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Coupled-cluster calculation of dispersion contributions to interaction energies and polarizabilities

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Abstract. The induced dipole dispersion-type contributions to the two-body and nonadditive three-body energies and electric dipole polarizabilities are studied for long-range interactions involving the He, Ne, Ar and Kr atoms and the H_2 and N_2 molecules. The coupled-cluster singles and doubles model and large basis sets are used. Comparison of the energy contributions with data derived from experiment shows in most cases the deviations to be less than 1%; therefore, it may be expected that the calculated polarizability increments are accurately determined and can be used to estimate the accuracy of approximate methods.

Key words: Interaction-induced properties – Electric dipole (hyper) polarizabilities – Cauchy coefficients – Coupled-cluster calculations – Weak long-range interactions

1 Introduction

The theory of weak long-range intermolecular forces is nowadays successfully applied to predict interaction energies [1]. The interaction-induced changes of atomic and molecular properties have been less well studied even though the changes in the electric polarizabilities and hyperpolarizabilities owing to intermolecular forces affect, for example, the collision-induced light scattering spectra [2] and dielectric and optical properties of compressed fluids [3–5].

Ab initio electronic structure studies of collision-induced pair polarizabilities have been carried out [6]. The accuracy of recent ab initio studies for the He dimer [7–11] is very high and the results have been successfully used to interpret the experimental data, see e.g. [12] for a study of collision-induced spectra. Similar studies for the Ar pair polarizability also show good overall agreement with the experimental data [8–10, 13].

The first step towards ensuring high accuracy is to investigate the long-range behaviour of the interaction-induced effects. Asymptotic expansions show, just like for the energies, that the interaction-induced polarizabilities can be decomposed into different contributions (induction, dispersion, etc.) that are proportional to the inverse powers of the interatomic or intermolecular distance; however, accurate expansion coefficients have been determined only for H, He and H_2 [14, 15].

We summarize here only briefly the theory for the dispersion energies and the dispersion polarizabilities, and refer the reader to Refs. [16, 17] for details. For the dispersion energies, we compare our results mainly with the dipole oscillator strength distribution (DOSD) values. They are generally used and apparently so far no ab initio values of similar accuracy have been obtained systematically.

More specifically, we refer to the work of Champagne et al. [17] for a description of the theory of the interaction-induced polarizabilities. The classical contribution is easily determined, as it depends only on the static polarizabilities of the interacting atoms or molecules [18]. The dispersion term is the computationally difficult one, for both two- and three-body interactions, and we concentrate in this work on this contribution. Apart from two-electron systems, primarily estimates based on static properties have been used to obtain the dispersion contributions [17]. In the so-called constant-ratio approximation (CRA) it is assumed that the ratio of integrals involving properties that depend on imaginary frequencies can be estimated from the ratio of corresponding static properties. This is a relatively crude approach, especially considering that frequency-dependent polarizabilities and hyperpolarizabilities can nowadays be computed accurately, at least for small atoms and molecules.

We present here the results for the interactions of rare-gas atoms and H_2 and N_2 molecules obtained within a coupled-cluster singles and doubles (CCSD)

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approach [19]. The details of response theory for a coupled-cluster parameterization of the wavefunction are discussed elsewhere. A general description of the method is given, for example, in Ref. [20]. The implementation of the dispersion coefficients for linear and cubic response properties in coupled-cluster response theory is described in Refs. [21, 22].

2 Theory and formulae

In this section we briefly summarize some of the highlights of the theory of interaction energy and electric dipole polarizabilities, mainly to provide some definitions and useful formulae.

2.1 Dispersion contribution to the interaction energy

The second-order dipole–dipole dispersion interaction energy between two non-overlapping closed shell atoms a and b is often approximated as [23] (atomic units, unless specified otherwise)

$$E^{(2)}_{ab}(R) = -\frac{C_6^{ab}}{R^6} \quad , \tag{1}$$

where $R = |\mathbf{R}_{ab}|$ is the interatomic distance and the dispersion force coefficient may be obtained from the so-called Casimir–Polder formula [24]

$$C_6^{ab} = \frac{3}{\pi}\int_0^\infty \alpha^a(-i\omega; i\omega)\alpha^b(-i\omega; i\omega)\mathrm{d}\omega \quad , \tag{2}$$

which relates the dispersion energy coefficient to an integral of electric dipole polarizabilities over imaginary frequencies. In the case of interaction between a closed shell atom a and a linear homonuclear molecule m in its totally symmetric ground state Eq. (1) is modified to [23]

$$E^{(2)}_{am}(R,\theta) = -\frac{C_6^{am}}{R^6}[1 + \Gamma_{am}P_2(\cos\theta)] \quad , \tag{3}$$

where θ is the angle between $\mathbf{R}$ and the molecular axis, whereas $P_2(\cos\theta)$ is the second-order Legendre polynomial. The coefficients C_6^{am} and Γ_{am} can be written as

