Dispersion Coefficients for van der Waals Complexes, Including C_{60}–C_{60}

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Abstract

A previously proposed and tested [*Phys. Rev. Lett.* **76**, 102 (1996), *Phys. Rev. Lett.* **77**, 2029 (1996)] van der Waals density functional is applied to van der Waals complexes. Dynamic polarizabilities, $\alpha(iu)$, and dispersion coefficients, C_6, are obtained with a useful accuracy and at a low computational cost using ground-state electron densities as input. We compare results for C_6 for small and medium-sized molecules with existing results obtained using more cumbersome methods. The computational simplicity of the functional opens up the possibility to treat large systems of real interest within different fields of physics, chemistry and biology. This is illustrated by the application to C_{60}. We present results for the static polarizability α_0 and the dispersion coefficient C_6 for two such molecules.

1. Introduction

While bonding within molecules mainly is of covalent character, interactions between molecules are governed by van der Waals forces. Recent development of theoretical and experimental tools have made studies of weak interactions possible. When a thorough understanding of the interaction in binary van der Waals complexes is attained, it will be possible to proceed to more complex systems that are of interest within physics, chemistry and biology. Examples of such systems are molecular solids, liquids, polymers and membranes [1].

Much work has been invested in the construction of molecular interaction potentials with input from calculations and from experiments. Such potentials are used in simulations of systems of large numbers of molecules and thus act as a bridge between theory and experiment and between microscopic and macroscopic properties.

The asymptotic non-retarded interaction energy between two molecules at a distance R is generally written on the form $-\sum_n C_n/R^n$. For van der Waals molecules, accurate values for the coefficients C_n, are needed for the construction of interaction potentials. Using quantum-mechanical perturbation- and variational schemes [2], these coefficients can be calculated with very high accuracy only for atoms and small and medium-sized molecules. It is not tractable to apply such methods to large molecules [3].

The density-functional theory (DFT) [4] is an alternative to such schemes. It has proved to be useful beyond all expectations of its founders [5,6], and DFT calculation schemes with local and semi-local approximations (LDA, GGA) for the unknown exchange-correlation energy have been successfully applied to atoms, molecules and solids [4,7]. One shortcoming of such schemes is their inability to correctly describe van der Waals interactions.

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The aim of our work is to construct a van der Waals density functional that can be included in DFT calculation schemes without any significant increase in computational effort. A van der Waals density functional has been proposed [8,9] and tested successfully on atom–atom [8], atom–surface [9] and surface–surface [31] interactions.

In this report we show that our approach is applicable also to van der Waals complexes by comparing dispersion coefficients, C_6, obtained using our functional with other, more elaborate, methods. This should be viewed as a critical test of the functional, since a failure would limit its applicability.

Ry atomic units are used throughout this paper.

2. van der Waals complexes

The interaction energy between two molecules can be written as [1],

$$V^{\text{int}} = V^{\text{short}} + V^{\text{elec}} + V^{\text{ind}} + V^{\text{disp}}. \qquad (1)$$

The first, short-ranged term, accounts for the repulsion that falls off exponentially with distance. V^{elec} is the energy from the interaction between the ground-state electron distributions of the molecules. When the Coulomb interaction operator is treated as a perturbation, this contribution is obtained as a first-order term. The induction energy originates from interactions between induced electric moments and ground-state charge distributions, and is a second-order term [10]. The dispersion interaction, finally, accounts for correlation between instantaneous electric moments of the two charge densities. Like the induction energy, it is obtained to second order in the Coulomb interaction [10]. Both the induction and the dispersion energies are proportional to R^{-6} at large separations between two molecules. For most interactions, induction is much less important than dispersion [1,11].

We consider the van der Waals interaction to be the dispersion interaction, that is the interaction between instantaneous fluctuating dipole moments. It is the only source of attraction between two molecules with filled subshells and no permanent dipole moments. In a wider sense, the van der Waals interaction also embraces the induction that arises when permanent dipole moments are present [12].

Two or more stable molecules held together by induction or dispersion interaction are called a van der Waals complex [1,2]. Sometimes hydrogen bonded systems are also referred to that group.

