The effect of intermolecular interactions on the electric properties of helium and argon. I. *Ab initio* calculation of the interaction induced polarizability and hyperpolarizability in He_2 and Ar_2

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The frequency-dependent interaction induced polarizabilities and second hyperpolarizabilities are calculated for He_2 at the coupled cluster singles and doubles and full configuration interaction levels and for Ar_2 at the coupled cluster singles and doubles level. The frequency-dependence is approximated by a power series to second-order in the frequency arguments using Cauchy moments and hyperpolarizability dispersion coefficients. Using large correlation consistent basis sets, results close to the basis set limit are obtained. The computed curves for the interaction induced (hyper-) polarizabilities are tabulated for a range of internuclear distances. The data are employed in a companion paper to make for the first time a direct comparison between the experimentally determined pressure dependence of an ESHG hyperpolarizability and *ab initio* calculated hyperpolarizability second virial coefficients. © *1999 American Institute of Physics.* [S0021-9606(99)31146-6]

I. INTRODUCTION

The interaction of molecules and light is an important research topic in chemistry and physics, both experimentally and theoretically. Linear one-photon optical processes can be observed with conventional light sources, whereas the experimental study of nonlinear optical effects is directly linked to lasers. The high intensity and the coherence that can be achieved with them make it possible to detect multiphoton second-, third-, and higher-order optical effects.[1–6] From a computational point of view, highly electron correlated methods as well as large basis sets are required to obtain results that compare well with experiment and have predictive power.

Accurate determination of frequency dependent polarizabilities and hyperpolarizabilities of molecules is important for the description of nonlinear optical experiments and it has become possible using recent response function approaches. A more complex situation is encountered if one is interested in the pressure-dependence and therewith also in the temperature-dependence of linear and nonlinear optical properties. This requires the determination of second and higher virial coefficients for the optical properties under investigation. In a previous article[7] we reported interaction induced polarizabilities and hyperpolarizabilities for the Ar_2 van der Waals complex for a range of internuclear distances. The frequency-dependence of the properties was accounted for through the expansion in the frequency arguments in terms of Cauchy moments and hyperpolarizability dispersion coefficients. We used the coupled cluster singles and doubles method (CCSD), which is known to describe dynamical correlation very efficiently and to be size-extensive, and selected an adequate basis set within Dunning's series. The results were employed to compute the dielectric, refractivity, Kerr, and hyperpolarizability second virial coefficients and in most cases good agreement with the available experimental data was found. Basis set incompleteness was found to be the largest source of error. Another source of error for the comparison of the hyperpolarizability second virial coefficient with a recent ESHG experiment was the unknown accuracy of the second virial coefficient for the hyperpolarizability of helium gas. This is needed since the experiment provided only data for the hyperpolarizability ratios between two gases. For the hyperpolarizability virial coefficient of the helium gas we used an *ab initio* value for the static limit result, which has been calculated quite recently.[8] The dispersion of the hyperpolarizability was thus not accounted for. Considering this, we proceed here by improving some of the Ar_2 results using a larger basis set and evaluate the frequency-dependent polarizability and hyperpolarizability

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for the He_2 dimer with a technique similar to that used for Ar_2.

A considerable number of publications on these properties is available in the literature. The theoretical studies highlight the difficulties encountered in evaluating contributions which are small compared to the properties of the noninteracting monomers. Among the most recent studies, Fowler *et al.* determined the He_2 pair polarizability functions and studied their long-range behavior, finding that between 5 and 8 bohr the R^{-6} and R^{-8} terms can be considered equally important in the parallel contribution, and that between 3 and 4.5 bohr the R^{-6} term dominates the power series expansion for the perpendicular contribution.[9] To evaluate the dynamic polarizabilities they used an electron uncorrelated method and a basis set containing up to *f* functions.

Moszynski *et al.* applied the symmetry-adapted perturbation theory (SAPT) to the study of the interaction-induced polarizability of He_2.[10–12] When the results were used in quantum-statistical calculations of the binary collision-induced Raman spectra, the agreement with experiment was found to be quite good. The authors also calculated the dielectric second virial coefficients, including first and second order quantum corrections[11] and with a fully quantum statistical method.[10] The quantum effects resulted to be significant for temperatures below 50 K. The discrepancies with respect to experiment were considerable, and the authors suggested that new measurements should be performed.

Bishop and Dupuis carried out an evaluation of the interaction induced hyperpolarizability of the He dimer using as best correlation treatment the fourth-order Møller–Plesset perturbation theory (MP4).[8] The results were analyzed in terms of long-range dispersion and dipole-induced-dipole effects and virial coefficients were evaluated.

The interaction polarizability of the argon dimer at different internuclear distances was calculated by Joslin *et al.* using second-order Møller–Plesset theory (MP2).[13] The approximation was not accurate enough to describe the property quantitatively and the results were far away from the experimental data.

The various experimental results for the second dielectric virial coefficients for hyperpolarizabilities show some discrepancies.[14–16] Only few measurements have been reported for the pressure dependence of second hyperpolarizabilities, in particular for the ESHG process. See, for example, Refs. 14–17. In one of the most recent studies Donley and Shelton measured the electric field induced second generation (ESHG) hyperpolarizability ratios $\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{Ar})/\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{H_2})$, $\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{N_2})/\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{H_2})$, and $\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{H_2})/\gamma_{\parallel}^{\mathrm{ESHG}}(\mathrm{He})$ as a function of the density with a 0.1% accuracy at a wavelength of 514.5 nm.[16,17]

A way of checking the quality of these data and of the underlying model employed in the expansion in virial coefficients is provided by *ab initio* calculations of accurate curves for the interaction induced properties followed by the evaluation of the virial coefficients using either a semiclassical approximation or a full quantum description.[10–12] In this paper we report the results of accurate calculations of the frequency-dependent interaction induced polarizabilities and hyperpolarizabilities for the He_2 van der Waals complex using the coupled cluster singles and doubles (CCSD) and the full configuration interaction (FCI) methods and improved CCSD calculations for the static interaction (hyper-) polarizabilities of Ar_2. In a companion paper (''Part II'' below), we employ these results to compute semiclassically the appropriate second virial coefficients.[18]

The article is organized as follows: In Sec. II the basic equations are summarized and the computational procedures are described, in Sec. III we present and discuss the results, and in the last section we give some concluding remarks.