$$C_6^{am} = 2C_6^{am}(\|) + 4C_6^{am}(\perp) \quad , \tag{4}$$

$$\Gamma_{am} = 2\frac{C_6^{am}(\|) - C_6^{am}(\perp)}{C_6^{am}} \quad , \tag{5}$$

respectively, where the parallel and perpendicular components of the dispersion coefficient may be expressed as

$$C_6^{am}(\|) = \frac{1}{2\pi}\int_0^\infty \alpha^a(-i\omega; i\omega)\alpha^m_\|(-i\omega; i\omega)\mathrm{d}\omega \quad , \tag{6}$$

$$C_6^{am}(\perp) = \frac{1}{2\pi}\int_0^\infty \alpha^a(-i\omega; i\omega)\alpha^m_\perp(-i\omega; i\omega)\mathrm{d}\omega \quad . \tag{7}$$

An average over all angles leads to

$$\langle E^{(2)}_{am}\rangle_\Omega = -\frac{C_6^{am}}{R^6} \quad . \tag{8}$$

A further step in the generalization of Eq. (1) leads to an expression for the second-order dipole–dipole dispersion energy for two interacting homonuclear diatomic molecules m and n. The expression is given explicitly for example, in Ref. [23] and involves the coefficients

$$C_6^{mn} = \frac{2}{3}[C_6^{mn}(\|,\|) + 4C_6^{mn}(\perp,\perp) + 2C_6^{mn}(\|,\perp) + 2C_6^{mn}(\perp,\|)] \quad , \tag{9}$$

$$\Gamma_{nm} = \frac{2}{3}\frac{[C_6^{mn}(\|,\|) - 2C_6^{mn}(\perp,\perp) + 2C_6^{mn}(\|,\perp) - C_6^{mn}(\perp,\|)]}{C_6^{mn}} \quad , \tag{10}$$

$$\Gamma_{mn} = \frac{2}{3}\frac{[C_6^{mn}(\|,\|) - 2C_6^{mn}(\perp,\perp) + 2C_6^{mn}(\perp,\|) - C_6^{mn}(\|,\perp)]}{C_6^{mn}} \quad , \tag{11}$$

$$\Delta_{mn} = \frac{2}{3}\frac{[C_6^{mn}(\|,\|) + C_6^{mn}(\perp,\perp) - C_6^{mn}(\|,\perp) - C_6^{mn}(\perp,\|)]}{C_6^{mn}} \quad , \tag{12}$$

with

$$C_6^{mn}(\|,\|) = \frac{1}{2\pi}\int_0^\infty \alpha^m_\|(-i\omega; i\omega)\alpha^n_\|(-i\omega; i\omega)\mathrm{d}\omega \tag{13}$$

and analogous definitions of $C_6^{mn}(\|,\perp)$, $C_6^{mn}(\perp,\|)$ and $C_6^{mn}(\perp,\perp)$ in terms of the parallel, $\alpha_\|(-i\omega; i\omega)$, and perpendicular, $\alpha_\perp(-i\omega; i\omega)$, components of the electric dipole polarizability at imaginary frequency. Once again, an average over the two sets of angles $\Omega \equiv \theta, \phi$ gives

$$\langle E^{(2)}_{mn}\rangle_{\Omega_m,\Omega_n} = -\frac{C_6^{mn}}{R^6} \quad . \tag{14}$$

The leading nonadditive long-range term for the three-body interaction energy can be written in terms of three-body dispersion energy coefficients C_9^{abc} [25–31], which satisfy [27]

$$C_9^{abc} = \frac{3}{\pi}\int_0^\infty \alpha^a(-i\omega; i\omega)\alpha^b(-i\omega; i\omega)\alpha^c(-i\omega; i\omega)\mathrm{d}\omega \quad . \tag{15}$$

In particular, the dipole–dipole–dipole energy term for three interacting molecules m, n, p involves combinations of isotropic and anisotropic terms – the last indicated as Γ_m, Γ_{mn} and Γ_{mnp} – which can all be expressed in terms of coefficients mixing perpendicular and parallel components of the imaginary electric dipole polarizability, for example $C_9^{mnp}(\|,\|,\|), C_9^{mnp}(\|,\perp,\|), \cdots C_9^{mnp}(\perp,\perp,\perp)$, using a self-explanatory notation [30, 31].

