Density functional results for isotropic and anisotropic multipole polarizabilities and C_6, C_7, and C_8 Van der Waals dispersion coefficients for molecules

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The generalized gradient-approximated (GGA) energy functionals used in density functional theory (DFT) provide accurate results for many different properties. However, one of their weaknesses lies in the fact that Van der Waals forces are not described. In spite of this, it is possible to obtain reliable long-range potential energy surfaces within DFT. In this paper, we use time-dependent density functional response theory to obtain the Van der Waals dispersion coefficients C_6, C_7, and C_8 (both isotropic and anisotropic). They are calculated from the multipole polarizabilities at imaginary frequencies of the two interacting molecules. Alternatively, one might use one of the recently-proposed Van der Waals energy functionals for well-separated systems, which provide fairly good approximations to our isotropic results. Results with the local density approximation (LDA), Becke–Perdew (BP) GGA and the Van Leeuwen–Baerends (LB94) exchange-correlation potentials are presented for the multipole polarizabilities and the dispersion coefficients of several rare gases, diatomics and the water molecule. The LB94 potential clearly performs best, due to its correct Coulombic asymptotic behavior, yielding results which are close to those obtained with many-body perturbation theory (MBPT). The LDA and BP results are systematically too high for the isotropic properties. This becomes progressively worse for the higher dispersion coefficients. The results for the relative anisotropies are quite satisfactory for all three potentials, however.
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I. INTRODUCTION

Density functional methods[1,2] have become very popular, because of the accuracy which can be obtained at low computational cost. There are however a few situations in which the present approximate functionals for the exchange-correlation energy clearly fail. These functionals are too crude to describe the small Van der Waals interaction energies, and the region of the potential energy surface near the Van der Waals minimum is usually not very well described.[3,4] Both the depth and the position of the well are generally not obtained with satisfactory accuracy. Second, the long-range part of the potential energy surface obtained with the local density approximation (LDA) and generalized gradient approximations (GGAs) does not behave as R^{-6}, as it should.

In order to overcome this problem, we proposed another way of constructing the long-range part of the potential energy surface within DFT,[5] by calculating the Van der Waals dispersion coefficient C_6 from frequency-dependent polarizabilities calculated with time-dependent density functional theory.[6]

A somewhat different DFT approach has been introduced recently. Both Andersson *et al.*[7–10] and Dobson and Dinte[11] have considered energy functionals which approximate the Van der Waals forces for two well-separated systems. Both these approaches and our own approach address the long-range behavior only. This means that a way to calculate Van der Waals minima reliably within DFT does not yet exist. We will not be concerned with this difficult, unsolved problem here, though it should certainly be possible to devise a scheme which connects the short-range and long-range potential energy surfaces. An outline of such a scheme has been given in Ref. 12.

In this paper, we will extend our previous work by calculating not only the C_6 dispersion coefficients, but also the C_7 and C_8 coefficients. These coefficients, connected with the R^{-7} and R^{-8} behavior of the potential energy surface, determine the form of this surface closer to the Van der Waals minimum. In order to do this, the code used for calculating frequency-dependent dipole–dipole polarizabilities was extended to general multipole–multipole polarizabilities. To the best of our knowledge, the results in this paper are the first within DFT on molecular quadrupole polarizabilities and C_7 and C_8 dispersion coefficients. Atomic results for higher multipole polarizabilities and dispersion coefficients have been obtained by Bartolotti and co-workers.[13,14]

The calculations were performed with the Amsterdam density functional[15–17] program (ADF). Because of limitations on the maximum *l*-value of the basis and fit sets in ADF, we restrict ourselves to the calculation of the lowest order dispersion coefficients. We emphasize that there is no fundamental problem in going beyond C_8 coefficients.

Since our implementation of the linear response equations of time-dependent DFT has already been described,[5] we will concentrate in the theoretical section on the generalizations which are needed when general multipole–multipole polarizabilities are required. For the sake of completeness, the equations which link the dispersion energy to the frequency-dependent polarizabilities are also given in detail.

It is widely acknowledged that the quality of the most popular LDA and GGA exchange-correlation potentials is unsatisfactory in the outer region of a molecule. They show an exponential decay, where the exact exchange-correlation potential tends to zero as $-1/r$. This leads to large errors in the one-electron energy of the highest occupied Kohn–Sham orbital[18] (which should be equal to the ionization potential in magnitude) and to systematic overestimations in polarizabilities.[19,20] We have shown previously[20] that this systematic overestimation is removed for the dipole polarizability, if one uses the Van Leeuwen–Baerends (LB94) potential,[18] which has the correct asymptotic $-1/r$ behavior by construction.

As the higher multipole polarizabilities are even more sensitive to the outer region, one would expect the normal exchange-correlation potentials, such as the Vosko–Wilk–Nusair (VWN)[21] parametrization of the LDA potential and the gradient-corrected Becke–Perdew (BP)[22,23] potential, to yield a larger overestimation here. We observed this trend for the atomic polarizabilities before.[20] For this reason the LB94 potential was included in our calculations, as well as the more common VWN (simply denoted by LDA in this work) and BP potentials.

II. THEORETICAL INTRODUCTION

A. Frequency-dependent linear response in DFT

We will use time-dependent DFT[6] for our calculations in this paper. Only recently, various applications of this theory in the field of quantum chemistry have appeared.[5,20,24–27] For recent reviews on time-dependent DFT we refer to Gross *et al.*[12] for a general overview of the field and to Casida[28] for the perspective of a quantum chemist. The book by Mahan and Subbaswamy[29] is also a valuable source of information and contains many of the earlier references.

Our implementation of the linear response equations (we refer to Ref. 5 for more details) had to be extended in order to calculate the linear response to a general multipole field. What we need to calculate is the frequency-dependent linear density response of a molecule $\delta\rho^{(lm)}(\mathbf{r},\omega)$ due to a scalar electric external field of general multipole form $\delta v_{\text{ext}}^{lm}(\mathbf{r},\omega)$, labeled with the quantum numbers l and m:

$$\delta v_{\text{ext}}^{lm}(\mathbf{r},\omega)=\sqrt{\frac{4\pi}{2l+1}}Er^{l}Z_{lm}(\hat{r})\cos(\omega t), \tag{1}$$

where the function Z_{lm} stands for a real combination of spherical harmonics Y_{lm}. It is important to note that, for $\delta\rho$, we use parentheses around the labels l and m in order to indicate that this density change was caused by an external field of lm symmetry. The density change will in general possess components of other $l'm'$ symmetries as well.