II. COMPUTATIONAL DETAILS

The interaction induced polarizability $\Delta\alpha(-\omega;\omega)$ and the parallel component of the second hyperpolarizability $\Delta\gamma_{\parallel}(\omega_0;\omega_1,\omega_2,\omega_3)$ (we use the symbol Δ to indicate interaction induced; see Ref. 7 for details on definitions and notations) depend on both the internuclear distance of the dimer and the frequency arguments of the property. To reduce the computational costs of the calculations we follow the approach devised in Ref. 7 and expand $\Delta\alpha(-\omega;\omega)$ and $\Delta\gamma_{\parallel}(\omega_0;\omega_1,\omega_2,\omega_3)$ as power series in the frequency arguments truncated to second order, i.e. after the lowest-order dispersion contribution,

$$\Delta\alpha(-\omega;\omega)=\Delta\alpha+\omega^2\Delta S(-4)+\mathcal{O}(\omega^4), \tag{1}$$

$$\Delta\gamma_{\parallel}(\omega_0;\omega_1,\omega_2,\omega_3) = \Delta\gamma_{\parallel}+(\omega_0^2+\omega_1^2+\omega_2^2+\omega_3^3)\Delta(\gamma_{\parallel}\times A)+\mathcal{O}(\omega_i^4), \tag{2}$$

where $\omega_0=-\omega_1-\omega_2-\omega_3$. The polarizabilities, Cauchy moments $[S(-4)]$, hyperpolarizabilities and hyperpolarizability dispersion coefficients $[(\gamma\times A)]$ are calculated for He_2 at the FCI and the CCSD levels, and for Ar_2 only at the CCSD level.

For the FCI calculations on the helium dimer we used the *d*-aug-cc-pVTZ basis set, developed by Dunning and co-workers,[19–23] extended with an uncontracted $(3s3p2d1f)$ set of midbond functions.[24,25] At the CCSD level we have used the *d*-aug-cc-pV5Z basis set, augmented with the same set of midbond functions. The same set has also been employed in the coupled cluster singles and doubles with connected triples [CCSD(T)] calculations of the potential energy. In the following, we will denote the two sets as ''*d*-aug-cc-pVTZ-3321'' and ''*d*-aug-cc-pV5Z-3321,'' respectively. They were chosen based on a study for He_2 at the equilibrium distance $R_e=5.6$ a.u., and whose results are summarized in Table I. The basis set convergence is quite different at the CCSD and at the FCI level for the interaction potential $V(R)$. Changes with basis sets similar to those seen at the FCI level are first obtained with CCSD(T). For the interaction induced (hyper-) polarizabilities instead the changes with the basis set at the CCSD level and at the FCI level proceed very much in parallel. Thus, for the average $\Delta\alpha_{\mathrm{ave}}$, the anisotropy $\Delta\alpha_{\mathrm{ani}}$ and for $\Delta\gamma_{\parallel}$ calculated in the *d*-aug-cc-pVTZ-3321 basis set at the FCI level the difference between the CCSD results in the *d*-aug-cc-pV5Z-3321 and the *d*-aug-cc-pVTZ-3321 sets should provide a reliable estimate of the remaining basis set error. After adding these corrections to the FCI/*d*-aug-cc-pVTZ-3321 results we

TABLE I. Helium. Basis set study for the potential V and the interaction induced changes of the polarizabilities α_{ave} and α_{ani} and the hyperpolarizability $\gamma_{\|}$ for He_2 at $R_e = 5.6$ a.u. The numbers in parentheses are the differences to the results obtained with basis set immediately above in the table, i.e., for the *d*-aug-cc-pVQZ-3321 the difference between this basis and the results obtained with the *d*-aug-cc-pVTZ-3321 basis.

	$V/10^{-6}$ a.u.			$\Delta\alpha_{ave}/10^{-3}$ a.u.		$\Delta\alpha_{ani}/10^{-3}$ a.u.		$\Delta\gamma_{\|}$/a.u.	
Basis set	CCSD	CCSD(T)	FCI	CCSD	FCI	CCSD	FCI	CCSD	FCI
aug-cc-pVDZ-3321	−27.9890	−32.1947	−33.3786	−1.513	−1.372	61.248	63.340	−1.1992	−1.1630
d-aug-cc-pVDZ-3321	−28.7950	−33.0038	−34.0725	−1.271	−1.128	61.086	63.171	−0.8564	−0.8136
	(−0.8060)	(−0.8091)	(−0.6939)	(0.242)	(0.244)	(−0.162)	(−0.169)	(0.3428)	(0.3494)
d-aug-cc-pVTZ-3321	−28.7168	−33.3251	−34.3923	−1.171	−1.048	59.931	62.023	−0.9115	−0.8821
	(0.0782)	(−0.3213)	(−0.3198)	(0.100)	(0.079)	(−1.155)	(−1.148)	(−0.0551)	(−0.0686)
d-aug-ccpVQZ-3321	−28.7894	−33.5571	−34.6103	−1.122	−0.995	59.858	61.957	−0.9048	−0.8760
	(−0.0726)	(−0.2320)	(−0.2180)	(0.049)	(0.054)	(−0.073)	(−0.066)	(0.0067)	(0.0062)
d-aug-cc-pV5Z-3321	−28.8513	−33.6612		−1.108		59.787		−0.8993	
	(−0.0619)	(−0.1041)		(0.014)		(−0.071)		(0.0055)	
d-aug-cc-pV6Z-3321	−28.8892	−33.7201		−1.109		59.774		−0.8961	
	(−0.0379)	(−0.0589)		(−0.001)		(−0.013)		(0.0032)	

expect an accuracy of a few percent for these properties, depending on the distance. For the interaction potential a good basis set correction is obtained by adding the difference between the CCSD(T)/*d*-aug-cc-pV5Z-3321 and the CCSD(T)/*d*-aug-cc-pVTZ-3321 potential energy curves to the FCI/*d*-aug-cc-pVTZ-3321 results. In the calculations on He_2 all four electrons have been correlated.

The interaction induced polarizability and hyperpolarizability of the argon dimer have recently been investigated[7] using the CCSD response approach and a *d*-aug-cc-pVTZ-33211 basis set, where ''33211'' denotes a $(3s3p2d1f1g)$ set of midbond functions.[24,25] In Ref. 7 it was found that, due to a cancellation of a large positive and a large negative contribution, the final results for the second virial coefficients were very sensitive to the choice of the basis set. In that study we chose the *d*-aug-cc-pVTZ-33211 basis set, since it provided an acceptable compromise between accuracy and computational costs for the calculation of both the static properties and the dispersion coefficients. The calculations showed, however, that the frequency-dependence of the interaction induced properties, and thereby also the dispersion of the virial coefficients, make a relatively small contribution to the total results for Ar_2. A computational more balanced approach for obtaining accurate results is therefore to calculate the less expensive static properties with a higher level basis set, and combine the static values with dispersion coefficients computed at a lower level. For the argon dimer we calculated new, improved curves for static interaction induced polarizabilities and hyperpolarizabilities using the larger *d*-aug-cc-pVQZ-33211 basis set, and combined them with the dispersion coefficients obtained in Ref. 7 with the *d*-aug-cc-pVTZ-33211 basis set. In the calculations on the argon dimer we have frozen the occupation of the lowest ten orbitals, which correspond to the $1s^2 2s^2 2p^6$ core of the argon atoms.