2.2 Dispersion contributions to the pair polarizability function

For a pair of atoms a and b at a distance R along z, the dispersion contributions to the parallel and perpendicular components of the van der Waals static pair polarizability can be written as [17, 32]

$$\Delta\alpha_{\parallel}^{ab} = \frac{A_6^{ab}(\parallel)}{R^6} + O\left\{\frac{1}{R^8}\right\} = \frac{1}{\pi R^6}(1+\wp^{ab})(3W_1^{ab} + 4W_2^{ab}) + O\left\{\frac{1}{R^8}\right\} , \quad (16)$$

$$\Delta\alpha_{\perp}^{ab} = \frac{A_6^{ab}(\perp)}{R^6} + O\left\{\frac{1}{R^8}\right\} = \frac{1}{\pi R^6}(1+\wp^{ab})(3W_1^{ab} + W_2^{ab}) + O\left\{\frac{1}{R^8}\right\} , \quad (17)$$

where

$$W_1^{ab} = \int_0^\infty \gamma_1^a(-i\omega; i\omega, 0, 0)\alpha^b(-i\omega; i\omega)\mathrm{d}\omega , \quad (18)$$

$$W_2^{ab} = \int_0^\infty \gamma_2^a(-i\omega; i\omega, 0, 0)\alpha^b(-i\omega; i\omega)\mathrm{d}\omega , \quad (19)$$

and $\wp^{ab}$ exchanges labels a and b. For atoms

$$\gamma_1(-i\omega; i\omega, 0, 0) = \gamma_\perp(-i\omega; i\omega, 0, 0) = \gamma_{xxzz}(-i\omega; i\omega, 0, 0) , \quad (20)$$

$$\gamma_2(-i\omega; i\omega, 0, 0) = \frac{\gamma_\parallel(-i\omega; i\omega, 0, 0) - \gamma_\perp(-i\omega; i\omega, 0, 0)}{2} = \frac{\gamma_{zzzz}(-i\omega; i\omega, 0, 0) - \gamma_{xxzz}(-i\omega; i\omega, 0, 0)}{2} . \quad (21)$$

The hyperpolarizabilities entering the equation describe the third-order response of the system to an applied external electric field **F** [33, 34]

$$\alpha_{\alpha\beta}^{\mathbf{F}}(-i\omega; i\omega) = \alpha_{\alpha\beta}(-i\omega; i\omega) + \tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}(-i\omega; i\omega, 0, 0)F_\gamma F_\delta + \cdots \quad (22)$$

evaluated at a purely imaginary frequency argument. The extension to molecules in their totally symmetric ground state requires the calculation of the appropriate rotational averages. The appropriate combinations of tensor components entering the definition of $\gamma_1(-i\omega; i\omega, 0, 0)$ and $\gamma_2(-i\omega; i\omega, 0, 0)$ for $D_{\infty h}$ molecules are given in Ref. [17].

Similarly to C_9, nonadditive three-body polarizability increments owing to the dispersion interaction can be defined [17]. The relevant integrals that are computed and discussed in this work are

$$W_1^{abc} = \int_0^\infty \mathrm{d}\omega \gamma_1^a(-i\omega; i\omega, 0, 0)\alpha^b(-i\omega; i\omega)\alpha^c(-i\omega; i\omega) , \quad (23)$$

$$W_2^{abc} = \int_0^\infty \mathrm{d}\omega \gamma_2^a(-i\omega; i\omega, 0, 0)\alpha^b(-i\omega; i\omega)\alpha^c(-i\omega; i\omega) . \quad (24)$$

We have not specified in detail the tensor components of the a, b and c subsystem (hyper)polarizabilities in the equations. For all the integrals discussed in this section, W_1^{ab}, W_2^{ab}, W_1^{abc} and W_2^{abc}, we use the same definitions as in Ref. [17], where further details can be found.

2.3 Power series expansions and frequency dispersion coefficients

The interaction properties introduced in the previous sections can thus all be written in terms of integrals over the frequency arguments of electric dipole (hyper)polarizabilities computed at purely imaginary frequencies (see Eqs. 2, 15, 18, 19, 23, 24). In recent years enormous progress has been made in the field of the ab initio determination of high-order optical properties, and it is this progress that allows us to carry out an accurate determination of the interaction properties.

The frequency dependence of the electric dipole (hyper)polarizabilities can be obtained by calculating the frequency dispersion coefficients. Response functions for a finite molecular or atomic system in its electronic ground state are analytical in the frequency arguments, except at the poles, where a frequency or a sum of frequencies is equal to an excitation energy; thus, for frequencies below the first pole, the linear, quadratic or cubic response functions can be expanded in power series [21, 22, 35, 36]. In the specific case of the electric dipole polarizability [21] and second hyperpolarizability [22], one can write

$$\alpha_{\alpha\beta}(-\omega; \omega) \propto \langle\langle \hat{r_\alpha}; \hat{r_\beta}\rangle\rangle_\omega = \sum_{n=0}^\infty \omega^{2n} S_{\alpha\beta}(-2n-2) , \quad (25)$$

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\beta - \omega_\gamma - \omega_\delta; \omega_\beta, \omega_\gamma, \omega_\delta) \propto \langle\langle \hat{r_\alpha}; \hat{r_\beta}, \hat{r_\gamma}, \hat{r_\delta}\rangle\rangle_{\omega_\beta,\omega_\gamma,\omega_\delta} = \sum_{n,m,r=0}^\infty \omega_\beta^n \omega_\gamma^m \omega_\delta^r D_{\alpha\beta\gamma\delta}(n, m, r) . \quad (26)$$