In time-dependent density functional response theory, this density change $\delta\rho^{(lm)}$ is given (in principle exactly) in terms of a single particle Kohn–Sham response function $\chi_s(\mathbf{r},\mathbf{r}',\omega)$ acting on an effective field $\delta v_{\text{eff}}^{(lm)}(\mathbf{r}',\omega)$ (which differs from the external field because of screening effects):

$$\delta\rho^{(lm)}(\mathbf{r},\omega)=\int d\mathbf{r}'\,\chi_s(\mathbf{r},\mathbf{r}',\omega)\,\delta v_{\text{eff}}^{(lm)}(\mathbf{r}',\omega), \tag{2}$$

where $\delta v_{\text{eff}}^{(lm)}(\mathbf{r},\omega)$ is the effective time-dependent potential evaluated to the first order in the perturbing potential:

$$\delta v_{\text{eff}}^{(lm)}(\mathbf{r},\omega)=\delta v_{\text{ext}}^{lm}(\mathbf{r},\omega)+\int d\mathbf{r}'\,\frac{\delta\rho^{(lm)}(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} + \delta v_{\text{xc}}^{(lm)}(\mathbf{r},\omega). \tag{3}$$

The response function $\chi_s(\mathbf{r},\mathbf{r}',\omega)$ is written in terms of (real) occupied and virtual Kohn–Sham orbitals and their respective energies, as well as the occupation numbers n, which can all be obtained in a standard DFT calculation:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega)=\sum_{i}^{\text{occ.}}\sum_{m}^{\text{virt.}} n_i\phi_i(\mathbf{r})\phi_m(\mathbf{r})\phi_m(\mathbf{r}')\phi_i(\mathbf{r}') \times\left(\frac{1}{(\varepsilon_i-\varepsilon_m)+\omega}+\frac{1}{(\varepsilon_i-\varepsilon_m)-\omega}\right). \tag{4}$$

The term for the change in the exchange-correlation potential is given by

$$\delta v_{\text{xc}}^{(lm)}(\mathbf{r},\omega)=\int d\mathbf{r}'\,f_{\text{xc}}(\mathbf{r},\mathbf{r}',\omega)\,\delta\rho^{(lm)}(\mathbf{r}',\omega). \tag{5}$$

The exchange-correlation kernel $f_{\text{xc}}(\mathbf{r},\mathbf{r}',\omega)$ is the Fourier transform of the functional derivative of the exchange-correlation potential with respect to the time-dependent density. The so-called adiabatic local density approximation (ALDA) provides the simplest approximation to this kernel. It was first employed by Zangwill and Soven.[30] It is obtained by taking the derivative of the time-independent LDA expression for v_{xc}. The result is a function which is frequency-independent and local in space:

$$f_{\text{xc}}^{\text{ALDA}}(\mathbf{r},\mathbf{r}',\omega)=\delta(\mathbf{r}-\mathbf{r}')\frac{d^2}{d\rho^2}[\rho\varepsilon_{\text{xc}}^{\text{hom}}(\rho)]|_{\rho=\rho_0(\mathbf{r})}, \tag{6}$$

where this function is evaluated at the converged SCF density $\rho_0(\mathbf{r})$. In this equation, $\varepsilon_{\text{xc}}^{\text{hom}}$ represents the exchange-correlation energy density for the homogeneous electron gas, in the VWN[21] parametrization.

The ALDA has been used in most of the time-dependent DFT calculations performed until now. In the low-frequency range, experience shows that it works quite well. We emphasize that we employ the ALDA for all potentials. This means that the potential which is used influences the results only through the response function and that finite-field calculations may differ from the results obtained here with the Becke–Perdew and LB94 potentials. In other words, we always take the VWN expression for ε_{xc} in Eq. (6).

Using this scheme, the change in the electron density $\delta\rho^{(lm)}(\mathbf{r},\omega)$ can be calculated by iteratively using Eqs. (2), (3) and (5) until self-consistency is obtained. After this has been done, the frequency-dependent polarizability $\tilde{\alpha}_{m,m'}^{l,l'}(\omega)$ is directly available. For an external potential specified by the quantum numbers l and m, as given by Eq. (1), one has:

$$\widetilde{\alpha}^{l,l'}_{m,m'}(\omega) = -\frac{2}{E}\int d\mathbf{r}\,\delta\rho^{(lm)}(\mathbf{r},\omega)\, r^{l'} \sqrt{\frac{4\pi}{2l'+1}}\, Z_{l'm'}(\hat{r}). \tag{7}$$

Here, the superindices l and l' determine the type of multipole–multipole polarizability considered ($l=l'=1$ representing the ordinary dipole–dipole polarizability), while the subindices m and m' determine the component of this polarizability tensor. The indices m and m' range from $-l$ to l and $-l'$ to l' respectively. In the practical implementation the polarizability is calculated by taking the trace of the product of the multipole moment matrix and the first order density matrix, which is a transcription of Eq. (7).

The tilde which has been attached to the polarizability tensor indicates that the multipole operators are based on real spherical harmonics $Z_{L,M}$, where we adopt the convention that a negative sign for the angular momentum quantum number M refers to the sine combination of two spherical harmonics. Explicit expressions can be found in Stone's book on intermolecular forces.[31] Stone also gives conversion tables which can be used for converting our results into those obtained by using other conventions (based on Cartesian tensors).

B. Van der Waals dispersion coefficients

There is an interesting relation between the polarizability tensors at imaginary frequencies and Van der Waals dispersion coefficients. The equations presented here exploit this relationship in order to obtain the dispersion coefficients. The equations have been derived and extensively used by Wormer and co-workers.[32–37] A detailed derivation of the equation for the dispersion energy[38] (which is given below) is also available from the authors.

One starts by considering molecules A and B with orientations in space determined by the sets of Euler angles ω_A and ω_B. Their position relative to each other is given by the vector $\mathbf{R}$. For this system one can write the dispersion energy in terms of a complete set of scalar-coupled functions:

$$\begin{aligned} E_{\text{disp}} = {} & \sum_{n\geqslant 6}\ \sum_{L_A,L_B,L}\ \sum_{K_A,K_B} C_n^{(L_A,K_A,L_B,K_B,L)} R^{-n} \\ & \times \sum_{M_A,M_B,M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & -M \end{pmatrix} \\ & \times [D^{L_A}_{K_A M_A}(\omega_A)]^* [D^{L_B}_{K_B M_B}(\omega_B)]^* \\ & \times \sqrt{\frac{4\pi}{2L+1}}\, Y_{L,-M}(\hat{\mathbf{R}}). \end{aligned} \tag{8}$$

Here the coefficients $C_n^{(L_A,K_A,L_B,K_B,L)}$ are the Van der Waals dispersion coefficients which we want to calculate. For large separations ($R \gg 1$), only the $n=6$ term remains, yielding the R^{-6} behavior. In this paper we will also be concerned with the terms $n=7$ and $n=8$. The quantity between brackets is a $3j$-symbol, while the matrices D are the Wigner rotation matrices. More details and further references can be found elsewhere.[32,33]