Van der Waals bond energies are typically very small – of the order of thermal energies, kT [13]. The interaction-energy minimum for the He dimer, which is one of the most weakly bound van der Waals complexes, is $70\,\mu Ry$ [14], which is vanishingly small compared to that of the covalently bonded H_2 molecule, 350 mRy [15].

The interaction potential between two molecules in a van der Waals complex is often anisotropic. For many systems, though, the dispersion interaction energy is less anisotropic than other contributions to the interaction. A typical degree of anisotropy is about 8% [17].

3. Method

In the standard treatment [10] of intermolecular interactions at large separations, $R,$ a multipole expansion of the Coulomb interaction leads to an inverse power series,

$$V^{\text{int}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots \tag{2}$$

The leading R^{-6} term comes from the dipole–dipole interaction and the van der Waals coefficient, C_6 obtained using second order perturbation theory is [10]

$$C_6 = \frac{3}{\pi} \int_0^\infty \mathrm{d}u \, \alpha_1(iu)\alpha_2(iu), \tag{3}$$

where $\alpha_i(iu)$ is the polarizability of molecule i at imaginary frequency.

Several authors [18–22] have directed their attention towards the problem of how to treat the long-ranged van der Waals interaction in DFT calculation schemes. In order to construct a van der Waals density functional we have followed and extended an approach by Rapcewicz and Ashcroft (RA) [20], describing long-ranged electron-electron interaction in terms of plasmon propagation. An expression for the long-ranged electron-electron interaction, obtained first by RA from diagrammatic perturbation theory, has been modified [8,23]. The result is a very useful local approximation for the response of an electron system. Within this approximation, the molecular polarizability in Eq. (3) is

$$\alpha(\omega) = \int_V \mathrm{d}^3 r \, \chi(\boldsymbol{r}; \omega), \tag{4}$$

where $\chi(\boldsymbol{r})$ is the long-wavelength density response of a homogeneous electron gas of density

$$\chi(\boldsymbol{r}; \omega) = \frac{1}{4\pi}\left[1 - \frac{1}{\varepsilon(\boldsymbol{r}; \omega)}\right] = \frac{1}{4\pi}\frac{\omega_p^2(\boldsymbol{r})}{\omega_p^2(\boldsymbol{r}) - \omega^2}. \tag{5}$$

In the expression above the plasmon frequency ω_p is related to the electron density $n(\boldsymbol{r})$ via the electron-gas expression $\omega_p^2(\boldsymbol{r}) = 4\pi e^2 n(\boldsymbol{r})/m$ [24]. The van der Waals interaction is thus described by the ground-state electron densities of the interacting species.

In the outer regions of a molecule, the length scale l_d for density variations is shorter than the screening length l_s of the electron gas. This causes our approximation Eq. (5) to overestimate the response. Since the true response in those regions is small, we instead approximate it by zero in regions where $l_d < l_s$. Following the analysis of Ref. [25] we use $l_s = (k_{TF}/\sqrt{3})^{-1} = v_F/\omega_p$, where the Thomas-Fermi wave

vector is $k_{TF}^2 = 4me^2(3n/\pi)^{1/3}$ and v_F is the Fermi velocity. For the density variations we use the same definition as Langreth and Mehl, $l_d^{-1} = |\nabla n|/6n$ [26,27]. In practice this means that the integration in Eq. (4) is carried out only in the region V where

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

using the molecular electron density $n(r)$.

The functional forms of the length-scales are of course unique, although it could be argued that the overall constants are not. This leaves, in principle, a free parameter to be fit to known data. The dispersion coefficients, however, are in general very sensitive to the cut-off criterium Eq. (6), and the fact that our calculations based on that criterium agree so well with known results strongly supports the above analysis.