Equation (25) is the usual Cauchy expansion [37] introducing the so-called Cauchy coefficients $S_{\alpha\beta}(-2n-2)$. For optical processes involving a single laser frequency, for example, in the direct current Kerr effect, special versions of Eq. (26) were derived [22], where the frequency dispersion coefficients depend only on one order parameter. For purely imaginary frequency arguments we obtain

$$\alpha_{\alpha\beta}(-i\omega; i\omega) = \sum_{n=0}^\infty (-1)^n \omega^{2n} S_{\alpha\beta}(-2n-2) , \quad (27)$$

$$\gamma_{\alpha\beta\gamma\delta}(-i\omega; i\omega, 0, 0) = \sum_{n=0}^\infty (-1)^n \omega^{2n} D_{\alpha\beta\gamma\delta}^{\mathrm{dc-Kerr}}(2n) , \quad (28)$$

where $D_{\alpha\beta\gamma\delta}^{\mathrm{dc-Kerr}}(2n) = D_{\alpha\beta\gamma\delta}(2n, 0, 0)$ [22]. Within coupled-cluster response theory the expansion coefficients in Eqs. (27) and (28) are obtained directly by exploiting their proportionality to the derivatives with respect to the frequency arguments of the frequency-dependent (hyper)polarizabilities [21, 22].

2.4 Padé approximants, interaction energies and (hyper) polarizabilities

It is well known that the electric dipole polarizability (Eq. 27) has the property of being a Stieltjes series [16, 38–42]. The proper convergence criterion being satisfied [41], one can introduce the Padé approximant $[n,m]_\alpha$ [16, 40–42]

$$[n,m]_\alpha = \frac{P_m(\omega)}{Q_n(\omega)} \ , \tag{29}$$

providing an analytic continuation to Eq. (27) outside the radius of convergence and effectively summing the series within the radius of convergence. The subindex α indicates that we are seeking an approximation to the electric dipole polarizability $\alpha_{\alpha\beta}(-i\omega; i\omega)$. The set of linear inhomogeneous equations defining the polynomials P_m and Q_n is easily derived [16, 40, 41]. In particular, the Padé approximants $[n, n-1]_\alpha$ exhibit the correct asymptotic behaviour as $i\omega \to \infty$ and can be used as a proper lower-bounding approximant. Upper bounds can be derived using functions of other approximants [16, 40, 41].

Using the Casimir–Polder formula, Eq. (2), we can write

$$C_6^{ab} \approx \frac{3}{\pi} \int_0^\infty [n, n-1]_\alpha^a [n, n-1]_\alpha^b \mathrm{d}\omega \quad n = 1, 2, \ldots \tag{30}$$

In practice, we observe good convergence in the series $n = 1, 2, \ldots$ as n increases, and we find no need to apply other approximants. The integrals in Eq. (30) can be computed using the appropriate quadrature scheme [43]. Similar procedures were developed and are applicable to higher-order multipole nonadditive interaction terms. Equation (15) is, for instance, cast in a form that allows the use of Padé approximants and the construction of bounds in a way that is analogous to the two-body case. Finally, we use the same technique to obtain from Eq. (28) the values of $\gamma_{\alpha\beta\gamma\delta}(-i\omega; i\omega, 0, 0)$ required in the integrals defining W_1^{ab}, W_2^{ab}, W_1^{abc} and W_2^{abc} (see Sect. 2.2).

3 Results

3.1 Computational details

Multiply- augmented correlation-consistent valence basis sets of Dunning and co-workers [44–47] were used. The calculations of the static polarizabilities, hyperpolarizabilities and Cauchy coefficients were carried out using a local version of the DALTON code [48].

All H_2 results are given for $R_0 = 1.449$ au. It was observed earlier [49, 50] and reconfirmed by several calculations that polarizabilities determined at this internuclear distance lead to much better agreement with experimental data than corresponding R_e values. The differences between R_0 and R_e for H_2 are significant; for example, we obtain $C_9 = 43.275$ for properties calculated at $R_e = 1.4$ au and 47.976 for R_0. For N_2 we use the experimental internuclear distance $R = 2.07432$ au [51].

Owing to the very large number of data (six systems, two- and three-body interactions) we discuss primarily the results obtained for X_2- and X_3-type systems and present only selected results for the mixed dimers and trimers.