The dispersion coefficients are the only quantities in this equation which are unknown. They can be calculated from the multipole–multipole polarizabilities of the monomers, which appear in the so-called Casimir–Polder integrals.[39] The final expression is based upon a double spherical harmonics expansion of the $1/r_{12}$ operator:

$$\begin{aligned} C_n^{(L_A,K_A,L_B,K_B,L)} & \\ = {} & \sum_{l_A,l'_A,l_B,l'_B}^{l_A+l'_A+l_B+l'_B+2=n} \zeta^{L_A,L_B,L}_{l_A,l'_A,l_B,l'_B} \\ & \times \sum_{m_A=-l_A}^{l_A} (-1)^{K_A} \begin{pmatrix} l_A & l'_A & L_A \\ m_A & K_A-m_A & -K_A \end{pmatrix} \\ & \times \sum_{m_B=-l_B}^{l_B} (-1)^{K_B} \begin{pmatrix} l_B & l'_B & L_B \\ m_B & K_B-m_B & -K_B \end{pmatrix} 8\pi \\ & \times \int_0^\infty \alpha^{l_A,l'_A}_{m_A,K_A-m_A}(i\omega)\, \alpha^{l_B,l'_B}_{m_B,K_B-m_B}(i\omega)\, d\omega . \end{aligned} \tag{9}$$

Here, the coefficients ζ are given by:

$$\begin{aligned} \zeta^{L_A,L_B,L}_{l_A,l'_A,l_B,l'_B} = {} & (-1)^{L_A+L_B+L}(-1)^{l_A+l'_A} \\ & \times \left[\frac{(2l_A+2l_B+1)!(2l'_A+2l'_B+1)!}{(2l_A+1)!(2l'_A+1)!(2l_B+1)!(2l'_B+1)!} \right]^{1/2} \\ & \times [(2L_A+1)(2L_B+1)(2L+1)] \\ & \times \begin{pmatrix} l_A+l_B & l'_A+l'_B & L \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{Bmatrix} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A+l_B & l'_A+l'_B & L \end{Bmatrix}, \end{aligned} \tag{10}$$

where the quantity between curly brackets is the Wigner $9j$-symbol. We note that our expression contains a phase factor $(-1)^{(L_A+L_B+L)}$, which was inadvertently[40] omitted in the review paper of Ref. 32. However, in the calculations of this paper, we always have that L_A+L_B+L is even, which makes the difference in phase irrelevant.

As l_A and l'_A are combined to L_A, the last quantity is limited in the following way (similarly for L_B and L):

$$\begin{aligned} & L_A = |l_A-l'_A|, |l_A-l'_A|+1, \cdots, l_A+l'_A, \\ & L_B = |l_B-l'_B|, |l_B-l'_B|+1, \cdots, l_B+l'_B, \\ & L = |L_A-L_B|, |L_A-L_B|+1, \cdots, L_A+L_B. \end{aligned} \tag{11}$$

As the polarizabilities α in these formulas are based on spherical harmonics $Y_{L,M}$ while the calculated $\widetilde{\alpha}$'s are based on real spherical harmonics $Z_{L,M}$ and include the Racah renormalization factor $\sqrt{4\pi/(2l+1)}$, the following conversion has to be made:

$$
\begin{aligned}
\alpha^{l,l'}_{m,m'} = {} & \frac{1}{4\pi}\sqrt{(2l+1)(2l'+1)}\frac{1}{2}(\sqrt{2})^{\delta_{m,0}+\delta_{m',0}}(-\sigma_m)^m \\
& \times(-\sigma_{m'})^{m'}\{\tilde{\alpha}^{l,l'}_{|m|,|m'|}-(1-\delta_{m,0}) \\
& \times(1-\delta_{m',0})\sigma_m\sigma_{m'}\tilde{\alpha}^{l,l'}_{-|m|,-|m'|} \\
& +i[\sigma_{m'}(1-\delta_{m',0})\tilde{\alpha}^{l,l'}_{|m|,-|m'|}+\sigma_m(1 \\
& -\delta_{m,0})\tilde{\alpha}^{l,l'}_{-|m|,|m'|}]\}, \qquad (12)
\end{aligned}
$$

in order to convert from (real) $Z_{L,M}$'s to $Y_{L,M}$'s. Here δ is the Kronecker delta and σ is the sign function. For the molecules considered here, the imaginary part of α vanishes on symmetry grounds.

III. COMPUTATIONAL DETAILS

The calculations were performed similarly to our calculations on dipole polarizabilities,[5,20] to which we refer for further details. We repeat the most important aspects of the calculations here, for ease of reference.

All calculations were performed with the Amsterdam density functional (ADF) package.[15–17] Because the properties we consider are very sensitive, the use of extensive basis and fit sets (used to make the evaluation of Coulomb potential cheaper) is required. The basis sets we use consist of a valence triple zeta Slater type basis with two polarization functions, augmented with two s, two p, two d and two f functions, all with diffuse exponents.

Because none of the atoms we consider in this paper possess d-electrons (a frozen core approximation is used, which includes the $3d$-shell for Kr) and we do not consider polarizabilities higher than octupole–dipole or quadrupole–quadrupole, g-functions are not essential in the basis set. The diffuse f-functions are indispensable on the other hand, as is also shown by our test calculations.

We assume that the major source of error in our calculations comes from the remaining incompleteness in the basis and fit sets. This incompleteness becomes more important for the higher multipole polarizabilities. Our test calculations show that the other possible sources of error (the use of a frozen core approximation, the numerical integration scheme) are smaller and can be neglected.

One more technical aspect of our calculations is worth mentioning. Because of the large basis sets with many diffuse functions which are used, problems with linear dependence in the basis sometimes occur. If this becomes a problem, the eigenvectors of the overlap matrix of the basis functions with the smallest eigenvalue are removed from the basis set. This is a standard method for solving this problem, and has been applied before by others[41,42] in similar situations.

In our calculations on water it was absolutely necessary to use this method, while the removal of dependent basis functions also affected the $C_8^{4,0,0,0,4}$ results for the diatomic-rare gas interactions. As the linear combinations of basis functions which are removed are close to being superfluous, the quality of the results is not expected to suffer much from this.

The criterion for the smallest eigenvalue in the overlap matrix was taken to be 10^{-4} for the H_2O, H_2, N_2 and 10^{-3} for Cl_2, CO and HCl. This lead to the removal of 7 functions for H_2O, and 4 functions for each of the diatomics. Considering the total number of basis functions (156 Slater type orbitals for H_2O, and at least 100 for all diatomics) this reduction in the basis is not very severe. Some results were insufficiently stable with respect to the criterion for removal of basis functions. These have either been left out of the tables or given in parentheses.

