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Nonadditivity and anisotropy of the polarizability of clusters: Relativistic finite-field calculations for the Xe dimer

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We present all-electron relativistic studies of the polarizability properties of the Xe dimer. The studies rely on finite-field calculations of the dimer energies obtained by *ab initio* methods including electron correlations. An extended set of basis functions is designed in order to ensure a high accuracy of the calculations. Particular attention is paid to the analysis of the nonadditivity and anisotropy of the polarizability of the dimer. It is found that the polarizability of the dimer relative to that of the atoms can be accurately described analytically, at least for internuclear distances around and larger than the equilibrium distance of the dimer.

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I. INTRODUCTION

The electric-dipole polarizability is an important property of atoms, molecules, and clusters. This is reflected by numerous theoretical and experimental studies; see, for example, the comprehensive book by Bonin and Kresin [1] and references therein. Manifestations of polarization properties include, for example, the Stark effect, dielectric constants, and refraction of radiation, as well as the stability of van der Waals systems. A great variety of these last systems remain in the focus of extensive research because of the challenge with respect to their accurate theoretical descriptions as well as in their experimental probes. Particularly important are clusters of the rare-gas atoms where, owing to the closed-shell electronic structure, the polarizability is a fundamental property related to the bonding. In addition, polarizability of these clusters plays an important role in electron attachment to the clusters. It has been theoretically shown (see, e.g., [2] and the references therein) that the extra electron can be attached to form stable anions if the number of cluster atoms exceeds some critical value found to be 7, 14, and 46 for Xe, Kr, and Ar clusters; these values reflect a reciprocal relationship to the atomic polarizabilities of 27.29 for Xe, 16.77 for Kr, and 11.08 for Ar. The above values of the polarizabilities, in atomic units, are the experimental values based on the measured dielectric constants of Xe by Miller and Benderson [3] and of Ar and Kr by Orcutt and Cole [4].

Our special interest in the polarizability of rare-gas clusters was spurred by the studies of *magnetically induced anions*, which evolved into an appealing area of research over the last few years visible in a series of theoretical works (see for example [5–8]). Such anions are formed in the presence of a magnetic field and have no analogs in the field-free space. In particular, species known to not form stable anions can even exhibit a few or many excited anionic states on top of the ground state when exposed to a magnetic field. Striking examples for this behavior are the rare-gas atoms themselves and their clusters with a number of atoms fewer than the critical values mentioned above. Their excited magnetically induced states are formed by attachment of the extra electron in a magnetically stabilized extended orbital, where interaction of the electron with the underlying neutral core happens by pure polarization attraction,

$$V_{\mathrm{pol}}(\mathbf{r}) = -\alpha_{\mu\nu} n_\mu n_\nu / (2r^4). \tag{1}$$

In this expression, $\alpha_{\mu\nu}$ is the polarizability tensor of the neutral counterpart, $\mathbf{r}$ denotes the location of the electron, $r = |\mathbf{r}|$, n_μ and n_ν are the components of the unit vector $\mathbf{r}/r$, and the Einstein summation convention is applied. The corresponding binding energies were explicitly evaluated in [5] for the isotropic polarizabilities $\alpha_{\mu\nu} = \alpha\delta_{\mu\nu}$, and the procedure can be equally well applied to systems with anisotropic polarizabilities. An accurate knowledge of the polarizability is therefore of great relevance for getting access to magnetically bound anions and requires detailed electronic structure calculations.

Early studies already revealed that the polarizabilities of bound complexes deviate from the sum of individual polarizabilities of the constituent parts, and are generally anisotropic even for the case of individual isotropic polarizabilities. The effects of the nonadditivity and anisotropy are a consequence of interactions between the parts and symmetry lowering in the complexes. A simple meaningful approximation to describe these effects is a model of the dipole-induced dipole (DID) interactions between the point-polarizable entities. This model was introduced by Silberstein [9] and further utilized by Applequist *et al.* [10]. It yields analytical estimates for the polarizabilities of complexes that are small in size or possess a high symmetry. In particular, for polyhedral clusters of cubic and icosahedral symmetry, closed-form analytical expressions for the polarizability tensor were derived [11].