3.2 Dispersion contribution to the interaction energy

The dependence of the C_6^{aa} and C_9^{aaa} coefficients on the choice of the basis set for the rare-gas atoms is illustrated in Table 1. As a reference we compare with the pseudo DOSD values of Kumar and Meath [28] and other semiempirical literature data [52–54] published prior to

Table 1. Basis set dependence of the dipole–dipole energy coefficient, C_6^{aa}, and of the triple-dipole coefficient, C_9^{aaa}, for the rare-gas atoms a = He, Ne, Ar and Kr. Atomic units

	He	Ne	Ar	Kr
C_6^{aa}				
d-aug-cc-pVQZ	1.4630	6.3958	65.3846	132.3651
t-aug-cc-pVQZ	1.4633	6.4163	65.4076	132.1820
d-aug-cc-pV5Z	1.4595	6.3711	65.0415	131.6223
t-aug-cc-pV5Z	1.4599	6.3704	64.8657	131.7913
d-aug-cc-pV6Z	1.4598			
t-aug-cc-pV6Z	1.4601			
Ref. [28]	1.458	6.383	64.30	129.6
Ref. [52]	1.47 ± 0.01	6.87 ± 0.4	67.2 ± 3.6	133 ± 9
Refs. [53, 54]	1.461	6.43	64.20	127.9
C_9^{aaa}				
d-aug-cc-pVQZ	1.4832	12.0774	530.7976	1635.8766
t-aug-cc-pVQZ	1.4834	12.1394	530.8278	1635.3663
d-aug-cc-pV5Z	1.4770	12.0074	526.8336	1617.4631
t-aug-cc-pV5Z	1.4774	12.0079	525.8923	1617.6288
d-aug-cc-pV6Z	1.4777			
t-aug-cc-pV6Z	1.4780			
Ref. [28]	1.472	11.95	518.3	1572
Ref. [52]	1.485 ± 0.06	12.75 ± 0.42	528.0 ± 12	1569 ± 36
Refs. [53, 54]	1.481	12.02	517.4	1554

Ref. [28]. For all the atoms we have almost reached convergence with respect to extension of the basis set, and the largest basis set C_6^{aa} and C_9^{aaa} coefficients are thus close to the CCSD basis set limit. Increasing the principal cardinal number always reduces the value of the coefficient. Increasing from the double to the triple level of augmentation generally leads to smaller corrections, with the sign of the change depending on the principal cardinal number.

All the results given in the following were obtained using the largest basis sets, i.e. the t-aug-cc-pV6Z basis for He and the t-aug-cc-pV5Z basis for the other atoms. For the molecules, we used the d-aug-cc-pV5Z basis for H_2 and the d-aug-cc-pVQZ basis for N_2.

Our best results for the rare-gas atom dimers and trimers are given in Table 2. Similar results for the H_2 and N_2 molecules are collected in Table 3. As an example of the accuracy that can be achieved for mixed system dimers, we present the rare gas–N_2 interaction coefficients in Table 4. We include for comparison reference values obtained in most cases again using semiempirical approaches. Deviations are in most cases less than 1%.

Table 2. Dipole–dipole, C_6^{ab}, and triple-dipole energy, C_9^{abc}, coefficients for the rare-gas atoms *a*, *b*, *c* = He, Ne, Ar and Kr. Atomic units. The basis set is the t-aug-cc-pV6Z for He and the t-aug-cc-pV5Z for Ne, Ar and Kr

System	This work	Literature
C_6^{ab}		
He–He	1.4601	1.458, 1.47 ± 0.01, 1.461[a]
He–Ne	3.0308	3.029, 3.13 ± 0.8, 3.041
He–Ar	9.5996	9.538, 9.82 ± 0.35, 9.546
He–Kr	13.517	13.40, 13.6 ± 0.6, 13.31
Ne–Ne	6.3704[b]	6.383, 6.87 ± 0.4, 6.43
Ne–Ar	19.613	19.50, 20.7 ± 1.3, 19.53
Ne–Kr	27.505	27.30, 28.7 ± 2.1, 27.12
Ar–Ar	64.866	64.30, 67.2 ± 3.6, 64.20
Ar–Kr	92.295	91.13, 94.3 ± 5.7, 90.44
Kr–Kr	131.79	129.6, 133 ± 9, 127.9
C_9^{abc}		
He–He–He	1.4780	1.472, 1.481[c]
He–He–Ne	2.9589	2.945, 2.961
He–He–Ar	10.296	10.21, 10.25
He–He–Kr	14.753	14.56, 14.55
He–Ne–Ne	5.9466	5.917, 5.95
He–Ne–Ar	20.469	20.28, 20.33
He–Ne–Kr	29.263	28.87, 28.80
He–Ar–Ar	73.022	72.15, 72.24
He–Ar–Kr	105.35	103.6, 103.3
He–Kr–Kr	152.36	149.1, 148.2
Ne–Ne–Ne	12.008	11.95, 12.02
Ne–Ne–Ar	40.814	40.41, 40.49
Ne–Ne–Kr	58.198	57.40, 57.20
Ne–Ar–Ar	144.37	142.5, 142.5
Ne–Kr–Kr	300.17	293.7, 291.2
Ar–Ar–Ar	525.89	518.3, 517.4
Ar–Ar–Kr	763.10	748.6, 744.6
Ar–Kr–Kr	1109.8	1083, 1074
Kr–Kr–Kr	1617.6	1572, 1554

