After Ref. [35].

face	d(0)	Z_0	Z_0^{ref}
111	1.05	0.69	0.61
100	1.32	0.87	0.83
110	2.08	1.32	1.27

$d(0)$ and Z_0^{ref} from Ref. [22, 74]

different faces of the same material thus have the same C_3-value but different Z_0-values.

Of course the jellium model is rather unphysical for the high-density (small r_s) surfaces, because the bulk seeks to be at a lower density, and the surface seeks to increase its area (negative surface tension). The result is that electrons spill out, making the selvage layer unphysically thick, and the $d(\omega)$ values unphysically large. As r_s increases, the unphysical spill-out decreases, and the image plane in this model moves closer to the jellium edge. The values of Z_0 follow this trend and also become smaller with increasing r_s. In addition to this spurious density dependence of Z_0, the possibility for dependence on crystalline face is missing entirely.

To test our approximation in a physically correct setting, we have applied it to a case [35], where there are results available that include the effects of the lattice in a realistic way, namely for the interaction between a hydrogen molecule and the low-indexed aluminum surfaces [22, 74]. The densities and the static image-plane for the Al surfaces are taken from a self-consistent DFT-calculation for jellium with laterally averaged pseudopotentials representing the ions in the four outermost layers [22, 74]. From this input we calculated the Z_0 values shown in Table 6. These turn out very close to those obtained by M. Persson [22, 74] in another approximation,[§] as also shown in the table.

A simpler way of introducing more realistic features and also face-dependent density profiles is to use a stabilized-jellium model with face corrugation [75, 76]. Hult and Kiejna [77] have recently calculated the van der Waals coefficient and the van der Waals plane for a large number of atoms and molecules outside face-dependent stabilized-jellium surfaces. The stabilized-jellium model gives increasing image-plane positions $d(0)$ with increasing r_s [76], as opposed to the jellium model. This is reflected in the results for the van der Waals plane, where in the more realistic stabilized-jellium model the dependence on r_s is rather weak, while the face-dependence is pronounced. The more open the surface is, the larger the value of Z_0. For fcc-metals the van der Waals plane is located at the smallest distance for the close-packed (111) surface and at the largest one for the open (110) surface. For the bcc-metals the (110) surface gives the smallest van der Waals plane and (111) the largest.

Parallel Surfaces

The van der Waals interaction between two surfaces is of interest for adhesion and scanning-force microscopy, among other examples. The standard reference in this case is the Lifshitz theory for dispersion [11], giving $E_{vdW} = -C_2/d^2$, where d is now the

[§] This calculation [74] used an interpolation formula [71] in the manner of Eq. (2) of Ref. [67]. The parameter λ in the interpolation formula was fixed from the stress sum rule [70, 71], which was generalized to the case of the quasi-one-dimensional pseudopotential model used to get self-consistently calculated electron densities.

separation between the two surfaces, which are assumed to be sharp. We have derived a modified expression [78], valid also for soft surface profiles, where van der Waals planes are introduced in the same way as in the case of a molecule outside a surface.

For the cases of atom–atom and atom–surface interactions, the second-order perturbation theory formula (4) is applicable and gives the right van der Waals expressions. For the interaction between two parallel surfaces, on the other hand, we cannot treat the Coulomb interaction as a perturbation, since there will be an infinite number of reflections going back and forth between the surfaces. The adiabatic-connection expression (1) can still be used [30], though, giving an interaction at large separations z between two surfaces A and B as [78]

$$E_{\rm vdW} = -\frac{C_2}{(z - Z_A - Z_B)^2} \,. \tag{27}$$

In this expression the van der Waals coefficient is

$$C_2 = \frac{1}{32\pi^2} \int_0^\infty du\, F(iu) \,, \tag{28}$$

where

$$F(\omega) = \int_0^\infty \frac{dx\, x^2\, e^{-x}}{\left(\frac{\epsilon_A(\omega)+1}{\epsilon_A(\omega)-1}\right)\left(\frac{\epsilon_B(\omega)+1}{\epsilon_B(\omega)-1}\right) - e^{-x}} \,, \tag{29}$$

and the outward displacements of the van der Waals planes from the respective jellium edges are given by

$$Z_{A/B} = \frac{\int_0^\infty du \frac{\epsilon_{A/B}(iu)}{\epsilon_{A/B}(iu)+1}\, d(iu) F(iu)}{\int_0^\infty du F(iu)} \,. \tag{30}$$

The expression for C_2 agrees with the standard one [11], while the expression for $Z_{A/B}$ appears to be a new result of Ref. [78]. Since the expressions for C_2 and $Z_{A/B}$ contain the same components as the corresponding atom–surface expressions we can use the same approximation here. Calculations have been done for jellium and the low-indexed aluminum surfaces [30], using the expressions above with surface electron densities and static image plane positions as input. In that process the same cut-off as used previously for surfaces was applied. The value Z_A for an aluminum surface A interacting with a similar aluminum surface B is very close the corresponding values of Z_0 obtained when the surface A interacts with molecules. The displacements $Z_{A/B}$ are larger for the more open surfaces [78].

Experimental data or better calculations for making comparisons with the results we have obtained are lacking. On the other hand, it might be fruitful to incorporate the result (27) into an interpolation formula like that of Ref. [79] in an attempt to obtain a formula useful at closer distances.

SUMMARY AND OUTLOOK

In this review we have described a simple, general, and approximate scheme to account for van der Waals interactions in density functional theory. This should provide the basis for numerous applications on interacting microscopic particles, such as atoms, molecules, and molecular complexes, and on macroscopic objects, such as atoms and molecules interacting with solid surfaces, parallel surfaces, and ultimately more generally shaped macroscopic objects. We give examples of results for the van der Waals interactions at intermediate distances, before the onset of the effect of retardation,

which illustrate that a useful accuracy can be achieved. A virtue of the scheme is that to get the forces between two objects, only the electron densities of each object are needed as input. This implies an applicability to systems of growing complexity far beyond what other, more fundamental methods can achieve.

Typically, for most of the experimental results presented so far, the interest is in intermediate-range van der Waals interactions. Here our present results should be adequate. However, some surface experiments, for example, selective-adsorption diffraction and scanning-force microscopy, point at the relevance of the close contact region. In particular, it would be very desirable to account for the region, where the attractive van der Waals interaction goes over into Pauli repulsion at short distances. To provide a general method for this transition region is an important task for the continued research on van der Waals functionals.

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