All in all, we believe our results to be close to the basis set limits in general. This is supported by the fact that the LB94 results are close to those obtained with MBPT. There are a few exceptions in which the agreement is less satisfactory. These will be discussed in more detail.

IV. POLARIZABILITY RESULTS

In a previous paper,[20] atomic quadrupole polarizabilities for the rare gases were presented. Here, the quadrupole–quadrupole polarizability tensors $\alpha^{2,2}_{m,m'}$ for the diatomics H_2, N_2, CO, HCl and Cl_2 are given. We use the following definitions of the mean quadrupole–quadrupole polarizability ($\overline{\alpha^{2,2}}$) and the relative first ($\gamma_{\Delta_{1,2}}$) and the second ($\gamma_{\Delta_{2,2}}$) anisotropy in the quadrupole–quadrupole polarizability:

$$
\begin{aligned}
&\overline{\alpha^{2,2}}=(\alpha^{2,2}_{0,0}+2\alpha^{2,2}_{1,1}+2\alpha^{2,2}_{2,2})/5,\\
&\Delta_1\alpha^{2,2}=\alpha^{2,2}_{0,0}+\alpha^{2,2}_{1,1}-2\alpha^{2,2}_{2,2},\\
&\Delta_2\alpha^{2,2}=(3\alpha^{2,2}_{0,0}-4\alpha^{2,2}_{1,1}+\alpha^{2,2}_{2,2})/4, \qquad (13)\\
&\gamma_{\Delta_{1,2}}=\frac{\Delta_1\alpha^{2,2}}{\overline{\alpha^{2,2}}},\\
&\gamma_{\Delta_{2,2}}=\frac{\Delta_2\alpha^{2,2}}{\overline{\alpha^{2,2}}}.
\end{aligned}
$$

In Tables I, II and III the mean quadrupole polarizability and the relative first and the second anisotropies are given. As the quadrupole polarizabilities depend upon the choice of the origin, one has to specify the geometry. We have performed all our calculations (also for the dispersion coefficients) with respect to the center of mass, which is the usual choice.

For the anisotropies we present the relative numbers in order to emphasize that the quality of the polarizability anisotropies is not bad for the LDA and BP polarizability tensor components. In this way the clear overestimation, which is present in all calculations with the LDA and BP potentials, is divided out. The results of Ref. 43 were linearly interpolated because they were given at several bond distances, but not at the experimental ones used in this work and in our previous work.[20]

In Table I, our results for the mean quadrupole polarizabilities of the diatomics are given. The LB94 potential gives

TABLE I. Mean quadrupole polarizability $\overline{\alpha}^{2,2}$ [cf. Eq. (13)] for diatomics using the LDA, BP and LB94 potentials.

Molecule	LDA	BP	LB94	*ab initio*
H_2	21.92	19.73	18.86	16.11,[a] 15.4122[b]
N_2	91.83	88.37	80.20	78.22,[a] 80.74[c]
CO	124.9	119.8	106.9	106.8,[a] 112.1,[d] 110.24,[e] 102.52,[f]
HCl	128.2	122.2	117.8	106.1[a]
Cl_2	402.4	390.6	371.1	345.2,[a] 339.0[g]

[a] Reference 37, many-body perturbation theory.

[b] Reference 47, sum-over-states with explicitly-correlated wave functions (SoS).

[c] Reference 48, finite field fourth order singles doubles quadruples-MBPT (SDQ-MBPT).

[d] Reference 49, finite field coupled cluster doubles (FF-CCD).

[e] Reference 50, singles doubles quadruples MBPT.

[f] Reference 51, finite field HF.

[g] Reference 52, finite field fourth order MBPT.

TABLE III. Relative second anisotropy $\gamma_{\Delta_{2,2}}$ [cf. Eq. (13)] in the quadrupole polarizability for diatomics using the LDA, BP and LB94 potentials.

Molecule	LDA	BP	LB94	*ab initio*
H_2	0.0217	0.0145	0.0114	0.0119,[a] 0.1367[b]
N_2	−0.206	−0.208	−0.222	−0.223,[a] −0.234[c]
CO	−0.261	−0.266	−0.285	−0.293,[a] −0.292,[d] −0.294,[e] −0.319[f]
HCl	0.148	0.150	0.171	0.144[a]
Cl_2	−0.402	−0.398	−0.383	−0.395,[a] −0.390[g]

[a] Reference 37, many-body perturbation theory.

[b] Reference 47, sum-over-states with explicitly correlated wave functions (SoS).

[c] Reference 48, finite field fourth order singles doubles quadruples-MBPT (SDQ-MBPT).

[d] Reference 49, finite field coupled cluster doubles (FF-CCD).

[e] Reference 50, singles doubles quadruples MBPT.

[f] Reference 51, finite field HF.

[g] Reference 52, finite field fourth order MBPT.

the best results of the three potentials used in this work, although the values of H_2, HCl and Cl_2 are a bit higher than the literature values. The LDA yields overestimations from 10 to 40%, while the BP result is slightly better with overestimations of 5 to 30%. These results confirm the trends which were observed in our earlier comparison of these three potentials.[20] The trends are more pronounced in the case of quadrupole polarizabilities than for dipole polarizabilities.

The results for the relative first and the second anisotropies (given in Tables II and III) obtained with the different potentials are of comparable quality. The results for diatomics containing a chloride-atom are somewhat worse than the others. Most of the results for the relative anisotropies of all the three methods are comparable to the *ab initio* literature values.

We also performed quadrupole polarizability calculations on water. They results are shown in Table IV. Because of the lower symmetry of this molecule, its dipole–quadrupole polarizability does not vanish and off-diagonal elements are allowed for the quadrupole–quadrupole tensor. For the dipole–quadrupole tensor the LB94 and MBPT values are very close to each other, the values of LDA and BP being somewhat higher and the values for the Hartree Fock method of Ref. 36 somewhat lower. Considering the excellent agreement between the LB94 and MBPT results, the CI values of Ref. 53 seem to be less accurate than either of these.

The LB94 results for the quadrupole–quadrupole polarizability are also in very good agreement with the MBPT results, except for the $\alpha^{2,2}_{2,0}$-component. The DFT results for this component have been given in parentheses, as test calculations have shown that our results for this component are unstable with respect to small changes in the basis set. We performed a calculation where extra basis and fit functions were added on the symmetry axis at 0.27 Å from the O-atom in the direction of the hydrogen atoms (with the same criterion for the removal of basis functions). This yielded a value for the LB94 potential of $\alpha^{2,0}_{2,2}=1.38$, in much better agreement with the other values. The other components are much more stable with respect to changes in the basis set or in the criterion for removal of basis functions and can be considered reliable. It is not completely clear, why this component is less stable than the other ones. The sole fact that it is small in magnitude, is not satisfactory as an explanation.