An extension of the DID model was introduced in [12] by representation of the interacting atoms by Drude dispersion oscillators. This approach was applied to simulate the clusters comprising 7–26 atoms; in particular, the minimum-energy configurations were determined for the pentagonal grow sequence, and the principal values of the polarizability tensor

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were computed for these configurations with 7, 13, 19, and 26 atoms. Both nonadditivity and anisotropy of the cluster polarizabilities were found to become more pronounced with increase in the value of the isotropic atomic polarizability. It was also observed that the α principal values exhibit larger differences for more anisotropic clusters. For highly symmetric cases such as the icosahedral structure made of 12 atoms in the shell and one at the origin, all three principal values are equal.

Ab initio determinations of polarizabilities are based on electronic structure calculations. The most direct and widely used approach is to compute the energy E of the system in a weak homogeneous external electric field $\mathbf{F}$ and make use of the well-known energy expansion [13] in powers of the field components. For systems with no net charge and permanent dipole moment, the leading field-dependent term of the expansion is determined by the static dipole polarizability,

$$E = E_0 - (1/2)\alpha_{\mu\nu} F_\mu F_\nu, \tag{2}$$

where E_0 is the energy at zero electric field. The polarizability tensor thus can be computed by numerical differentiation of the energy with respect to the field components or by construction of a polynomial fit to the energy dependence on the field components. Inclusion of higher-order polynomial powers in the latter fit generally improves the accuracy of the polarizability values as well as allowing one to evaluate the related hyperpolarizabilities of the system. The corresponding calculations are of the finite-field type, where different theoretical approaches to compute the energy have been applied. In the standard way, the self-consistent-field (SCF) procedure is used first in order to obtain an initial approximation for the wave function and is followed by different methods to account for electron correlation. Among the latter methods the second-order many-body perturbation (MBPT2) method is quite inexpensive with respect to computational resources. Highly accurate but considerably more expensive are the coupled-cluster methods with single and double excitations (CCSD) and with extension to perturbational triples corrections [CCSD(T)].

Our studies are focused on Xe clusters, which are promising candidates to form the magnetically induced anions mentioned above. Since the Xe atom possesses the largest polarizability among the rare-gas atoms, some small Xe clusters can already be expected to support magnetically induced anionic states with experimentally detectable binding energies. In this work we study the Xe dimer.

According to symmetry, the dimer polarizability has two principal values $\alpha_\perp$ and $\alpha_\parallel$, and in the coordinate system with the interatomic axis being the z axis, the nonzero components of the polarizability tensor are $\alpha_{xx} = \alpha_{yy} = \alpha_\perp$ and $\alpha_{zz} = \alpha_\parallel$. In the DID model, these principal values are given by the simple formulas

$$\frac{\alpha_\perp}{2\alpha} = \left(1 + \frac{\alpha}{R^3}\right)^{-1}, \quad \frac{\alpha_\parallel}{2\alpha} = \left(1 - \frac{2\alpha}{R^3}\right)^{-1}, \tag{3}$$

where α is the (isotropic) atomic polarizability, and R is the interatomic distance. Quantum mechanical calculations of the dimer polarizability have already been undertaken by different research groups. To be mentioned are the finite-field calculations by Dacre [14] using SCF energies and by Maroulis *et al.* [15] using MBPT2 energies. These studies employ atomic basis sets optimized for a maximum agreement with experimental values for the atomic xenon polarizability. Dacre [14] used the reference value 27.106 of the atomic Xe polarizability according to [16] and obtained an SCF polarizability that represents 94% of this value. Maroulis *et al.* [15] referred to more recent experimental values 27.12 and 27.16 reported in [17] and [18], respectively, whereas their MBPT2 calculations yielded a Xe polarizability of 27.71 significantly exceeding these values. In [14], computed pair Xe polarizabilities are compared to the results of the DID model. In [15], theoretical results are compared to recent experimental measurements of the anisotropy $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ [19]. Both studies [14,15] paid special attention to computation of the *interaction* polarizability with high accuracy. This interaction property is defined as the dimer polarizability minus the sum of the individual atomic polarizabilities. The well-known counterpoise correction method [20] was employed in order to eliminate basis set superposition errors (BSSE) when computing the anisotropy.

The studies cited here treated the Xe dimer in an essentially nonrelativistic manner. Relativistic effects, however, are already pronounced for the Xe atom and need to be taken into account properly. Their impact on the Xe polarizability was demonstrated by Nicklass *et al.* [21] employing scalar relativistic pseudopotentials together with the CCSD(T) method for obtaining the perturbed energies. These calculations yielded an atomic polarizability value of 27.685, which was compared with the experimental values of 27.16 and 27.815 reported in [22] and [23], respectively. For the Xe dimer and larger Xe clusters, to the best of our knowledge, no accurate relativistic polarizability calculations have yet been performed. Evidence for the importance of a relativistic treatment for the dimer is supported by calculations based on the model potential by Andzelm *et al.* [24] showing, in particular, that relativistic effects lower the SCF energies quite substantially at distances close to the van der Waals minimum.