All reported interaction energies and interaction induced properties are counterpoise corrected using the scheme by Boys and Bernardi.[26] For the FCI calculations we used the LUCIA program.[27] The CCSD calculations are carried out using the implementation of the CCSD response approach[28] in the integral-direct coupled cluster program described in Refs. 29–33, which is part of the DALTON program package.[34]

III. RESULTS AND DISCUSSION

In Fig. 1 we have plotted the potential energy curves obtained at the CCSD/*d*-aug-cc-pVTZ-3321, the CCSD/*d*-aug-cc-pV5Z-3321, the CCSD(T)/*d*-aug-cc-pVTZ-3321 and the FCI/*d*-aug-cc-pVTZ-3321 levels in comparison with the HFD-B3-FCI1 and potential of Aziz *et al.*,[35] which is currently considered as the most accurate (semiempirical) potential for He_2. The plot shows clearly that although the *d*-aug-cc-pVTZ-3321 basis set was chosen as a compromise between accuracy and computational costs for the interaction induced (hyper-) polarizabilities and dispersion coefficients, it has the flexibility to describe very accurately the intermolecular interaction in the helium dimer; the FCI results for the equilibrium distance r_0 and for the well depth D_0 are within, respectively, 0.2% and 0.9% of the HFD-B3-FCI1 values. Very recently van de Bovenkamp and van

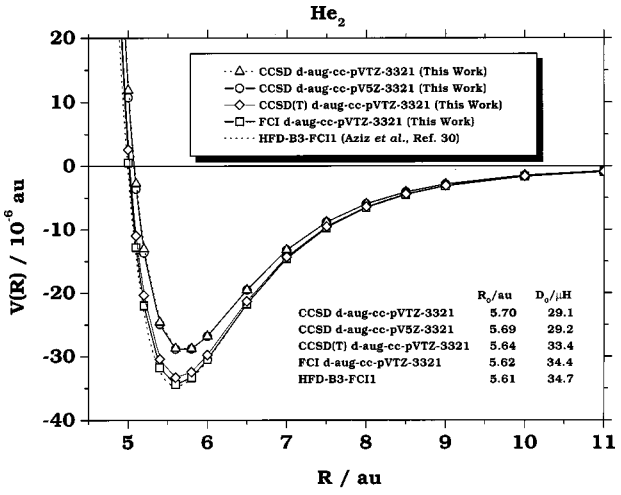


FIG. 1. Potential energy curves for the helium dimer calculated at various levels of approximation in comparison with the HFD-B3-FCI1 potential of Ref. 35.

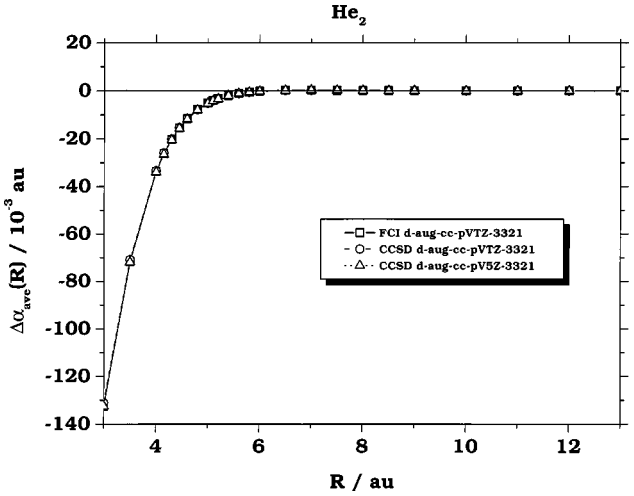


FIG. 2. The interaction induced change of the static isotropic polarizability in He_2 at various levels of approximation.

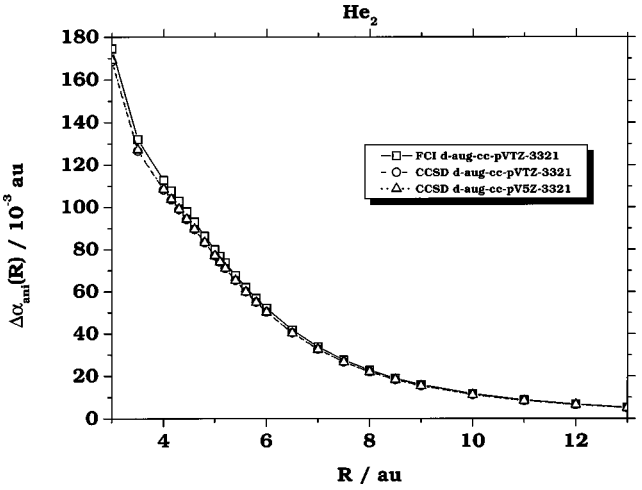


FIG. 4. The interaction induced polarizability anisotropy in He_2.

Duijnefeldt[36] obtained a best estimate for the interaction potential at $R=5.6$ a.u of 10.99 ± 0.02 K or $34.80\pm0.06\times10^{-6}$ a.u. from a large MRCI calculation and a basis set incompleteness correction calculated at the CCSD(T) level. Our FCI/*d*-aug-cc-pVTZ value for the interaction potential is within 1.2% of this benchmark result; at the FCI/*d*-aug-cc-pVQZ level the difference is reduced to 0.5%. The CCSD potential curves, on the other hand, are off by about 20% around the equilibrium distance, although they are asymptotically correct. The CCSD(T) potential recovers about 80% of the correlation effects beyond CCSD. This shows the well-known fact that for such weakly bound van der Waals complexes the inclusion of at least connected triples in the correlation treatment is mandatory to obtain accurate potential energy curves.[37–39] It is therefore surprising that correlation effects, beyond the CCSD level, apparently have only minor effects on the isotropic interaction induced polarizability $\Delta\alpha_{\mathrm{ave}}$ and the hyperpolarizability $\Delta\gamma_{\parallel}$, shown in Figs. 2 and 3, respectively. In the range of distances investigated here, 3–13 a.u., the CCSD results in the *d*-aug-cc-pVTZ-3321 and *d*-aug-cc-pV5Z-3321 and the FCI results in the *d*-aug-cc-pVTZ-3321 basis sets are almost indistinguishable on the scales of Figs. 2 and 3. The same holds in the case of the lowest-order dispersion coefficients for these properties, $\Delta S_{\mathrm{ave}}(-4)$ and $\Delta(\gamma_{\parallel}\times A)$. Only for the induced polarizability anisotropy $\Delta\alpha_{\mathrm{ani}}$, shown in Fig. 4, and for the corresponding induced Cauchy moment $\Delta S_{\mathrm{ani}}(-4)$ the differences between the FCI and the CCSD results are somewhat larger, but they are still small compared to the effect on the potential energy V. The final results at the FCI/*d*-aug-cc-pVTZ-3321 and CCSD/*d*-aug-cc-pV5Z-3321 levels for 25 interatomic distances are collected in Tables II and III.