4. Implementation

Combining Eq. (4), Eq. (5) and Eq. (6) yield the following numerical integration:

$$\alpha(iu) = \int \mathrm{d}^3 r \, \kappa(\boldsymbol{r}) \frac{4n(\boldsymbol{r})}{16\pi n(\boldsymbol{r}) + u^2}, \tag{7}$$

where $n(\boldsymbol{r})$ is the electron density, and $\kappa(\boldsymbol{r})$ is the cut-off condition given by

$$\kappa(\boldsymbol{r}) = \theta\left(1 - \frac{|\nabla \log(n(\boldsymbol{r}))|}{Cn^{1/6}(\boldsymbol{r})}\right). \tag{8}$$

Here $\theta(x)$ is the Heaviside step function, and C is derived from Eq. (6). We have integrated Eq. (7) on a uniform grid, with a quadrature calculated from cubic splines. The input to our calculations is merely the electron density. With the accuracy of approximation Eq. (7) in regard, we have omitted the effect of small variations in the density profile, due to different approximations of the exchange-correlation energy, such as LDA, GGA, and the various parametrizations therein. The overall accuracy of the calculation is streamlined to provide sufficient data for the aim of this work, showing the statistical correlation between our simple approach and more elaborate calculations.

5. Results

We calculate isotropic dispersion coefficients for a number of combinations of atoms and molecules by evaluating Eqs. (3–6). The results are presented and compared with others in Fig. 1 and in Tables I–IV. In Tables V–VI, we mainly present predictions that might be of interest. Average deviations of the relative differences are included in the tables. Molecular electron densities are calculated within DFT, using the DMol program, which is part of the Biosym program package [32], while Hartree-Fock electron densities are used for the atoms [33].

In particular, van der Waals complexes formed through the interaction of molecules with rare-gas atoms are of special interest, since the rare gas atom can be thought of as a probe of the molecular potential [11], giving information valid also for the molecule in a more complex environment. In addition,
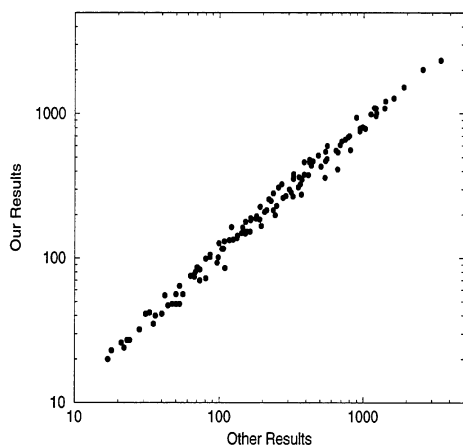
Fig. 1. Summary of our values for C_6 of the about 100 van der Waals complexes studied, compared with other results.

there are only three intermolecular degrees of freedom, since the rare gas atom is spherically symmetric. Many *ab initio* studies have accordingly concerned such systems.

We have made calculations for most systems that we have found first-principles results for. Among those are rare gas atoms interacting with HF, HCl, HBr, O_2, N_2, H_2O, H_2S, NH_3, Cl_2, CO, CO_2, C_2H_2 and C_6H_6, as well as interactions between these molecules. We also give dispersion coefficients for rare gas atoms interacting with the C_{60} molecule, for which there exist no concluding results.

5.1. *Comparison with other results*

There are various types of first-principles calculations with which we may compare our results. Questions still exist concerning the best methods to use for calculating dispersion interaction energies [3]. Using *ab initio* methods such as time-dependent coupled Hartree-Fock (TDCHF) [34] or many-body perturbation theory (MBPT) [35,36], molecular dynamic polarizabilities can be obtained with very high accuracy. These are used to calculate the C_6 coefficient via Eq. (3).

One problem with such methods is that they scale unfavorably with the number of electrons (N^4 or worse [2]), making their applicability restricted to small molecules [2]. The prospects for application of semi-empirical methods to van der Waals interactions are not encouraging, the methods being too crude [2].

Calculation of the total interaction energy between two molecules as a function of separation is a very demanding task, but in return yields extensive structural and energetic information. If the calculation is carried out for sufficiently large separations, van der Waals coefficients can be extracted. Also here TDCHF and MBPT are used. The basis sets need to be very large, though, and large numbers of polarization functions are required [11]. MBPT gives a better description of correlation than TDCHF does, but is on the other hand more time-consuming.

Potential-energy surfaces have been calculated for a number of small van der Waals complexes [37,38]. Such results contain much information, but in order to study the dynamics of a certain complex, analytical representations of the potentials are required [38]. These are in general written as the sum of a repulsive part and an attractive van der Waals

part on the form $-C_6/R^6$. Parameters extracted for such potentials are often rather poor measures of the van der Waals dispersion coefficient, since they in most cases are obtained through an optimization of the total potential at equilibrium separation. The R^{-6} term is often used to correct for deficiencies of the repulsive potential, and also to account for the absence of R^{-8} and R^{-10} terms, which are of significant importance at equilibrium separation. A close agreement between our results for the dispersion coefficients and such potential parameters should thus not be expected.