In the present paper we describe all-electron *ab initio* studies of the polarizability of the Xe dimer. Relativistic effects are taken into account by the Douglas-Kroll method [25,26], and the finite-field technique is employed for the determination of the polarizability. Becaue of the closed-shell character of the constituent cluster units, spin-orbit effects do not have a large effect on the total energy of the system and are hereby ignored. Otherwise, a four-component calculation would have been the method of choice but is much more expensive computationally. The Hartree-Fock and correlated calculations are done with the MOLCAS package [27]. In order to achieve a balance between accuracy and acceptable computational costs of the most reliable coupled-cluster studies, we optimized an atomic basis set comprising 104 Gaussian-type primitives. The relativistic benchmark polarizability calculations employing this basis set are compared to previously obtained theoretical results. In the practical realization of the finite-field approach, we compute the ground-state dimer energies for zero electric field and, with the field being applied along and perpendicular to the dimer axis, for a few values of the field strength. The latter values, in most cases, were selected to be equal, in atomic units, to the square roots of 3×10^{-5}, 5×10^{-5}, 7×10^{-5}, and

9×10^{-5}. The dependence of the energies on the field strength squared was then approximated by second-order polynomials. A standard polynomial fit procedure was applied, and the fit control parameter was verified to indicate a high accuracy of the fits over all the series of calculations performed. From these fits, the polarizability values were obtained from the coefficients at the first polynomial power. Inclusion of the second polynomial power, with respect to the field strength squared, into the fits was found to additionally improve the accuracy of the polarizability values.

The paper is organized as follows. In Sec. II we describe the construction of the atomic basis set and provide the corresponding results for the atomic Xe polarizability. Section III presents detailed studies of the Xe dimer polarizability over a wide range of internuclear distances. Also computed is the BSSE-free interaction energy of two Xe atoms. Finally, the SCF, MBPT2, CCSD, and CCSD(T) dimer polarizabilities are scaled by the sums of the atomic polarizabilities computed at the same levels of theory, and the scaled quantities are benchmarked versus the results according to Eqs. (3) of the DID model. Section IV contains the concluding remarks. There, we also discuss the influence of the nonadditivity and anisotropy of the dimer polarizability on the binding energies of the excited magnetically induced anionic states.

TABLE I. Exponents of the $[9s9p8d4f]$ and $[10s10p9d5f]$ primitive sets optimized for the relativistic polarizability calculations.

s	p	d and f
60 101 513.1	27 087 78.86	3214.543 35
12 985 501.3	404 117.936	1411.0798
3 505 397.19	83 972.4822	638.269 163
1 055 748.62	21 769.3904	296.394 814
347 921.943	6812.080 47	140.646 374
123 160.172	2474.936 19	68.170 0583
46 325.7162	1003.182 48	33.667 2652
18 322.7937	439.646 552	16.885 2926
7548.288 12	203.709 419	8.607 947 91
3214.543 35	98.322 0219	4.265 325 81
1411.0798	48.597 7963	2.052 560 45
638.269 163	23.592 5739	0.947 760 887
296.394 814	11.761 7187	0.382 343 355
140.646 374	5.799 142 23	0.15
68.170 0583	2.870 109 71	0.07
33.667 2652	1.372 047 12	0.035
16.885 2926	0.544 650 485	0.018
8.607 947 91	0.228 802 914	0.009
4.265 325 81	0.088 370 9199	
2.052 560 45	0.038 370 9199	
0.947 760 887	0.018	1.78
0.382 343 355	0.007	0.712
0.144 991 653	0.0027	0.2848
0.05		0.113 92
0.02		0.045 568
0.008		
0.004 5		