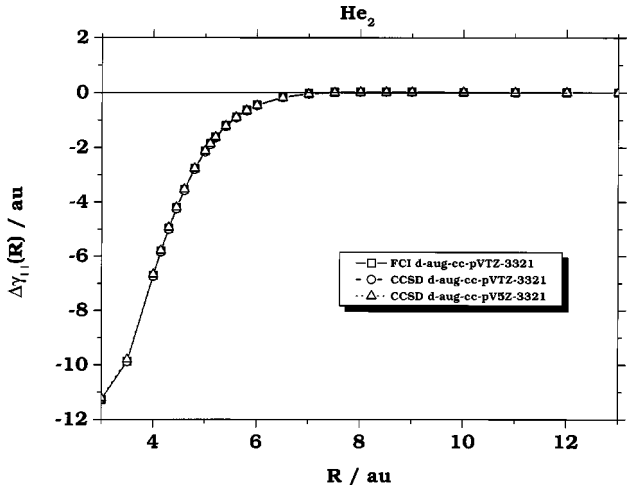


FIG. 3. The interaction induced change of the static isotropic hyperpolarizability in He_2.

The interaction induced static polarizability $\Delta\alpha_{\mathrm{ave}}$ of He_2 has been computed previously by Dacre[40] at the SCF and configuration interaction singles and doubles (CISD) levels. Bishop and Dupuis have recently calculated $\Delta\alpha_{\mathrm{ave}}$ and $\Delta\gamma_{\parallel}$ at the SCF, MP2, and MP4 levels using a basis set of 59 functions on each helium atom.[8] The results of Dacre and those of Bishop and Dupuis are in reasonable good qualitative, but not quantitative, agreement with our results for the static interaction induced properties. The trends in the SCF, MP2, and MP4 results of Ref. 8 support our finding that the static interaction induced properties are only moderately sensitive to the level of the correlation treatment.

In Table IV we have collected the static interaction induced polarizability and hyperpolarizability for the argon dimer, calculated at the CCSD/*d*-aug-cc-pVQZ-33211 level. The improved results for the interaction induced hyperpolarizability $\Delta\gamma_{\parallel}$ are shown in Fig. 5 in comparison with the *d*-aug-cc-pVTZ-33211 results taken from Ref. 7. As anticipated in Ref. 7, the positive branch of $\Delta\gamma_{\parallel}(R)$, i.e., for $R>8$ a.u., becomes somewhat smaller in the more complete basis set—on the average by about 15%–20%. Also for the negative branch, in particular in the range of 5.5–6.0 a.u., the absolute values in the *d*-aug-cc-pVQZ-33211 basis set become slightly smaller, opposite to what has been estimated in Ref. 7 based on the *t*-aug-cc-pVQZ-33211 result for an internuclear distance of 7.0 a.u. Nevertheless, these changes in the curve for $\Delta\gamma_{\parallel}(R)$ result in a considerable decrease of the weighted integral entering the hyperpolarizability second virial coefficient B_{γ}, which will make the disagreement between the semiclassical approximation for B_{γ} and experi-

TABLE II. Helium. FCI results for He_2 in the *d*-aug-cc-pVTZ-3321 basis set for the dependence of the potential V (in 10^{-6} a.u.), the interaction induced polarizabilities $\Delta\alpha_{ave}$ and $\Delta\alpha_{ani}$ (in 10^{-3} a.u.), Cauchy moments $\Delta S_{ave}(-4)$ and $\Delta S_{ani}(-4)$ (in 10^{-3} a.u.), hyperpolarizability $\Delta\gamma_{\parallel}$ (in a.u.), and hyperpolarizability dispersion $\Delta(\gamma_{\parallel}\times A)$ in (a.u.) on the interatomic distance R (in a.u.).

R	V	$\Delta\alpha_{ave}$	$\Delta S_{ave}(-4)$	$\Delta\alpha_{ani}$	$\Delta S_{ani}(-4)$	$\Delta\gamma_{\parallel}$	$\Delta(\gamma_{\parallel}\times A)$
3.00	12058.7808	−132.476	−339.090	174.603	283.439	−11.2692	−29.7428
3.50	3566.7686	−71.650	−212.383	131.981	174.013	−9.8709	−29.0999
4.00	944.7841	−33.684	−114.433	112.790	158.382	−6.7124	−21.2324
4.15	610.6509	−26.229	−92.936	107.842	157.809	−5.8095	−18.7754
4.30	383.1701	−20.205	−74.762	102.911	157.220	−4.9741	−16.4366
4.45	229.9731	−15.391	−59.583	97.955	156.136	−4.2166	−14.2584
4.60	128.1917	−11.585	−47.045	92.977	154.309	−3.5411	−12.2650
4.80	45.3906	−7.770	−33.824	86.365	150.582	−2.7669	−9.9112
5.00	0.5364	−5.068	−23.881	79.872	145.464	−2.1289	−7.9027
5.10	−12.8184	−4.040	−19.918	76.703	142.456	−1.8567	−7.0223
5.20	−22.0063	−3.188	−16.523	73.600	139.201	−1.6131	−6.2199
5.40	−31.7459	−1.905	−11.160	67.631	132.112	−1.2030	−4.8325
5.60	−34.3923	−1.048	−7.313	62.023	124.514	−0.8821	−3.7052
5.80	−33.3218	−0.491	−4.597	56.812	116.689	−0.6346	−2.8017
6.00	−30.4918	−0.139	−2.713	52.009	108.870	−0.4463	−2.0866
6.50	−21.7544	0.226	−0.282	41.750	90.380	−0.1596	−0.9200
7.00	−14.5979	0.267	0.480	33.724	74.415	−0.0322	−0.3353
7.50	−9.7126	0.217	0.604	27.503	61.299	0.0173	−0.0676
8.00	−6.5306	0.156	0.526	22.676	50.776	0.0318	0.0398
8.50	−4.4699	0.109	0.410	18.901	42.394	0.0321	0.0723
9.00	−3.1224	0.075	0.308	15.915	35.704	0.0276	0.0732
10.00	−1.6176	0.038	0.173	11.593	25.973	0.0174	0.0507
11.00	−0.8970	0.022	0.103	8.708	19.476	0.0103	0.0305
12.00	−0.5256	0.015	0.066	6.708	14.981	0.0062	0.0181
13.00	−0.3219	0.010	0.043	5.275	11.770	0.0039	0.0108