5.1.1. Ab initio *MBPT*

In Ref. [40], Hettema *et al.* use *ab initio* MBPT to calculate dynamic polarizabilities for N_2, Cl_2, CO, HCl and HBr. They are combined with the polarizabilities for rare gas atoms to give anisotropic (and isotropic) dispersion coefficients via Eq. (3).

We compare our results with those of Hettema *et al.* in Table I. For interactions of HCl, HBr and CO with rare gas atoms, our results are a few percent below, while those for N_2 are a few percent above. For Cl_2, though, the coefficients are on average 28% larger than those of Ref. [40].

Rijks *et al.* [41,42] present C_6 values for small molecules, calculated using MBPT. Our corresponding coefficients are on average 13% larger than theirs (see Table II).

Table I. *vdW-coefficients* C_6 *(Ry atomic units).*

	Our result	Ref. [40]
HCl–He	31	28
HCl–Ne	56	56
HCl–Ar	185	190
HCl–Kr	261	276
HCl–Xe	376	412
ave. dev.	5.5%	
HBr–He	39	36
HBr–Ne	69	73
HBr–Ar	230	248
HBr–Kr	325	362
HBr–Xe	470	543
ave. dev.	9.3%	
Cl_2–He	48	53
Cl_2–Ne	85	109
Cl_2–Ar	276	369
Cl_2–Kr	360	539
Cl_2–Xe	558	808
ave. dev.	28.0%	
CO–He	27	24
CO–Ne	48	50
CO–Ar	153	163
CO–Kr	215	236
CO–Xe	308	351
ave. dev.	8.9%	
N_2–He	26	21
N_2–Ne	47	44
N_2–Ar	149	142
N_2–Kr	209	205
N_2–Xe	299	303
ave. dev.	7.2%	

Table II. *vdW-coefficients* C_6 *(Ry atomic units).*

	Our result	Refs. [41,42]
O_2–O_2	133	117
O_2–He	24	18
O_2–Ne	41	40
O_2–H_2	64	53
O_2–NH_3	163	144
O_2–H_2O	116	106
ave. dev.	14.0%	
H_2O–He	20	17
H_2O–Ne	35	35
H_2O–H_2	56	50
H_2O–CO	138	132
ave. dev.	8.0%	
NH_3–H_2O	143	133
NH_3–He	24	22
NH_3–Ne	48	47
NH_3–H_2	80	68
NH_3–N_2	190	164
NH_3–CO	195	180
ave. dev.	9.5%	
CO–He	27	22
CO–Ne	48	47
CO–H_2	78	67
CO–N_2	183	164
ave. dev.	12.2%	
HF–HF	55	42
HF–H_2	41	31
HF–N_2	99	80
HF–O_2	86	70
HF–NH_3	105	86
HF–H_2O	75	63
HF–CO	102	86
ave. dev.	21.5%	

Table III. *vdW-coefficients* C_6 *(Ry atomic units)*

	Our result	Ref. [43]
HF–Ne	27	23
HF–Ar	83	73
HF–Kr	116	104
ave. dev.	13.2%	
H_2O–H_2O	101	98
H_2O–N_2	134	124
ave. dev.	5.4%	
CO–CO	188	178
CO–Ar	153	154
CO–Kr	215	212
ave. dev.	2.5%	
C_2H_6–C_2H_6	698	794
C_2H_6–H_2	148	150
C_2H_6–CO_2	430	504
C_2H_6–NH_3	378	386
C_2H_6–N_2O	541	542
ave. dev.	6.5%	
N_2–Ne	48	43
N_2–Ar	149	140
N_2–Kr	209	201
ave. dev.	7.0%	
N_2O–N_2O	421	372
CO_2–CO_2	267	322
ave. dev.	15.5%	

5.1.2. Time-dependent DFT

Van Gisbergen and co-workers [43,44] have recently reported on the calculation of polarizabilities within a time-dependent density-functional scheme, employing the adiabatic local density approximation, scaling as N^3 They extract C_6 coefficients using the calculated polarizabilities and find them to be somewhat larger than results from TDCHF and MBPT. The rather unfavorable scaling and the necessity to use large basis sets still makes this method unrealistic for large molecules [43,44]. The results given in Table III on average deviate 9% from those obtained by Van Gisbergen and co-workers.