II. ATOMIC BASIS SET

Polarizability calculations require basis sets of high flexibility in order to properly account for the changes in electron density caused by the presence of the external electric field. A maximum of flexibility is provided by fully uncontracted sets, and we first constructed such a set of Gaussian-type orbitals (GTOs) yielding a Xe polarizability close to the experimental values. These are mentioned in the preceding section and vary from 27.106 to 27.815, not allowing for a definite conclusion regarding the most reliable value. We therefore took care to obtain polarizability values that fit the above range and saturate with extension of the size of the basis set. The GTOs comprising a $(23s19p13d)$ primitive set were first optimized with respect to energy minimization at the SCF level. Then softer functions were added in order to reach a limiting value for α at the SCF level as well as at the correlation levels of theory. In this way a $(26s22p17d4f)$ primitive set was obtained whose exponents can be found in Table I. For many-atom clusters a calculation with an uncontracted basis set is, of course, prohibitive. We therefore contracted the set of Table I in order to reduce the number of the basis functions while maintaining the same level of accuracy. In order to achieve this, the ratio of the molecular orbital coefficients with and without application of the external field were calculated and yielded a set of outer valence basis functions that were most responsive to the field. Consequently, these functions were then all left uncontracted, and a very good compromise between accuracy and numerical efficiency could be achieved by this procedure. In this way the set $[9s9p8d4f]$ was obtained, where 22 of 26 s, 17 of 22 p and 11 of 17 d functions were included in the contraction. In order to check the saturation of the polarizability values with respect to increase in the basis set, the latter set was extended to the $[10s10p9d5f]$ set by addition of one more uncontracted primitive per each angular momentum value. The corresponding exponents are the softest exponents included in Table I.

With the $[9s9p8d4f]$ basis set constructed above, all-electron *relativistic* SCF calculations yield the Xe polarizability of 26.7505, which deviates by a negligible 0.005% from the SCF value obtained with the $[10s10p9d5f]$ basis set. The same saturation behavior with respect to increase in the basis set is exhibited by the MBP2, CCSD, and CCSD(T) polarizability values. We have also examined how sensitive the values of α are to inclusion of the core orbitals into the correlation calculations. For this reason, the MBPT2, CCSD, and CCSD(T) calculations were performed correlating all the orbitals as well as with the lowest 18 orbitals kept frozen and not taken into the correlations. The results obtained show that the core correlation contributions increase α only by 0.19% for the MBPT2 treatment and by 0.23% for the CCSD and CCSD(T) treatments. These numbers represent estimates of uncertainty in our correlation polarizability values. Given the small values of these estimates, the core correlation contributions can be safely neglected, providing considerable numerical savings in the CCSD and CCSD(T) treatments. We will therefore employ the frozen-core approximation when computing the dimer polarizabilities within the correlation MBPT2, CCSD and CCSD(T) approaches. Naturally, the same $[9s9p8d4f]$ basis set, when attributed to both dimer atoms, yield more orbitals involved in the correlations than the orbitals correlated for the single atom. Therefore we can expect

TABLE II. Atomic xenon polarizabilities and zero-field ground-state SCF energies (in atomic units) at various levels of theory. The last column indicates the number of core orbitals frozen for the correlation treatment. Values displayed in italics were not provided in the corresponding references and have been computed in the present work using the basis sets given in these references.

			Polarizability				
Reference	Basis	SCF energy	SCF	MBPT2	CCSD	CCSD(T)	Frozen
[14][a]	$11s9p5d$	−7224.8161	25.61	*26.34*	*26.61*	*26.71*	18
				26.42	*26.68*	*26.79*	0
[15][a]	$9s8p7d5f$	*−7226.8597*	27.05	27.71	*27.70*	*27.87*	18
				27.80	*27.80*	*27.96*	0
This work[b]	$9s8p7d5f$	−7361.0230	26.17	26.91	26.92	27.08	18
				26.99	27.00	27.17	0
This work[c]	$9s9p8d4f$	−7441.4835	26.75	27.13	27.16	27.36	18
				27.18	27.22	27.42	0

[a] Nonrelativistic calculations.

[b] All-electron relativistic (Douglas-Kroll) calculations with the basis set of Ref. [15].

[c] All-electron relativistic (Douglas-Kroll) calculations with the original basis set given in Table I.

the frozen-core approximation to yield an accuracy of the dimer polarizabilities not worse than the above 0.19%–0.23% accuracy of the atomic polarizabilities. Including the uncertainty estimates in parentheses, our reference CCSD(T) polarizability value for the Xe atom is 27.36(6) a.u.