TABLE III. Helium. CCSD results for He_2 in the *d*-aug-cc-pV5Z-3321 basis set for the dependence of the potential V (in 10^{-6} a.u.), the interaction induced polarizabilities $\Delta\alpha_{ave}$ and $\Delta\alpha_{ani}$ (in 10^{-3} a.u.), Cauchy moments $\Delta S_{ave}(-4)$ and $\Delta S_{ani}(-4)$ (in 10^{-3} a.u.), hyperpolarizability $\Delta\gamma_{\parallel}$ (in a.u.), and hyperpolarizability dispersion $\Delta(\gamma_{\parallel}\times A)$ in (a.u.) on the interatomic distance R (in a.u.).

R	V	$\Delta\alpha_{ave}$	$\Delta S_{ave}(-4)$	$\Delta\alpha_{ani}$	$\Delta S_{ani}(-4)$	$\Delta\gamma_{\parallel}$	$\Delta(\gamma_{\parallel}\times A)$
3.00	12086.0857	−130.984	−334.376	169.055	274.314	−11.2215	−30.1778
3.50	3600.3362	−70.876	−209.056	127.135	166.533	−9.7998	−29.1749
4.00	970.3292	−33.408	−112.685	108.524	151.252	−6.6715	−21.2278
4.15	631.6651	−25.984	−91.562	103.731	150.767	−5.7094	−18.7699
4.30	404.8795	−20.165	−73.709	99.085	150.424	−4.9416	−16.4314
4.45	247.4413	−15.342	−58.794	94.295	149.488	−4.2040	−14.2602
4.60	143.3526	−11.578	−46.472	89.526	147.878	−3.5356	−12.2741
4.80	57.8589	−7.800	−33.471	83.186	144.476	−2.7689	−9.9307
5.00	10.7433	−5.119	−23.687	76.954	139.708	−2.1365	−7.9323
5.10	−3.5919	−4.098	−19.784	73.909	136.882	−1.8666	−7.0567
5.20	−13.6695	−3.249	−16.438	70.927	133.811	−1.6248	−6.2587
5.40	−24.9453	−1.968	−11.150	65.185	127.092	−1.2179	−4.8793
5.60	−28.8513	−1.108	−7.352	59.787	119.858	−0.8993	−3.7587
5.80	−28.8126	−0.545	−4.667	54.767	112.385	−0.6536	−2.8601
6.00	−26.8248	−0.186	−2.801	50.139	104.900	−0.4666	−2.1484
6.50	−19.5528	0.199	−0.381	40.254	87.152	−0.1814	−0.9843
7.00	−13.2315	0.256	0.393	32.520	71.798	−0.0535	−0.3958
7.50	−8.8306	0.218	0.537	26.523	59.165	−0.0023	−0.1209
8.00	−5.9467	0.164	0.473	21.864	49.015	0.0144	−0.0053
8.50	−4.0758	0.119	0.367	18.218	40.923	0.0171	0.0354
9.00	−2.8499	0.085	0.271	15.335	34.466	0.0150	0.0437
10.00	−1.4759	0.044	0.144	11.163	25.081	0.0088	0.0327
11.00	−0.8171	0.025	0.079	8.379	18.815	0.0047	0.0196
12.00	−0.4778	0.015	0.046	6.450	14.477	0.0025	0.0115
13.00	−0.2922	0.009	0.028	5.071	11.380	0.0016	0.0073

TABLE IV. Argon. CCSD results for Ar_2 in the *d*-aug-cc-pVQZ-33211 basis set for the dependence of the polarizabilities $\Delta\alpha_{ave}$ and $\Delta\alpha_{ani}$ (in a.u.), and the hyperpolarizability $\Delta\gamma_{\|}$ (in a.u.) on the interatomic distance R (in a.u.).

R	$\Delta\alpha_{ave}$	$\Delta\alpha_{ani}$	$\Delta\gamma_{\|}$
5.50	−0.21327	3.19923	−72.5366
6.00	−0.10604	2.72571	−82.2740
6.50	−0.03473	2.32834	−62.8980
6.75	−0.01213	2.14717	−50.1890
7.10	0.00811	1.91131	−32.9991
8.00	0.02326	1.40366	−2.4230
9.00	0.01775	1.00010	9.0222
10.00	0.01063	0.72823	9.1699
12.00	0.00349	0.41801	4.2673
15.00	0.00086	0.21280	1.1246
20.00	0.00015	0.08951	0.1651
30.00	0.00001	0.02648	0.0091

mental results even more apparent (see Part II, Ref. 18).

A measure of the quality of our potential energy curves for the rare gas dimers is given by their capability of reproducing rovibrational spacings and transport properties as well as by the degree of accuracy they furnish in the calculation of the second gas virial coefficients. At temperatures high enough that quantum-statistical effects can be neglected, the second gas virial coefficient of a diatomic molecule can be obtained by the classic expression[41]

$$B(T) = -2\pi N_A \int_0^\infty (\exp^{-[V(R)/kT]} - 1) R^2 dR. \tag{3}$$

At very low temperatures quantum effects become important, and the classical integration is substituted by an appropriate quantum expression, containing a so-called ''perfect gas'' contribution, a contribution from the rovibrational bound states and a dynamical contribution associated with the scattering phase shifts.[42–44]

The gas virial coefficients have been determined experimentally by several authors.[41] A wide range of temperatures was covered in the work of Wiebe *et al.*,[45] White *et al.*,[46] Witonsky and Miller,[47] Gammon,[48] Kell *et al.*,[49] Kemp *et al.*,[50] and Kalfoglou and Miller[51] on the helium dimer. For the Ar_2 complex, Hahn *et al.* determined the coefficient in the 200.5–493.0 K range,[52] whereas Schramm and Hebgen measured it at lower temperatures.[53] A considerable amount of data is also available, for instance, in the work of Michels.[54,55]