[a] The literature results for C_6^{ab} are taken from Ref. [28], Ref. [52] and Refs. [53, 54] in this order

[b] Same coupled-cluster singles and doubles result as in Ref. [21]. See also references to other previous theoretical results therein

[c] The literature results for C_9^{abc} are taken from Ref. [28] and Refs. [53, 54] in this order

The results presented here were obtained using the CCSD approach and large basis sets and provide the presently most accurate theoretical values of the asymptotic dispersion coefficients for the energy. To describe all the dispersion effects more general formulas including damping functions are applied [55]; however, the asymptotic behaviour, given by the coefficients discussed here, is important as the limiting case. The good agreement between our results and the DOSD results confirms that we can use with confidence the same approach also to study the interaction effects on the electric dipole polarizability.

3.3 Dispersion contributions to the interaction polarizabilities

To estimate the accuracy of our results for the electric dipole polarizabilities we can compare our static properties with reference literature data. For atoms, we obtain (t-aug-cc-pV6Z basis set for He, t-aug-cc-pV5Z for the other atoms) $\alpha(\text{He}) = 1.3828$, $\alpha(\text{Ne}) = 2.6757$, $\alpha(\text{Ar}) = 11.1062$, $\alpha(\text{Kr}) = 16.9120$ and $\gamma(\text{He}) = 43.13$, $\gamma(\text{Ne}) = 110.21$, $\gamma(\text{Ar}) = 1169.2$ and $\gamma(\text{Kr}) = 2513.0$ au. Note that our definition of γ includes an extra factor of 3 in comparison with Ref. [17]. Our results are close to other recent reference state-of-the-art values: $\alpha(\text{He}) = 1.383192$ [56] $\alpha(\text{Ne}) = 2.673$ [57], $\alpha(\text{Ar}) = 11.15$ and $\alpha(\text{Kr}) = 16.85$ [58], $\gamma(\text{He}) = 43.104$ [14], $\gamma(\text{Ne}) = 110.2$, $\gamma(\text{Ar}) = 1179.0$ [59] and $\gamma(\text{Kr}) = 2810 \pm 90$ au [60]. We note that self-consistent-field values of the hyperpolarizabilities for Ne and Ar and a semiempirical value for Kr were used in Ref. [17] and that some of these differ significantly from the accurate results. For the H_2 molecule, we have $\bar{\alpha} = 5.17744$, $\Delta\alpha = 1.81947$ and $\gamma_{\|} = 621.34$ au at $R = 1.4$ au, to be compared with $\bar{\alpha} = 5.18149$, $\Delta\alpha = 1.80900$ [61] and $\gamma_{\|} = 603.6$ au [62]. For N_2 we obtain $\bar{\alpha} = 11.648$, $\Delta\alpha = 4.478$ and $\gamma_{\|} = 889.02$ au. For comparison, we have $\bar{\alpha} = 11.562$, $\Delta\alpha = 4.431$ au [63] and $\gamma_{\|} = 868.2 \pm 6$ au [59] as a best estimate from an unrelaxed CCSD d-aug-cc-pV5Z basis set calculation. This confirms that our static polarizabilities and hyperpolarizabilities are accurate also for the molecules studied.

For interaction polarizabilities in the dimers, both the asymptotic coefficients $A_6(\|)$ and $A_6(\perp)$ as well as the integrals which determine their values (Eqs. 18, 19) have been discussed in the literature. To simplify the comparison with literature data we have given the results for all the quantities in Table 5. For the nonadditive three-body contributions to the polarizability following Ref. [17] we give in Tables 6, 7 and 8 only the raw integrals as defined in Eqs. (23) and (24). In addition, similarly to Ref. [17], we use for molecules the symbol $< \ldots >$ to denote an isotropic average, which, for example, for the polarizability is $(\alpha_{\|} + 2\alpha_{\perp})/3$.

For He and H_2 previous results have been obtained using the accurate data of Refs. [14, 15]. For these two-electron systems the CCSD polarizabilities and hyperpolarizabilities differ from those of Refs. [14, 15]

Table 3. Isotropic dispersion energy coefficients, C_6^{mm}, C_9^{mmm}, and corresponding anisotropic coefficients for $m = H_2$ and N_2. Atomic units. The basis sets are d-aug-cc-pV5Z for H_2 and d-aug-cc-pVQZ for N_2. For the hydrogen molecule an interatomic distance corresponding to R_0 was employed in the calculations, see text