Table II lists the results for α obtained with the basis sets from the literature and with our own basis. Particularly relevant for comparison with our results are the results of nonrelativistic calculations [14,15]. As already discussed, Ref. [14] reports only SCF values for α and Ref. [15] provides nonrelativistic SCF and MBPT2 polarizability values. For the sake of completeness of the analysis, we have performed nonrelativistic MBPT2, CCSD, and CCSD(T) calculations with the $[11s9p5d]$ basis set of Ref. [14] and CCSD, CCSD(T), calculations with the $[9s8p7d5f]$ basis set of Ref. [15]. The more complete basis set of Ref. [15] was also tested in relativistic calculations.

Analysis of the polarizability values presented in Table II shows that inclusion of f functions leads to a substantial increase of the polarizability values for all levels of the theory. It is also observed that, except for the rather poor $[11s9p5d]$ basis set, the MBPT2 and CCSD polarizabilities are very close to each other. One can therefore skip the expensive CCSD procedure and achieve good accuracy already with perturbation methods if one is not interested in triples corrections, which always lead to the largest values of α. Overall, electron correlations lead to a remarkable increase of the polarizabilities over the SCF values.

Let us now focus on the CCSD(T) values calculated within the frozen-core approximation and on the experimental values collected in the Introduction: 27.106, 27.12, 27.16, 27.29, and 27.815 according to Refs. [16–18], [3] and [23], respectively. The value 27.36 obtained from the relativistic calculations with our $[9s9p8d4f]$ basis set turns out to be closest to the experimental value 27.29 extracted from the measurements of the dielectric constant [3]. This relativistic CCSD(T) polarizability of 27.36 exceeds by 0.67 the value 26.71 from the nonrelativistic calculations with the $[11s9p5d]$ basis set, and is by 0.51 smaller than the value 27.87 obtained from the nonrelativistic calculations with the $[9s8p7d5f]$ basis set. Although the theoretical value of 27.87 is quite in favor of the more recently measured [23] Xe polarizability 27.815, the corresponding basis set of Ref. [15] yields a remarkably smaller CCSD(T) polarizability of 27.08 when applied for the relativistic calculations. The latter relativistic theoretical value is also smaller than our benchmark result 27.36. While it is indeed difficult to judge which experimental value is the most accurate, it is legitimate to estimate the mean polarizability value for the set of five experimental results cited above. This mean value is 27.298 and is in fact nearly the same as the measured Xe polarizability according to Ref. [3] and close to our theoretical result 27.36. It is also worthy of note that, among the all sets of calculations presented in Table II, the zero-field ground-state SCF energy is minimal, −7441.4835 a.u., for the relativistic calculations with our $[9s9p8d4f]$ basis set, approaching very well the basis-set-free limit −7445.6817 a.u. For a reference, we have computed the latter limit energy value using the GRASP package [28,29] for grid numerical integration of the Dirac Hartree-Fock equations. Given all the above discussion, we can conclude our theoretical polarizability value of Xe to be a reliable benchmark.

III. DIMER INTERACTION PROPERTIES

With the basis set designed in the preceding section, we have performed finite-field polarizability calculations for the Xe dimer. Two main values of the polarizability were computed for a broad range of internuclear separations R by the *ab initio* SCF, MBPT2, CCSD, and CCSD(T) methods. In order to diminish the influence of the BSSE on our results, we have followed the widely used approach by computing the interaction quantities

$$\alpha^{\rm int}_{\parallel,\perp}(R) = \alpha_{\parallel,\perp}(1,2) - \alpha_{\parallel,\perp}(1,X) - \alpha_{\parallel,\perp}(X,2). \qquad (4)$$

In this equation, $\alpha_{\parallel,\perp}(1,2)$ are the polarizabilities for the dimer obtained from the *ab initio* calculations with the basis orbitals attributed to the atoms 1 and 2, $\alpha_{\parallel,\perp}(1,X)$ are the polarizabilities of atom 1 in the presence of the ghost basis orbitals for atom 2, and $\alpha_{\parallel,\perp}(X,2)$ are the polarizabilities of atom 2 in the presence of the ghost basis orbitals for atom 1. Since the atoms are identical, $\alpha_{\perp}(1,X)$ and $\alpha_{\perp}(X,2)$ are