TABLE II. Relative first anisotropy $\gamma_{\Delta_{1,2}}$ [cf. Eq. (13)] in the quadrupole polarizability for diatomics using the LDA, BP and LB94 potentials.

Molecule	LDA	BP	LB94	*ab initio*
H_2	0.479	0.485	0.498	0.474,[a] 0.527[b]
N_2	1.388	1.391	1.456	1.388,[a]1.562[c]
CO	1.511	1.522	1.601	1.567,[a] 1.606,[d] 1.611,[e] 1.594[f]
HCl	0.321	0.318	0.474	0.271[a]
Cl_2	1.788	1.811	1.835	1.781,[a] 1.822[g]

[a] Reference 37, many-body perturbation theory.

[b] Reference 47, sum-over-states with explicitly-correlated wave functions (SoS).

[c] Reference 48, finite field fourth order singles doubles quadruples-MBPT (SDQ-MBPT).

[d] Reference 49, finite field coupled cluster doubles (FF-CCD).

[e] Reference 50, singles doubles quadruples MBPT.

[f] Reference 51, finite field HF.

[g] Reference 52, finite field fourth order MBPT.

TABLE IV. Polarizability tensor elements for water, using LDA, BP and LB94.

Tensor component	LDA	BP	LB94	TDCHF[a]	MBPT[a]	CI-value[b]
$\alpha^{2,1}_{0,0}$	−3.44	−3.30	−2.70	−1.959	−2.633	−2.194
$\alpha^{2,1}_{2,0}$	−2.75	−2.88	−2.73	−2.717	−2.853	−3.433
$\alpha^{2,1}_{1,1}$	−8.11	−8.22	−7.87	−7.143	−7.843	−7.785
$\alpha^{2,1}_{-1,-1}$	−3.60	−3.39	−2.56	−1.822	−2.509	−2.062
$\alpha^{2,2}_{2,2}$	59.7	57.9	46.4	40.732	45.947	
$\alpha^{2,2}_{2,0}$	(3.9)[c]	(3.6)[c]	(0.06)[c]	1.228	1.843	
$\alpha^{2,2}_{1,1}$	64.7	62.8	54.9	46.425	51.375	
$\alpha^{2,2}_{0,0}$	55.8	53.7	43.3	37.149	42.368	
$\alpha^{2,2}_{-1,-1}$	58.4	55.9	42.8	38.043	43.398	
$\alpha^{2,2}_{-2,-2}$	58.6	56.4	44.0	37.604	42.809	

[a] Reference 36.

[b] Reference 53.

[c] Values in parentheses are unstable with respect to basis changes.

TABLE V. C_8 Van der Waals coefficients for the rare gases.

Atom–Atom	LDA	BP	LB94	*ab initio*	TDCHF[a]
He–He	20.97	18.13	14.15	14.1179[b]	
He–Ne	48.20	44.01	34.32	36.175[c]	
He–Ar	215.0	197.2	171.8	167.47[c]	
He–Kr	344.0	317.5	268.8	279.99[c]	
Ne–Ne	109.6	105.2	82.02	90.344[c]	73.458
Ne–Ar	461.5	444.3	379.5	390.12[c]	344.51
Ne–Kr	726.4	703.1	583.0	638.14[c]	560.17
Ar–Ar	1877	1808	1709	1623.2[c]	1553.0
Ar–Kr	2904	2811	2578	2616.7[c]	2487.3
Kr–Kr	4455	4337	3862	4187.3[c]	3953.0
Av. abs. error wrt MBPT	18.9%	12.8%	5.1%		
Av. error wrt MBPT	18.9%	12.8%	-3.5%		

[a] Reference 54, TDCHF.

[b] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).

[c] Reference 54, many-body perturbation theory (MBPT).

A. Results for Van der Waals coefficients

The dispersion coefficients were calculated from Eq. (9), using a stand-alone program called ''disper,'' which was based upon a similar program by Dr. P.E.S. Wormer and co-workers. The program uses the output of polarizability calculations with the ADF program. The Casimir–Polder integrals, which appear in Eq. (9), are evaluated by Gauss–Chebyshev quadrature[34] in 20 frequency points. Because the Casimir–Polder integrals are even functions of the frequency ω, the frequency-dependent polarizabilities are needed in ten frequencies only. Test calculations with a larger number of integration points have shown that the resulting changes are minimal.

All the calculations were done for LDA, BP and the LB94 potentials. Although the program disper is able to calculate the C_n Van der Waals coefficients up to arbitrary n, only the results up to C_8 are given. Higher order dispersion coefficients would not be reliable due to the limitations in basis and fit sets. The results given in this section will be concentrated on the coefficients for which literature values exist.

First we will consider C_8-coefficients for interactions between rare gases in Table V. The BP and LDA potentials overestimate this coefficient in all cases with respect to the *ab initio* values, while the Hartree Fock values are consistently too low. The LB94 potential gives good results, though the results involving Kr are somewhat too low. This is due to the underestimation of the quadrupole polarizability of Kr by the LB94 potential.[20]

The average errors and average absolute errors with respect to the MBPT values have been included in the table. The first one gives an impression of the general quality of the results, while the second gives information about the nature of the error. Clearly, the LB94 results are superior to the BP results, which are in turn better than the LDA results. The error in the LDA and BP results is very systematic, while the errors in the LB94 results are of a more random nature.

After the rare gas-rare gas interactions, the interactions between diatomics and rare gases were considered. Because the number of independent components is greatly reduced in this case, a more compact notation for the dispersion coefficients is used in the literature, based on Legendre polynomials $P_{L,M}$. In the Legendre convention one has coefficients C_n^L which are related to the coefficients $C_n^{L,0,0,0,L}$ by:[35]

$$C_n^L = \frac{C_n^{L,0,0,0,L}}{(-1)^L \sqrt{2L+1}}. \tag{14}$$

The diatomic-rare gas interactions are completely determined by the C_n^L coefficients. All the results for the diatomic-rare gas interactions are given in the Legendre convention. Some of the LDA dispersion coefficients presented here in Tables VI and Tables VIII, were calculated by us before.[5] In these cases very small differences occur, mainly due to the fact that we use somewhat larger basis sets in the present work. The present values have to be considered slightly more accurate for this reason.

First the isotropic dispersion coefficients will be discussed. The C_6^0-coefficients are given in Table VI. For these coefficients accurate constrained dipole oscillator strength distribution (DOSD) results[44–46] are available. These are obtained by the use of available oscillator strength data and a system of quantum mechanical sum rule constraints and can be used as reference values, where these results are available.

In Table VI, we have given the average absolute error and average error of our results with respect to both the DOSD and the MBPT results. This has been done, because the DOSD results can be considered the benchmark, but the MBPT results are available for all the molecules. The previously noted general trend of an overestimation for LDA and BP potentials and results closer to the literature values for the LB94 potential can again be observed for these Van der Waals coefficients. Looking at the potentials individually, several trends can be noted.