	This work	Ref. [29]	Others (DOSD)	Others (calc)
$C_6^{H_2H_2}$	12.043	12.09	12.10 [64], 12.38 [65, 66], 12.1 [23]	12.09 [67], 12.14 [49], 12.30 [68], 12.15 [69], 12.62 [70]
$\Gamma_{H_2H_2}$	0.1017	0.1006	0.1007 [65, 66], 0.112 [23]	0.103 [67], 0.105 [49], 0.1021 [68], 0.1009 [69]
$\Delta_{H_2H_2}$	0.01091	0.0108	0.0108 [65, 66], 0.013 [23]	0.0112 [67], 0.0117 [49], 0.0109 [68], 0.0107 [69]
$C_6^{N_2N_2}$	73.555	74.43	73.33 [64], 73.8 [23]	71.46 [68], 75.63 [70]
$\Gamma_{N_2N_2}$	0.1101	0.1068	0.106 [23]	0.1175 [68], 0.1293 [70]
$\Delta_{N_2N_2}$	0.01258	0.0121	0.012 [23]	0.0147 [68], 0.0174 [70]
	This work	**Ref. [71]**		
$C_9^{H_2H_2H_2}$	47.976	48.50		
Γ_{H_2}	0.10980	0.1098		
$\Gamma_{H_2H_2}$	0.01231	0.01240		
$\Gamma_{H_2H_2H_2}$	0.001401	0.001427		
$C_9^{N_2N_2N_2}$	617.53	619.93		
Γ_{N_2}	0.1177	0.1166		
$\Gamma_{N_2N_2}$	0.01405	0.01391		
$\Gamma_{N_2N_2N_2}$	0.001694	0.001685		

Table 4. $C_6^{aN_2}$ and Γ_{aN_2}, where a = He, Ne, Ar and Kr. Atomic units

	This work	Ref. [29]	Others (DOSD)	Others (calc)
$C_6^{HeN_2}$	10.254	10.23	10.22 [64], 10.30 [23], 10.10 [72, 73, 74]	9.795 [68], 10.27 [70]
$C_6^{NeN_2}$	21.015	20.97	20.95 [28, 29, 64], 21.8 [23], 21.44 [72, 73, 74]	18.88 [68], 21.75 [70]
$C_6^{ArN_2}$	69.174	68.69	68.64 [28, 29, 64], 71.6 [23], 69.02 [72, 73, 74]	
$C_6^{KrN_2}$	98.027	97.28	97.20 [28, 29, 64], 101 [23]	
Γ_{HeN_2}	0.1071	0.1027	0.101 [23], 0.1143 [72, 73, 74]	0.1126 [68], 0.1253 [70]
Γ_{NeN_2}	0.1048	0.0999	0.096 [23], 0.1108 [72, 73, 74]	0.1088 [68], 0.1226 [70]
Γ_{ArN_2}	0.1107	0.1074	0.103 [23], 0.1194 [72, 73, 74]	
Γ_{KrN_2}	0.1120	0.1087	0.107 [23]	

Table 5. Dispersion contribution to pair polarizabilities of X_2, for X = He, Ne, Ar, Kr. W_1^{aa} and W_2^{aa} were defined in Eqs. (18) and (19). The last two columns report data obtained assuming Kleinman's symmetry, i.e. $\gamma_{xxzz} = \gamma_{zzzz}/3$. The rows labelled Ref. [17] were filled in this work using the values for the frequency integrals given in that reference. The purely classical values were subtracted from the data of Ref. [18]

	W_1^{aa}	W_2^{aa}	$A_6^{aa}(\parallel)$	$A_6^{aa}(\perp)$	$A_6^{aa,K}(\parallel)$	$A_6^{aa,K}(\perp)$
He–He						
This work	9.4621	8.4105	39.488	23.426	39.042	22.310
Ref. [17]	9.4167[a]	8.4170[a]	39.418	23.343	38.994	22.282
Ref. [18]			35	20		
Ref. [32][a]			39.42	23.34		
Ref. [7]			40.19	23.39		
Ne–Ne						
This work	43.612	40.708	186.96	109.21	185.72	106.13
Ref. [17]	40	36	168	99	166	95
Ref. [18]			200	114		
Ar–Ar						
This work	1486.9	1191.5	5873.8	3598.3	5748.5	3284.8
Ref. [17]	1240	1120	5220	3081	5169	2954
Ref. [18]			5490	3150		
Ref. [75][b]					4981	
Kr–Kr						
This work	3602.8	3305.5	15298	8985.2	15172	8669.7
Ref. [17]	3760	3390	14609	8580	15657	8947
Ref. [18]			17333	9333		

[a] Based on the data of Refs. [14, 15]
[b] Multiconfiguration self-consistent field

only through the use of a finite basis set and our final results for the interaction-induced polarizabilities are therefore also very similar. We do not discuss in detail all the dimers and trimers involving only He atoms and H_2 molecules; selected results are given in the tables. We concentrate instead on the interactions involving the heavier atoms and N_2 molecules.