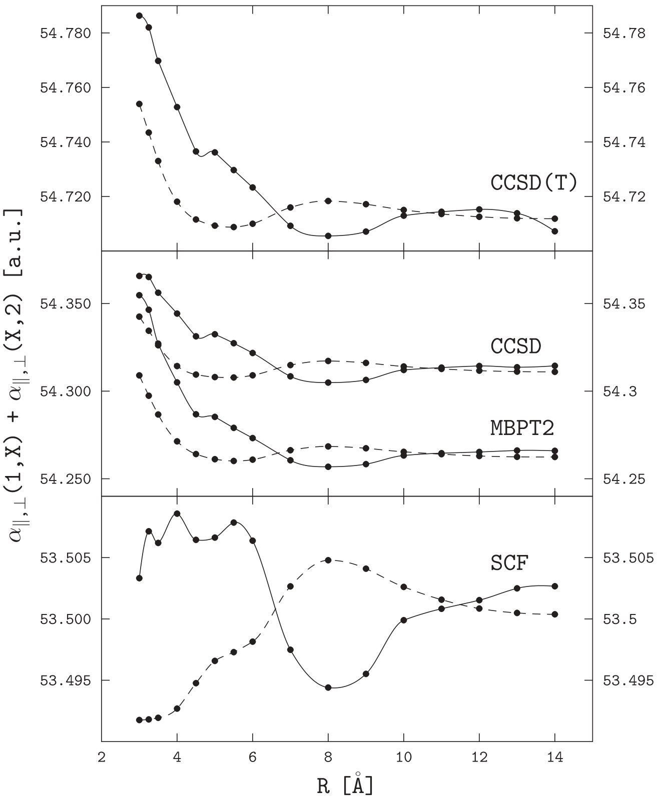

FIG. 1. Sum of the polarizabilities of the independent atoms separated by the distance R. The polarizability of each atom is obtained in the presence of the ghost basis set attributed to the location of the other atom. Dots are the results of the finite-field polarizability calculations for the discrete values of R. Solid lines connect the polarizability values for the electric field directed along the interatomic axis, and dashed lines connect the polarizability values for the perpendicular field direction.

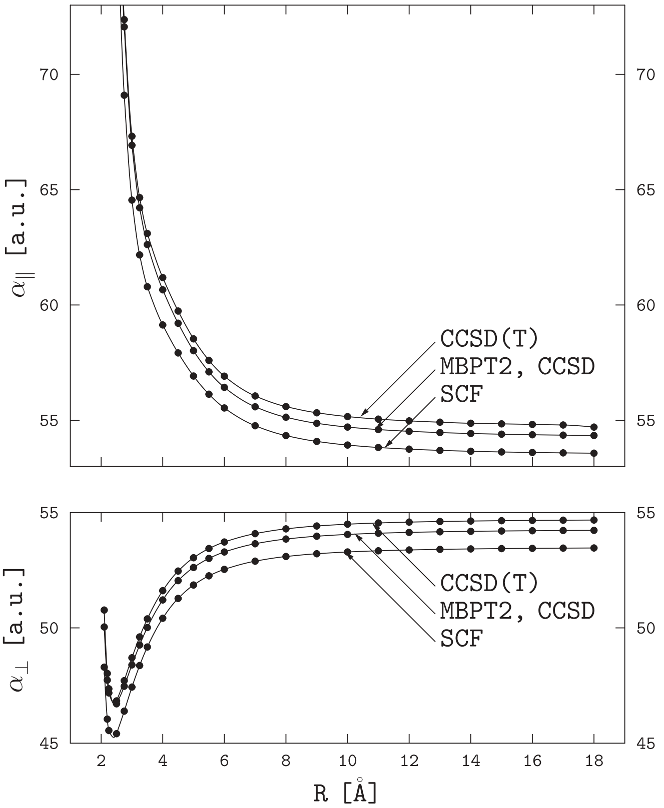

FIG. 2. Dimer polarizabilities as functions of the internuclear distance. The top and bottom panels show the longitudinal and transverse polarizabilities, respectively. Dots represent the results computed for the discrete values of the distance and are connected by the smooth solid lines for visualization of the curves. Different curves correspond to the different theoretical finite-field approaches labeled by SCF, MBPT2, CCSD, and CCSD(T) (MBPT2 and CCSD results are indistinguishable in the figure).

the same on the grounds of symmetry. The polarizabilities $\alpha_{\parallel}(1,X)$ and $\alpha_{\parallel}(X,2)$, when computed for the same direction of the electric field along the dimer axis, generally differ from each other: for one atom the presence of the ghost orbitals increases the polarizability with respect to that computed without the ghost basis set, while for the other atom the ghost basis contributes to a decrease of the polarizability. Numerically, the BSSEs lead to some small variations of the atomic polarizabilities which are more pronounced for smaller separations between the atoms. This is seen from Fig. 1, where we show the sums $\alpha_{\parallel}(1,X) + \alpha_{\parallel}(X,2)$ and $\alpha_{\perp}(1,X) + \alpha_{\perp}(X,2)$ obtained with different levels of *ab initio* treatments.