For the LDA and BP potentials most values give the expected overestimation, but the overestimation is lower for the C_6-coefficients involving Kr. This can be explained from the LDA and BP values for the dipole polarizability of Kr, which also show a smaller overestimation. The general overestimation of BP is smaller than the one of LDA (4.7% versus 9.8%).

With an average absolute error of 3.2%, the LB94 results approach the DOSD values best of the three exchange-correlation potentials. The MBPT results are even better, with an average absolute error of 2.0%. The average errors show that the LDA and BP errors are clearly of a systematic nature, which is not true for the LB94 and MBPT results. The errors with respect to the MBPT results show that the picture does not change if the Cl_2 molecule is taken into account as well.

In Table VII the C_8^0 results are presented. The trends are the same as in the previous tables. Taking the MBPT results as a reference, the average LDA, BP and LB94 errors are 20.5%, 13.2% and 4.2% respectively. For the LDA and BP results, these errors are clearly larger than those for the C_6^0 results. This was to be expected, since the C_8^0 coefficients are

TABLE VI. C_6^0-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]	DOSD[b]	SoS[c]
H_2	He	4.789	4.327	4.102	3.913	4.007[d]	4.012 81
H_2	Ne	9.187	8.679	7.961	8.027	8.091[d]	
H_2	Ar	30.36	28.54	28.84	27.12	27.64[d]	
H_2	Kr	42.46	40.13	39.59	39.47	39.44[d]	
N_2	He	11.77	11.00	9.939	9.773	10.23[d]	
N_2	Ne	23.01	22.43	19.73	20.25	20.97[d]	
N_2	Ar	73.22	71.16	68.23	65.60	68.69[d]	
N_2	Kr	101.6	99.32	93.00	94.52	97.28[d]	
CO	He	12.23	11.39	10.21	10.83	10.69[e]	
CO	Ne	23.80	23.16	20.18	22.34	21.87[e]	
CO	Ar	76.47	74.15	70.52	73.36	72.26[e]	
CO	Kr	106.4	103.7	96.32	106.1	102.5[e]	
HCl	He	15.44	14.31	13.36	13.33	13.33[f]	
HCl	Ne	29.71	28.77	26.02	27.34	27.05[f]	
HCl	Ar	97.57	94.18	93.56	91.48	91.21[f]	
HCl	Kr	136.3	132.3	128.3	132.9	129.9[f]	
Cl_2	He	26.75	24.90	23.04	23.48		
Cl_2	Ne	51.47	50.04	44.88	47.98		
Cl_2	Ar	169.0	163.8	161.5	161.5		
Cl_2	Kr	236.2	230.2	221.6	234.8		
Av. abs. error wrt. DOSD		9.8%	4.7%	3.2%	2.0%		
Av. error wrt. DOSD		9.8%	4.7%	−2.0%	−0.5%		
Av. abs. error wrt. MBPT		9.7%	5.2%	3.8%	−		
Av. error wrt. MBPT		9.7%	4.8%	−1.8%	−		

[a] Reference 37, MBPT, results were linearly interpolated.
[b] Constrained dipole oscillator strength distribution results.
[c] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).
[d] Reference 44.
[e] Reference 45.
[f] Reference 46.

more sensitive to the description of the outer region of the molecule. The errors are quite similar to those of the rare gases in Table V.

Now we turn to the anisotropies in the dispersion coefficients. In Table VIII, the relative anisotropic dispersion coefficients γ_6^2 are shown. They are defined by:

$$\gamma_6^2 = \frac{C_6^2}{C_6^0}. \tag{15}$$

In our earlier work[5] we used the symbol Γ for γ_6^2. Similarly, we define

$$\gamma_8^2 = \frac{C_8^2}{C_8^0},$$

$$\gamma_8^4 = \frac{C_8^4}{C_8^0}, \tag{16}$$

$$\gamma_7^3 = \frac{C_7^3}{C_7^1}.$$

In Table VIII, the DOSD values can again be considered the reference. Unfortunately, they are only available for H_2, N_2 and CO. The errors with respect to the DOSD values (5.9%, 4.2%, 4.1% and 11.1% for the LDA, BP and LB94 potentials and for the MBPT results respectively) show that, for the molecules considered here, our results are in better

TABLE VII. C_8^0-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]	SoS[b]
H_2	He	77.31	67.13	59.74	53.60	55.38
H_2	Ne	167.6	153.5	133.7	128.4	
H_2	Ar	720.7	663.2	644.0	576.5	
H_2	Kr	1135	1051	989.5	953.6	
N_2	He	284.3	259.7	222.4	219.7	
N_2	Ne	599.1	574.2	481.4	498.7	
N_2	Ar	2334	2240	2068	1986	
N_2	Kr	3552	3429	3074	3145	
CO	He	334.0	304.9	257.9	262.7	
CO	Ne	693.6	664.2	548.9	588.9	
CO	Ar	2689	2576	2348	2355	
CO	Kr	4072	3923	3474	3726	
HCl	He	364.9	332.2	298.5	284.1	
HCl	Ne	764.5	730.6	639.8	643.7	
HCl	Ar	3048	2914	2815	2638	
HCl	Kr	4667	4487	4201	4219	
Cl_2	He	1026	946.1	849.4	810.3	
Cl_2	Ne	2086	2013	1758	1770	
Cl_2	Ar	7758	7479	7186	6764	
Cl_2	Kr	11 539	11 184	10 439	10 505	
Av. abs. error wrt. MBPT		20.5%	13.2%	4.2%	−	
Av. error wrt. MBPT		20.5%	13.2%	1.8%		

[a] Reference 37, MBPT, results were linearly interpolated.
[b] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).

TABLE VIII. γ_6^2-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]	DOSD[b]	SoS[c]
H_2	He	0.0875	0.0915	0.0931	0.0902	0.0924[d]	0.0946
H_2	Ne	0.0852	0.0893	0.0902	0.0883	0.0901[d]	
H_2	Ar	0.0905	0.0947	0.0971	0.0946	0.0971[d]	
H_2	Kr	0.0917	0.0960	0.0984	0.0961	0.0986[d]	
N_2	He	0.1040	0.1064	0.1107	0.0824	0.1027[d]	
N_2	Ne	0.1010	0.1034	0.1068	0.0803	0.0999[d]	
N_2	Ar	0.1068	0.1095	0.1145	0.0857	0.1074[d]	
N_2	Kr	0.1079	0.1108	0.1157	0.0870	0.1087[d]	
CO	He	0.0833	0.0856	0.0884	0.1023	0.0930[e]	
CO	Ne	0.0814	0.0837	0.0860	0.1001	0.0916[e]	
CO	Ar	0.0842	0.0868	0.0899	0.1054	0.0942[e]	
CO	Kr	0.0845	0.0873	0.0903	0.1064	0.0943[e]	
HCl	He	0.0330	0.0337	0.0431	0.0368		
HCl	Ne	0.0324	0.0332	0.0419	0.0361		
HCl	Ar	0.0329	0.0337	0.0440	0.0375		
HCl	Kr	0.0328	0.0337	0.0443	0.0378		
Cl_2	He	0.1323	0.1334	0.1346	0.1355		
Cl_2	Ne	0.1281	0.1295	0.1294	0.1310		
Cl_2	Ar	0.1374	0.1390	0.1415	0.1437		
Cl_2	Kr	0.1395	0.1412	0.1437	0.1469		
Av. abs. error wrt. DOSD		5.9%	4.2%	4.1%	11.1%		
Av. abs. error wrt. MBPT		12.7%	11.6%	13.8%	−		

[a] Reference 37, MBPT, results were linearly interpolated.