5.2. *Some particularly interesting systems*

5.2.1. *CO_2 –Ar, N_2 and O_2*

Interactions of CO_2 with other gas atoms, in particular N_2 and O_2, are of great interest because of their importance in atmospheric chemistry [37]. What is relevant to study in this context is how the IR-spectrum for CO_2 depends on collisions with other molecules present. This can be simulated with scattering calculations, using intermolecular potentials. There is a practical problem, though, in that no accurate studies of the long-ranged interaction between CO_2 and N_2, or O_2 have been performed, due to limitations of quantum-chemical calculational schemes [37]. The inter-

action potential for the simpler van der Waals complex CO_2–Ar has been studied within various schemes, however, and since the interaction between CO_2 and Ar atoms is believed to be similar to those with N_2 and O_2, such interaction potentials are of interest. Several potentials have been constructed for the CO_2–Ar complex [37] by fitting to experimental results, none of which has been of satisfactory quality.

Our result for the CO_2–Ar dispersion coefficient is 183 Ry a_0^6, which is close to the similar systems CO_2–N_2 and CO_2–O_2, shown in Table V. Thus the idea to use CO_2–Ar as a model system for CO_2–N_2 and CO_2–O_2 seems reasonable.

5.2.2. *Benzene*

Interactions between a benzene molecule and a rare gas atom or a water molecule have also been the subject of a number of theoretical studies, stretching quantum chemistry to the limit of its capability [45]. Much attention has also been directed towards studies of solid benzene, where empirical intermolecular potentials have been used [46].

One reason for the interest in such systems is that the benzene ring is the prototype for aromatic π-electron systems, which play important roles in many biological systems. Examples are the tertiary structure of proteins, base-base interactions in DNA, and the intercalation of drugs into DNA [45].

Benzene–rare gas atom complexes are held together by dispersion interaction. The contribution from induction is negligible [47]. In Ref. [48] two different types of inter- molecular potentials on Lennard-Jones form for benzene-rare gas atom complexes are extracted by fitting to measured properties. For the benzene–Ar complex, the potential most

Table IV. *vdW-coefficients* C_6 *(Ry atomic units).*

	Our result	Ref. [49]
C_2H_2–O	131	108
C_2H_2–He	42	33
C_2H_2–Ne	74	67
C_2H_2–Ar	249	227
C_2H_2–Kr	353	324
C_2H_2–Xe	512	483
C_2H_2–HF	164	121
C_2H_2–HCl	380	326
C_2H_2–HBr	477	420
C_2H_2–H_2	127	99
C_2H_2–N_2	298	242
C_2H_2–O_2	256	220
C_2H_2–NO	280	235
C_2H_2–N_2O	461	386
C_2H_2–H_2O	227	191
C_2H_2–H_2S	378	420
C_2H_2–NH_3	325	270
C_2H_2–CO	308	256
C_2H_2–CO_2	363	356
C_2H_2–CH_4	371	325
C_2H_2–C_2H_6	596	558
C_2H_2–CH_3OH	468	422
C_2H_2–C_2H_5OH	711	657
C_2H_2–C_3H_7OH	939	890
ave. dev.	14.2%	
C_6H_6–C_6H_6	2324	3446
C_6H_6–O	286	312
C_6H_6–He	93	96
C_6H_6–Ne	167	194
C_6H_6–Ar	538	660
C_6H_6–Kr	755	940
C_6H_6–Xe	1084	1400
C_6H_6–HF	357	350
C_6H_6–HCl	802	948
C_6H_6–HBr	1000	1221
C_6H_6–SO_2	1214	1418
C_6H_6–H_2	269	288
C_6H_6–N_2	641	703
C_6H_6–O_2	554	641
C_6H_6–NO	605	685
C_6H_6–N_2O	989	1122
C_6H_6–H_2S	961	1220
C_6H_6–H_2O	485	554
C_6H_6–NH_3	687	782
C_6H_6–CO	661	744
C_6H_6–CO_2	786	1026
C_6H_6–CH_4	789	944
C_6H_6–C_2H_6	1272	1620
C_6H_6–C_2H_2	1088	1186
C_6H_6–CH_3OH	1005	1230
C_6H_6–C_2H_5OH	1521	1910
C_6H_6–C_3H_7OH	2011	2586
ave. dev.	16.6%	