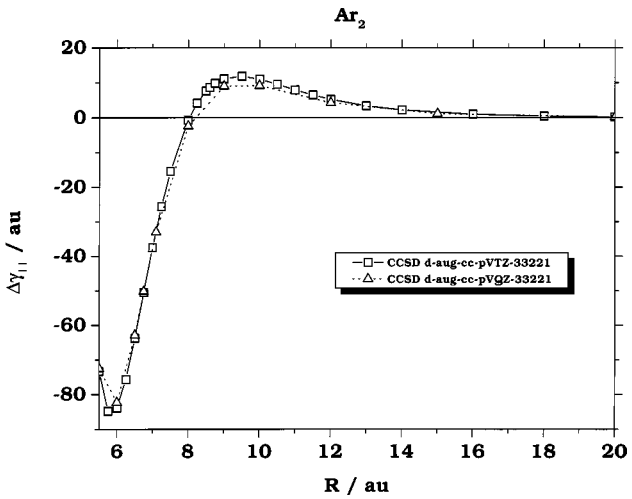


FIG. 5. The interaction induced static hyperpolarizability of Ar_2 obtained at the CCSD/*d*-aug-cc-pVQZ-33211 level compared to the CCSD/*d*-aug-cc-pVTZ-33211 results of Ref. 7.

TABLE V. Helium. The gas viral coefficient, $B(T)$ in $cm^3\,mol^{-1}$. We report results obtained using both the FCI/*d*-aug-cc-pVTZ-3321 and FCI/*d*-aug-cc-pVTZ-3321 corrected potential curves (see text), those obtained in this work using Aziz *et al.* potential curve (Ref. 35) and the experimental data.

T/K	FCI	FCI/Corr.	Aziz	Expt	Ref.
50.09	7.42	7.36	5.75	8.06	46
55.00	8.24	8.18	6.72	8.96	46
60.03	8.91	8.85	7.51	9.55	46
69.00	9.80	9.75	8.59	10.30	46
75.01	10.24	10.20	9.13	10.70	46
80.02	10.54	10.50	9.50	11.01	46
90.04	11.01	10.97	10.08	11.60	46
100.02	11.34	11.31	10.51	11.85	46
125.03	11.83	11.80	11.17	12.18	46
150.04	12.05	12.02	11.49	12.15	46
175.02	12.12	12.10	11.65	12.24	46
200.11	12.12	12.10	11.71	12.23	46
203.00	12.12	12.10	11.71	11.9	45
238.00	12.05	12.03	11.70	11.9	45
249.99	12.01	11.99	11.68	12.15	46
273.00	11.93	11.92	11.63	11.7	45
273.16	11.93	11.91	11.63	12.08	46
299.99	11.83	11.82	11.56	11.99[a]	46
303.00	11.82	11.81	11.55	11.4	51
323.00	11.74	11.73	11.49	11.4	45
373.00	11.54	11.53	11.32	11.3	45, 51
448.00	11.24	11.23	11.06	10.9	47
473.00	11.15	11.13	10.98	10.9,10.7	45, 51
523.00	10.96	10.95	10.81	10.7	47
573.00	10.78	10.77	10.65	10.3	51
598.00	10.70	10.69	10.57	10.7	47
673.00	10.45	10.44	10.34	9.7	47
748.00	10.23	10.22	10.13	9.7	51, 47
773.00	10.16	10.15	10.06	9.4	51

[a]Also 11.7, at $T = 296.15$ K, Ref. 66.

Aziz *et al.* have calculated gas virial coefficients for a large number of temperatures within 2.6 and 623.15 K using their analytical representation of the *ab initio* potential[35] and have claimed an accuracy that exceeds that of experiment. We have computed semiclassical values of $B(T)$ for the helium gas by employing both our FCI/*d*-aug-cc-pVTZ-3321 potential curve and the curve obtained by adding the difference between the CCSD(T)/*d*-aug-cc-pV5Z-3321 and the CCSD(T)/*d*-aug-cc-pVTZ-3321 *ab initio* results to the FCI/*d*-aug-cc-pVTZ-3321 data (results labeled ''FCI/Corr'' in Table IV and Fig. 6, see below). A CCSD(T) potential curve was employed in the calculation of $B(T)$ of argon.[56] In the Tables V and VI we compare our results with those we obtained employing the semiempirical potential determined by Aziz *et al.* (see Ref. 35 for He_2 and Ref. 57 for Ar_2) and with experiment. The comparison is also shown in Figs. 6 and 7. The integration in Eq. (3) requires accurate knowledge of the integrand at a quite large range of internuclear distances, and in particular—for the interval of temperatures of the tables—

TABLE VI. Argon. The gas virial coefficient, $B(T)$ in $cm^3\,mol^{-1}$. Together with the results obtained using the CCSD(T) potential curve (Ref. 56) we give in the table also those obtained in this work using Aziz's potential (Ref. 57) and the corresponding experimental estimates.

T	CCSD(T)	Aziz	Expt.	Ref.
50.0	−766.7	−773.3		
60.0	−510.8	−504.7		
70.0	−374.0	−364.2		
77.3	−309.4	−298.7	−303.0	53
80.0	−290.1	−279.4		
87.2	−247.7	−236.9	−239.0	53
90.2	−232.9	−222.3	−224.0	53
100.0	−193.7	−183.4		
120.0	−140.3	−131.2		
140.0	−106.6	−98.6		
160.0	−83.5	−76.3		
180.0	−66.6	−60.3		
200.5	−53.6	−47.9	−47.7	52
210.9	−48.1	−42.7	−42.4	52
220.0	−43.8	−38.7		
231.5	−39.0	−34.1	−43.1	52
251.5	−31.9	−27.4	−27.4	52
273.2	−25.5	−21.4	−21.6	52
280.0	−23.7	−19.8		
296.0	−19.9	−16.2	−16.2[a]	52
308.0	−17.4	−13.9	−14.0	52
320.0	−15.1	−11.7		
340.0	−11.6	−8.5		
360.0	−8.6	−5.7		
374.0	−6.8	−4.0	−13.8	52
395.0	−4.2	−1.6		
413.8	−2.2	0.2	0.8	52
430.0	−0.6	1.7		
453.4	1.4	3.6	4.0	52
493.0	4.3	6.3	7.0	52

[a]Also −16.2, at $T=296.15$ K, Ref. 66.

the contribution at low internuclear distances is still sizeable. To be able to stretch the integration limit well beyond the range of values for which we have computed the curve, we have fitted the calculated points to the same functional form