[b] Constrained dipole oscillator strength distribution results.

[c] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).

[d] Reference 44.

[e] Reference 45.

agreement with the DOSD results than the MBPT results are. The quality of the LDA, BP and LB94 results is very similar. This implies that reliable estimates for the *relative* anisotropies can be obtained at the LDA or BP level, because the overestimations affect the different polarizability tensor components in similar fashion.

Table IX gives the results for the relative anisotropic dispersion coefficients γ_8^2. We have calculated the average absolute errors with respect to the MBPT results. The DFT anisotropies are slightly higher than the MBPT anisotropy for Cl_2. The average errors show that the LDA and BP values tend to be very similar to each other and slightly lower than those obtained with MBPT, while the LB94 values are slightly higher. In general the agreement between the DFT results and the MBPT results is very satisfactory in this table.

Though the results for the isotropic dispersion coefficients calculated at the MBPT level are of higher quality than our DFT results, the errors of Table VIII indicate that the MBPT results for the relative anisotropies need not necessarily be better than ours. As still higher level calculations are lacking, it remains unclear which of the columns in Table IX gives the most reliable results.

Table X contains the results for γ_8^4. We have chosen not to include results for Cl_2, as we were unable to obtain converged results. The changes resulting from the removal of one or a few basis functions were too large to allow for a reliable quantitative estimate of this coefficient. The other dispersion coefficients and other molecules were much more stable with respect to small changes in the basis.

TABLE IX. γ_8^2-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]	SoS[b]
H_2	He	0.2786	0.2870	0.3064	0.2950	0.3080
H_2	Ne	0.2520	0.2588	0.2739	0.3233	
H_2	Ar	0.2161	0.2197	0.2290	0.2184	
H_2	Kr	0.2016	0.2049	0.2138	0.2018	
N_2	He	0.8864	0.8944	0.9465	0.9227	
N_2	Ne	0.8270	0.8353	0.8748	0.8488	
N_2	Ar	0.6927	0.6931	0.7228	0.7003	
N_2	Kr	0.6399	0.6402	0.6708	0.6428	
CO	He	0.9932	1.0046	1.0637	1.0424	
CO	Ne	0.9279	0.9352	0.9841	0.9600	
CO	Ar	0.7936	0.7970	0.8322	0.8151	
CO	Kr	0.7375	0.7406	0.7764	0.7553	
HCl	He	0.1615	0.1671	0.2127	0.1861	
HCl	Ne	0.1546	0.1590	0.1997	0.1744	
HCl	Ar	0.1236	0.1268	0.1630	0.1397	
HCl	Kr	0.1132	0.1161	0.1515	0.1277	
Cl_2	He	1.5042	1.5389	1.4979	1.4946	
Cl_2	Ne	1.4301	1.4595	1.4170	1.4060	
Cl_2	Ar	1.2751	1.2994	1.2588	1.2497	
Cl_2	Kr	1.2046	1.2279	1.1951	1.1778	
Av. abs. error wrt. MBPT		5.5%	5.0%	6.5%	−	
Av. error wrt. MBPT		−4.9%	−3.3%	4.5%	−	

[a] Reference 37, MBPT, results were linearly interpolated.

[b] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).

TABLE X. γ_8^4-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]	SoS[b]
H_2	He	0.0098	0.0092	0.0082	0.0091	0.0099
H_2	Ne	0.0092	0.0085	0.0074	0.0076	
H_2	Ar	0.0063	0.0058	0.0052	0.0062	
H_2	Kr	0.0055	0.0051	0.0046	0.0055	
N_2	He	−0.0208	−0.0212	−0.0200	−0.0217	
N_2	Ne	−0.0176	−0.0180	−0.0163	-0.0179	
N_2	Ar	−0.0181	−0.0183	−0.0177	−0.0192	
N_2	Kr	−0.0174	−0.0176	−0.0171	−0.0187	
CO	He	−0.0392	−0.0402	−0.0361	−0.0379	
CO	Ne	−0.0345	−0.0354	−0.0308	−0.0322	
CO	Ar	−0.0337	−0.0345	−0.0315	−0.0334	
CO	Kr	−0.0323	−0.0330	−0.0303	−0.0325	
HCl	He	0.0621	0.0658	0.0768	0.0777	
HCl	Ne	0.0555	0.0586	0.0675	0.0682	
HCl	Ar	0.0483	0.0509	0.0594	0.0598	
HCl	Kr	0.0445	0.0469	0.0552	0.0552	
Av. abs. error wrt. MBPT		8.6%	7.5%	6.4%		
Av. error wrt. MBPT		−3.4%	−3.2%	−6.4%		

[a] Reference 37, MBPT, results were linearly interpolated.

[b] Reference 47, sum-over-states with explicitly electron-correlated wave functions (SoS).

Once again, the agreement between the DFT results and the MBPT results is very good, considering the highly anisotropic character of this coefficient. The DFT values tend to be somewhat lower than the MBPT values. The average absolute errors are comparable for the three exchange-correlation potentials.

Finally, we come to our results for the C_7-coefficients. As these are zero for the centrosymmetric molecules, only results for HCl-rare gas and CO-rare gas interactions are presented in Table XI, where the coefficient C_7^1 is considered. Once again, the LDA values are too high. To lesser extent, this also holds for the BP values, though the BP coefficient for HCl-Kr is slightly lower than the MBPT value. The LB94 and MBPT results are in good agreement, though the MBPT values are slightly higher than the LB94 values for CO.

Table XII is the last table on the diatomic-rare gas interactions. It contains the relative anisotropic coefficient γ_7^3. Very good agreement between the LDA, BP, LB94 and MBPT results is obtained for the interactions involving HCl. This is not the case for those involving CO, where the DFT results are in very good mutual agreement, but in disagreement with the MBPT results. These results represent the largest differences we found between all the DFT and MBPT results in this paper. It is not *a priori* clear which results should be more trustworthy, and more advanced calculations are needed in order to draw definite conclusions. However, the fact that the DFT results are in very good mutual agreement (which might be expected only for the LDA and BP results), as well as the fact that the DFT results for CO are in better agreement with the DOSD results for γ_6^2 speak in favor of the DFT numbers.