The differences between our results and those of Champagne et al. [17] are due to their use of the CRA. Moreover, they used values of atomic (hyper)polarizabilities which, as discussed previously, are not sufficiently accurate. In the CRA (cf. Eqs. 44, 51 of Ref. [17]) the ratio γ/α is required. We can rescale the results of Champagne et al. for identical atoms using the coefficient $(\gamma/\alpha)_{\mathrm{this,work}}/(\gamma/\alpha)_{\mathrm{Champagne}}$. For He, the rescaling factor is 1.0009, and it is irrelevant. For the larger atoms the change is instead significant. In particular, for Ne γ^{SCF} is far too small, the rescaling coefficient is 1.4274, and it leads to a much overestimated correction. For example, for the two-body interactions (for which a similar approximation was applied in Ref. [17]), the rescaled values are $A_6^{\mathrm{NeNe}}(\|) = 239.9$ and $A_6^{\mathrm{NeNe}}(\perp) = 141.7$, whereas using the accurate W_1^{NeNe} and W_2^{NeNe} integrals we obtain 186.96 and 109.21 (Table 5). For Ar, the rescaling coefficient is 1.1811 and using the same procedure we obtain 6165 and 3639, in much better agreement with our results. Finally, for Kr, we multiply by 1.1113 and get 16236 and 9535, again overestimating the correction to the original values. Similar results are obtained for the three-body nonadditive CRA terms. The rescaling overestimates the corrections, in particular for Ne.

Significant savings in the computational effort may be achieved assuming Kleinman's approximation, $\gamma_{xxzz} = \gamma_{zzzz}/3$, a relation which is exact for atomic static hyperpolarizabilities. As shown in Table 5, for all the atoms the $A_6^{aa,K}$ coefficients derived within this approximation are relatively close to the accurate A_6^{aa} values. For three-atom interactions, Kleinman's approximation implies $W_1^{abc} = W_2^{abc}$ (Eqs. 20, 21), and, as can be seen from Table 7, such an estimate can be applied, although it is less accurate than for two-body effects.

Table 6. Dispersion contribution to pair polarizabilities for some binary A–B species. See text and caption to Table 5

A	B	W_1^{ab}		W_2^{ab}	
		This work	Ref. [17]	This work	Ref. [17]
$\langle H_2 \rangle$	He	93.887	92.638	84.120	83.184
$\langle H_2 \rangle$	$\langle H_2 \rangle$	325.00	320.94	297.17	293.73
$\langle N_2 \rangle$	$\langle N_2 \rangle$	1037.1	1130	981.29	1020

Table 7. Dispersion contribution to triple-dipole polarizabilities of X_3, for X = He, Ne, Ar, Kr. W_1^{aaa} and W_2^{aaa} were defined in Eqs. (23) and (24). The data in Ref. [17] were based on accurate ab initio calculations for He, whereas those for Ne, Ar and Kr were originally obtained using constant-ratio approximations, see text, and self-consistent-field static α and γ values (semiempirical value for Kr α)

X	W_1^{aaa}		W_2^{aaa}	
	This work	Ref. [17]	This work	Ref. [17]
He	11.305	11.280	10.336	10.338
Ne	101.92	87.4	97.721	80.6
Ar	13453	11700	11834	10800
Kr	53343	53300	50505	49200

4 Conclusions

In this article we have discussed only the dispersion contributions to interaction polarizabilities. As shown in Ref. [17], for both dimers and trimers the other contributions can be obtained more easily, requiring only the knowledge of the static polarizability. We have not discussed the higher multipole contributions. In principle, these can easily and straightforwardly be calculated at the CCSD level; however, the basis set requirements increase for the quadrupole, octupole, etc., polarizabilities, making calculations of the higher multipole contributions at the same level of accuracy more complicated.

In summary, accurate results can be obtained for interaction-induced polarizabilities at large internuclear distances. Separate calculations for the subsystems enable the use of large basis sets and proper treatment of correlation effects. The most complicated dispersion contributions require only the knowledge of hyperpolarizabilities that depend on one imaginary frequency and they can be obtained from frequency dispersion expansions.

Similarly to C_6 and C_9, long-range coefficients can be used to determine accurate asymptotic values of dispersion contributions to two- and three-body polarizabilities. They are needed even if shorter internuclear distance exchange and overlap are taken into account and/or some damping functions are applied in the R^{-n} expansion. Also, accurate long-range coefficients provide benchmark values for simpler approximations, such as the CRA approach, which may be applied for larger molecules.

Table 8. Dispersion contribution to triple-dipole polarizabilities for some ternary A–B–C species. See text and caption to Table 8

A	B	C	W_1^{abc}		W_2^{abc}	
			$\gamma_1(-i\omega; i\omega, 0, 0)$	Ref. [17]	$\gamma_2(-i\omega; i\omega, 0, 0)$	Ref. [17]
$\langle H_2 \rangle$	He	He	120.26	118.75	109.54	108.25
$\langle H_2 \rangle$	He	$\langle H_2 \rangle$	423.07	418.06	391.19	386.61
$\langle H_2 \rangle$	$\langle H_2 \rangle$	$\langle H_2 \rangle$	1511.8	1494.7	1413.6	1397.5
$\langle N_2 \rangle$	$\langle N_2 \rangle$	$\langle N_2 \rangle$	10616	11200	10176	10300

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