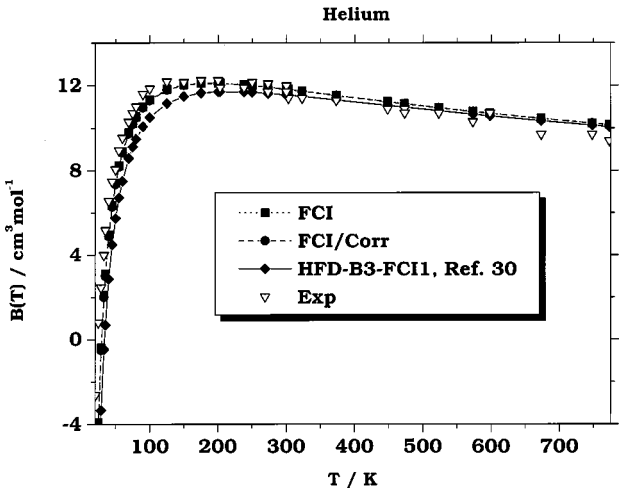


FIG. 6. The second gas virial coefficient $B(T)$ of helium. Comparison of results obtained at the FCI level with and without basis set correction (see text) with those obtained with the Aziz *et al.* analytical potential (Ref. 35) and with experiment.

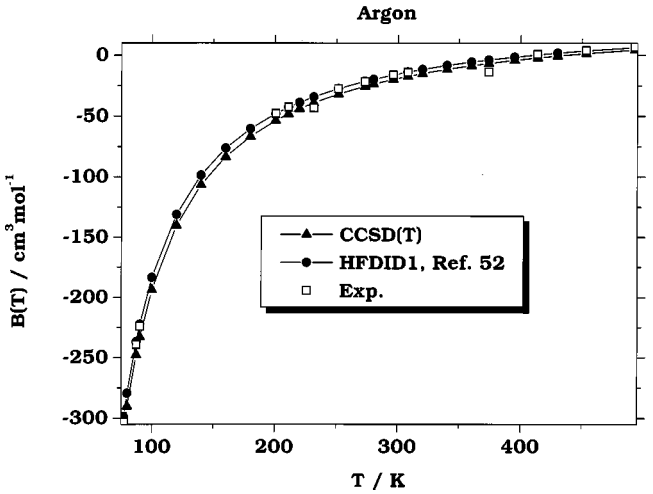


FIG. 7. The second gas virial coefficient $B(T)$ of argon. Comparison of results obtained with the CCSD(T) potential of Ref. 56 with those obtained with the Aziz *et al.* semiempirical analytical potential (Ref. 57) and with experiment.

as that used by Aziz and co-workers.[35,57] The results in the tables show an excellent agreement in the whole range of temperatures. We do not expect that the residual disagreement between calculations and experiment might be due to quantum effects, especially for helium, since for ^{4}He Aziz *et al.* have shown that the effect of the single bound state of the dimer is negligible at all temperatures, whereas that of scattering in the continuum dominates everywhere and it is essentially the one that corresponds to the semiclassical approximation.[44] Thus, our semiclassical values agree with experiment and with the quantum statistical results of Aziz also at temperatures below 50 K. This might be different for the argon dimer, which supports a larger number of bound states. However, no experimental data are available for temperatures lower than 77 K for argon gas, cf. Table VI.

In Tables VII–X we present the parameters of least square fits of analytic functions to the calculated points of the interaction induced properties. These functions reproduce accurately the *ab initio* calculated points in the investigated

TABLE VII. Helium. Parameters of the least square fits of the function $P_{\rm fit}(r)=-D\exp(-(r-\sigma)^2/\rho)+A_6 r^{-6}$ to the interaction induced isotropic polarizability $\Delta\alpha_{\rm ave}$ and Cauchy moment $\Delta S_{\rm ave}(-4)$ calculated at the CCSD/*d*-aug-cc-pVTZ-3321, CCSD/*d*-aug-cc-pV5Z-3321, and FCI/*d*-aug-cc-pVTZ-3321 levels and to the extrapolated FCI/*d*-aug-cc-pV5Z-3321 results.

	CCSD/pVTZ	CCSD/pV5Z	FCI/pVTZ	extr. FCI/pV5Z
		$\Delta\alpha_{\rm ave}$		
σ	−1.8364	−2.2863	−2.0519	−2.5288
D	4.4949	6.5401	5.5801	8.3152
ρ	7.3468	7.8978	7.5696	8.1515
A_6	39.164	43.066	43.090	47.094
		$\Delta S_{\rm ave}(-4)$		
σ	−1.3660	−1.2421	−1.1651	−1.0570
D	5.7349	5.2117	5.0684	4.6597
ρ	7.8152	7.5957	7.4685	7.2720
A_6	116.944	111.708	114.914	110.136

TABLE VIII. Helium. Parameters of the least square fits of the function $P_{\rm fit}(r)=\exp(-(r-\sigma)^2/\rho)+A_3r^{-3}+\Sigma_{n=0}^{2}A_{6+2n}r^{-6-2n}$ to the interaction induced polarizability anisotropy $\Delta\alpha_{\rm ani}$ and Cauchy moment $\Delta S_{\rm ani}(-4)$ calculated at the CCSD/*d*-aug-cc-pVTZ-3321, CCSD/*d*-aug-cc-pV5Z-3321, and FCI/*d*-aug-cc-pVTZ-3321 levels and to the extrapolated FCI/*d*-aug-cc-pV5Z-3321 results.

	CCSD/pVTZ	CCSD/pV5Z	FCI/pVTZ	extr. FCI/pV5Z
		$\Delta\alpha_{\rm ani}$		
σ	2.8387	2.8426	2.8569	2.8609
ρ	0.6104	0.6085	0.6076	0.6057
A_3	11.083	11.010	11.438	11.364
A_6	51.695	57.018	50.835	56.140
A_8	6878.4	6909.0	7100.6	7135.3
A_{10}	−35046	−35307	−36067	−36348
		$\Delta S_{\rm ani}(-4)$		
σ	3.6249	3.6144	3.6343	3.6243
ρ	0.7184	0.7154	0.7146	0.7116
A_3	23.756	23.648	24.488	24.378
A_6	1328.8	1280.2	1326.4	1278.8
A_8	7299.0	7763.7	7737.6	8200.8
A_{10}	−68316	−69711	−70439	−71849

range of distances (3–13 a.u. for He_2 and 5.5–30.0 a.u. for Ar_2) and can also be employed to extrapolate the interaction properties at large distances. They can be used to evaluate the integrals in the calculation of the dielectric, the refractivity, the Kerr and the hyperpolarizability second virial coefficients.