Table V. *vdW-coefficients* C_6 *(Ry atomic units).*

	Our result	Ref. [16]
CO_2–Ar	183	202
CO_2–N_2	218	–
CO_2–O_2	189	–

Table VI. *vdW-coefficients* C_6 *(kRy atomic units).*

	Our result	Ref. [54]
C_{60}–C_{60}	130	200, 350
C_{60}–He	0.71	–
C_{60}–Ne	1.28	–
C_{60}–Ar	4.05	–
C_{60}–Kr	5.67	–
C_{60}–Xe	8.11	–

those reported in Ref. [49] (see Table IV). For corresponding interactions for benzene, our results are on average 17% too small.

6. C_{60}

Much effort has been put into studies of the properties of the fascinating C_{60} molecule [50,51]. None of the first-principles methods described above can be applied to this system consisting of 60 carbon atoms. Simpler methods have been used, though, ranging from the summation of atom–atom interactions [52,53] and summation of multipole fields [54], to self-consistent treatments of the response function of C_{60} [55].

We have calculated the electron density for C_{60} using the density-functional-based program DMol [32]. Our result for the static polarizability, $\alpha(0)$, is 530 a_0^3, which is in agreement with the experimental result $\alpha(0) = 520 - -620$ a_0^3, determined from data for the solid phase of C_{60} [56]. An approach where a single shell model is used to calculate the linear response of a C_{60} molecule [57] yields $\alpha(0) = 770$ a_0^3.

Our calculated dispersion coefficient for the interaction between two C_{60} molecules is 130 kRy a_0^6. There exist various results for this quantity obtained from the treatments mentioned above. Girard *et al.* [54] present results for C_6 obtained both from a summation of C–C interactions, c_6/r^6, and from a calculation of dipole modes using a discrete dipole model. The former value, $C_6 = 200$ kRy a_0^6, is dependent of the choice of C–C interaction parameter, C_6. The discrete dipole model yields $C_6 = 350$ kRy a_0^6.

7. Summary and Conclusions

Van der Waals interactions between molecules are governed by their respective polarizabilities. The latter are quite subtle functions of frequency, determined by the excitation frequencies and oscillator strengths. It is interesting that our easily computed van der Waals density functional captures the physics of such subtle interactions. Earlier we have showed that dynamic polarizabilities compare favorably with first-principles calculations [8].

Summarizing our results, our van der Waals coefficients on average deviate less than 20% from benchmark results covering four orders of magnitude. The latter are first-principles

appropriate for describing van der Waals interactions has a C_6 coefficient of 628 Ry a_0^6, which is quite close to our result of 538 Ry a_0^6. In Ref. [49], dipole–dipole isotropic dispersion coefficients are calculated from dipole oscillator strength distributions, which in turn are constructed using quantum mechanical constraint techniques combined with experimental data. Isotropic van der Waals coefficients for a large number of interactions of acetylene and benzene with themselves and with other molecules are considered. Our results for acetylene interacting with rare gases, inorganic molecules and hydrocarbons are on average 14% larger than

calculations, when available (mostly for small molecules), or potential fits to measured quantities. Our van der Waals density functional is thus able to describe small and medium-sized molecules with reasonable accuracy. Since it has previously been shown to work well also for atom-atom and atom-surface interactions, it is now time to apply it to systems too complex to be treated using quantum chemistry. In order to illustrate the possibilities that open up with the use of our functional we have applied it to the C_{60} molecule. Other examples of interesting systems are proteins, DNA bases, liquid crystals, polymers and biosurfaces.

The strength of our approach is that it gives polarizabilities and C_6 values with a useful accuracy, only uses ground-state electron densities as input, and is very easily evaluated.

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