Summing up the results for the anisotropic parts of the diatomic-rare gas interactions, one can say that the DFT and MBPT results are in very satisfactory agreement for the relative anisotropic dispersion coefficients (except for the case just mentioned).

The final results obtained for this work are the Van der Waals coefficients for the water–water interaction, presented in Table XIII. Only those coefficients are shown for which comparison to MBPT literature values was possible. This means that very small dispersion coefficients are not included in the table. The results for the coefficients $C_6^{0,0,0,0,0}$, $C_7^{1,0,0,0,1}$ and $C_8^{0,0,0,0,0}$ once again show the overestimation in the LDA and BP results. The other components

TABLE XI. C_7^1-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]
CO	He	35.23	32.17	27.12	28.69
CO	Ne	66.12	63.04	51.06	57.25
CO	Ar	230.8	219.1	197.9	204.9
CO	Kr	325.8	312.1	274.9	302.3
HCl	He	21.33	19.57	19.23	18.54
HCl	Ne	40.95	39.28	37.30	37.72
HCl	Ar	135.2	129.1	135.4	128.0
HCl	Kr	189.2	181.6	186.0	186.5

[a] Reference 37, MBPT, results were linearly interpolated.

TABLE XII. γ_7^3-Van der Waals coefficients for diatomic-rare gas.

Diatomic	Rare gas	LDA	BP	LB94	MBPT[a]
CO	He	−0.0448	−0.0443	−0.0428	−0.0216
CO	Ne	−0.0432	−0.0430	−0.0404	−0.0191
CO	Ar	−0.0488	−0.0484	−0.0484	−0.0279
CO	Kr	−0.0504	−0.0501	−0.0502	−0.0306
HCl	He	0.2495	0.2649	0.2627	0.2669
HCl	Ne	0.2437	0.2588	0.2549	0.2615
HCl	Ar	0.2553	0.2719	0.2717	0.2759
HCl	Kr	0.2575	0.2746	0.2745	0.2792

[a] Reference 37, MBPT, results were linearly interpolated.

TABLE XIII. Van der Waals coefficients for H_2O–H_2O.

Coefficient	LDA	BP	LB94	MBPT[a]
$C_6^{0,0,0,0,0}$	50.37	48.65	43.17	46.433
$\gamma_6^{2,2,0,0,2}$	0.041	0.044	0.077	0.0647
$\gamma_6^{2,2,2,2,4}$	0.0059	0.0065	0.016	0.0112
$C_7^{1,0,0,0,1}$	113.7	111.80	96.48	102.16
$\gamma_7^{2,2,1,0,3}$	−0.027	−0.029	−0.055	−0.0460
$\gamma_7^{3,0,0,0,3}$	−0.244	−0.25	0.277	−0.2779
$\gamma_7^{3,2,0,0,3}$	0.315	0.331	0.366	0.3578
$\gamma_7^{3,0,2,2,5}$	−0.027	−0.030	−0.064	−0.0529
$\gamma_7^{3,2,2,2,5}$	0.036	0.041	0.084	0.0681
$C_8^{0,0,0,0,0}$	1426	1361	1115	1141.7
$\gamma_8^{1,0,1,0,2}$	−0.150	−0.157	−0.162	−0.1636
$\gamma_8^{2,0,0,0,2}$	(0.066)[b]	(0.064)[b]	(0.066)[b]	0.0626
$\gamma_8^{2,2,0,0,2}$	(0.040)[b]	(0.051)[b]	(0.206)[b]	0.1179
$\gamma_8^{3,2,1,0,4}$	−0.048	−0.053	−0.061	−0.0603
$\gamma_8^{3,0,3,0,6}$	−0.043	−0.048	−0.061	−0.0615
$\gamma_8^{3,2,3,0,6}$	0.055	0.063	0.080	0.0791
$\gamma_8^{3,2,3,2,6}$	−0.071	−0.082	−0.105	−0.1019
$\gamma_8^{4,0,0,0,4}$	−0.075	−0.075	−0.098	−0.0977
$\gamma_8^{4,2,0,0,4}$	0.078	0.081	0.094	0.0865

[a] Reference 36.

[b] Values in parentheses are unstable with respect to basis changes.

have been given relative to these values and are denoted by γ. One has, for example, that $\gamma_7^{3,2,0,0,3} = C_7^{3,2,0,0,3}/C_7^{1,0,0,0,1}$. The DFT results for $\gamma_8^{2,0,0,0,2}$ and $\gamma_8^{2,2,0,0,2}$ have been given in parentheses, as they depend strongly upon the quadrupole–quadrupole polarizability tensor component $\alpha_{2,0}^{2,2}$ of Table IV. The instability of this polarizability component clearly influences these dispersion coefficients. We performed some test calculations which show that the other components are influenced far less. Consequently, both the good agreement between the LB94 and MBPT results for $\gamma_8^{2,0,0,0,2}$ and the bad agreement for $\gamma_8^{2,2,0,0,2}$ should be considered accidental. The test calculation with extra diffuse functions in the center of the molecule, to which we referred earlier, yielded values of 0.052 and 0.162 for the $\gamma_8^{2,0,0,0,2}$ and $\gamma_8^{2,2,0,0,2}$ components for the LB94 potential.

In general, the LB94 potential clearly gives the best agreement with the *ab initio* values, in this case also for the relative anisotropies. This agreement can be considered very satisfactory.

It holds for all dispersion coefficients that all the discrepancies in the results can be explained by looking at the differences in the polarizability results. The frequency dependence is not of decisive importance, because it is similar for all the used methods.

V. CONCLUDING REMARKS

We have presented calculations with three different exchange-correlation potentials within time-dependent DFT on molecular quadrupole polarizabilities and Van der Waals coefficients. These are the first such calculations within DFT. By comparing to *ab initio* literature values we have been able to analyze the strengths and weaknesses of these potentials. The LB94 results for the isotropic properties are superior to the LDA and Becke–Perdew results, which overestimate the isotropic coefficients. This is due to the fact that the LB94 potential exhibits the correct Coulombic asymptotic behavior, which the ordinary LDA and GGA potentials do not. For the relative anisotropies, the results obtained with the three potentials are of similar quality. The anisotropic DFT results are in good agreement with the MBPT values, and seem to be of competitive quality.

Our results indicate that it is possible to obtain reliable long-range potential energy surfaces within the framework of density functional theory. An important next step would be to link this long-range potential energy surface with the short-range part, in order to obtain a reliable description of Van der Waals minima.

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