The dipole-induced-dipole (DID) model suggests the functional form of the functions employed for the fits at large distances.[13,8] Thus, the long range leading terms for the average polarizability, the anisotropy and the hyperpolarizability depend on R as R^{-6}, R^{-3} and R^{-6}, respectively, see also Refs. 40, 58, 59. Buckingham *et al.*[60] have obtained closed-form expressions which account for all powers of R, also for the mean second hyperpolarizability. Exponential-type short range models have been proposed for example by Proffitt *et al.*[61,62] for the average interaction polarizability and by Proffitt *et al.*[63] and by Meinander *et al.*[64] for the anisotropy, see also Refs. 13, 58. Dacre discusses several exponential models for the short range interaction anisotropy, and checked functions of the form $\Delta\alpha_{\rm ani}=A/R^3+B/R^6-C\exp^{-DR^x}$. Several attempts have been made to find the best functional forms to obtain reliable fits of the properties for a range of internuclear distances as large as possible. The models employed in Tables VII–X correspond to the choice that best mimics the properties. The fits for He_2 are used in Ref. 18 for the calculation of the virial coefficients of helium gas to supplement the *ab initio* calculated data for the interaction induced properties beyond 13 a.u., when the long range contribution is important.

TABLE IX. Helium. Parameters of the least square fits of the function $P_{\rm fit}(r)=-\exp(-S_1(x-R_1))+D_2\exp(-S_2(r-R_2)^2)+A_6r^{-6}+A_8r^{-8}$ to the interaction induced isotropic hyperpolarizability $\Delta\gamma_{\parallel}$ and hyperpolarizability dispersion $\Delta\gamma_{\parallel}\times A$ calculated at the CCSD/*d*-aug-cc-pVTZ-3321, CCSD/*d*-aug-cc-pV5Z-3321, and FCI/*d*-aug-cc-pVTZ-3321 levels and to the extrapolated FCI/*d*-aug-cc-pV5Z-3321 results.

	CCSD/pVTZ	CCSD/pV5Z	FCI/pVTZ	extr. FCI/pV5Z
		$\Delta\gamma_{\parallel}$		
R_1	4.0724	4.0892	4.0739	4.0736
S_1	3.3223	3.3312	3.3163	3.3267
D_2	−9732.4	−3871.2	−10087.1	−3121.4
R_2	−6.7338	−5.2774	−6.7274	−4.9459
S_2	0.0571	0.0664	0.0573	0.0687
A_6	12257	6290	13868	8064
A_8	333134	384945	324004	353917
		$\Delta\gamma_{\parallel}\times A$		
R_1	4.2663	4.2354	4.2829	4.2485
S_1	3.1195	3.1789	3.0905	3.1482
D_2	−1261.5	−891.21	−1361.18	−952.18
R_2	−2.9361	−2.4029	−2.9976	−2.4496
S_2	0.0743	0.0803	0.0741	0.0803
A_6	45138	31368	51179	37497
A_8	341208	412986	310285	376052

TABLE X. Argon. Parameters of the least square fits of the function $P_{\rm fit}(r)=-\exp(-(r-\sigma)/\rho)+\Sigma_{n=0}^{3}A_{6+2n}r^{-6-2n}$ to the interaction induced polarizability average $\Delta\alpha_{\rm ave}$, $P_{\rm fit}(r)=-\exp(-(r-\sigma)/\rho)+A_3r^{-3}+\Sigma_{n=0}^{2}A_{6+2n}r^{-6-2n}$ to the interaction induced polarizability anisotropy $\Delta\alpha_{\rm ani}$, and of $P_{\rm fit}(r)=D_1\exp(-S_1(r-R_1)^2)+D_2\exp(-S_2(r-R_2)^2)+A_6r^{-6}$ to the interaction induced isotropic hyperpolarizability $\Delta\gamma_{\parallel}$ of Ar_2 calculated at the CCSD/*d*-aug-cc-pVQZ-33211 level.

$\Delta\alpha_{\rm ave}$		$\Delta\alpha_{\rm ani}$		$\Delta\gamma_{\parallel}$	
σ	6.1589	σ	6.8654	D_1	−610.46
ρ	0.7028	ρ	0.7635	R_1	3.2433
A_6	8876.3	A_3	724.35	S_1	0.1248
A_8	−450859	A_6	−56735	D_2	59.043
A_{10}	1.2318×10^{8}	A_8	8.5664×10^{6}	R_2	−3.9056
A_{12}	-1.7660×10^{9}	A_{10}	-8.4989×10^{7}	S_2	0.0130
				A_6	6.4254×10^{6}

IV. CONCLUSIONS

We have reported the results of the first electron correlated *ab initio* calculations of the frequency-dependent interaction induced (hyper-) polarizabilities of He_2 and have improved the calculations of the static interaction induced (hyper-) polarizabilities of Ar_2. The combination of these two calculations allows, for the first time, to compare directly the experimentally measured pressure dependence of ESHG hyperpolarizabilities with *ab initio* calculated hyperpolarizability second virial coefficients (see Part II, Ref. 18).

We find that going beyond the *d*-aug-cc-pVTZ-3321 with the basis set and introducing correlation effects beyond the CCSD level has very small effects of equal magnitude for the isotropic properties $\Delta\alpha_{\rm ave}$, $\Delta\gamma_{\parallel}$, $\Delta S_{\rm ave}(-4)$, and $\Delta(\gamma_{\parallel}\times A)$, whereas the higher-order correlation effects are considerably more important, although still small, for the potential energy and for the anisotropic properties, $\Delta\alpha_{\rm ani}$ and $\Delta S_{\rm ani}(-4)$.

For Ar_2, the isotropic interaction induced properties are considerably more sensitive to the choice of the one-particle basis set. Even more important, we show in Part II that, due to a near cancellation of positive and negative regions of the weighted integrand, the balance between these regions is critical for the accuracy of the second virial coefficients for these properties.

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APPENDIX: CONVERSION FACTORS

Conversion factors from atomic units to SI and to esu,[65]

(1) 1 a.u. of $\omega \equiv \hbar a_0^{-2} m_e^{-1} \cong 4.13414 \times 10^{16}$ s^{-1};
(2) 1 a.u. of $\alpha \equiv e^2 a_0^4 m_e \hbar^{-2} \cong 1.64878 \times 10^{-41}$ $C^2\,m^2\,J^{-1}$ $\cong 1.64878 \times 10^{-47}$ cm^{-3}(esu);
(3) 1 a.u. of $\gamma \equiv e^4 a_0^{10} m_e^3 \hbar^{-6} \cong 6.23538 \times 10^{-65}$ $C^4\,m^4 J^{-3}$ $\cong 5.03669 \times 10^{24}$ esu.

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