With the BSSE-corrected interaction polarizabilities (4), the dimer polarizabilities for given internuclear separation R are determined by the relation

$$\alpha_{\parallel,\perp}(R) = \alpha^{\mathrm{int}}_{\parallel,\perp}(R) + 2\alpha, \qquad (5)$$

where α is the atomic polarizability computed in the preceding section. The results of the calculations of $\alpha_{\parallel,\perp}(R)$ are presented in Fig. 2. For each value of R, the dimer polarizabilities obtained by the post-SCF methods exceed the SCF values, with the CCSD(T) values being the largest in the sets of those for the MBPT2, CCSD, and CCSD(T) methods. This observation holds for both transverse and longitudinal dimer polarizabilities and is the same as that for studies of the isotropic atomic polarizability. Another observation, similar to the case of the atom, is that the MBPT2 and CCSD values for the dimer polarizabilities appear to be very close to each other. In the scale of the figure, small deviations between the MBPT2 and CCSD curves would make it difficult to distinguish between these curves. We therefore opted to omit the CCSD curves from the figure and to introduce the common label "MBPT2, CCSD" for the MBPT2 results.

As seen in Fig. 2, the transverse and longitudinal dimer polarizabilities obtained at the same levels of *ab initio* treatments differ from each other and from the doubled atomic polarizability 2α determined at the same theoretical level. These differences quantify the effects of the anisotropy and nonadditivity of the dimer polarizability and diminish in the limit of large internuclear separations where interaction between the atoms vanishes. We have the general inequality $\alpha_{\parallel}(R) > 2\alpha > \alpha_{\perp}(R)$, reflecting the fact that interaction between the induced atomic-dipole moments is attractive for the electric field applied along the dimer and repulsive for the field direction perpendicular to the dimer.

In order to compare the *ab initio* results with the results of the DID model, we have scaled the curves from Fig. 2

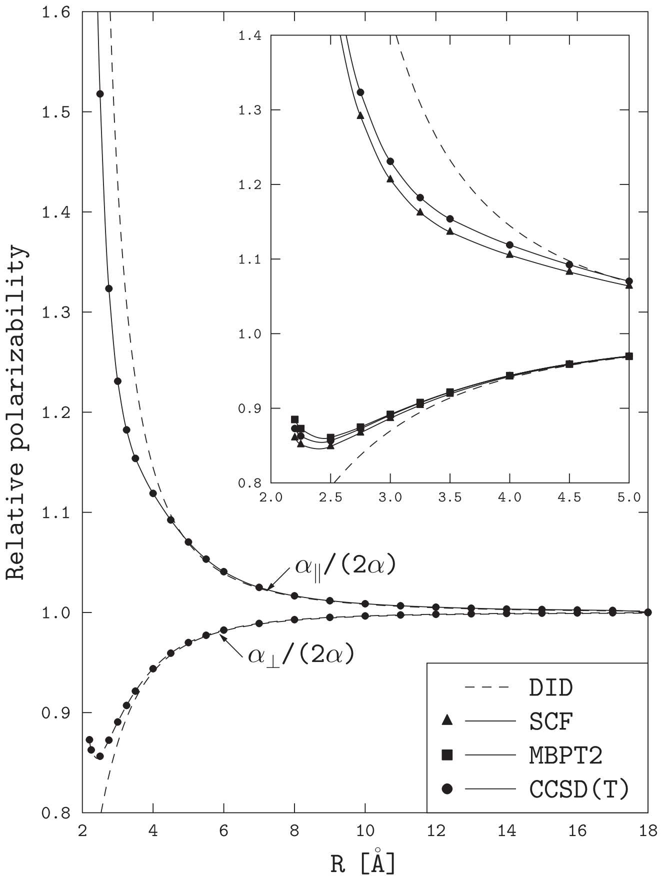

FIG. 3. Relative polarizabilities versus internuclear distance. Triangles, squares, and dots (connected by the smooth solid lines) show the SCF, MBPT2, and CCSD(T) results. Dashed lines are the polarizability curves according to the DID model. The inset shows the curves for the domain of small distances where the finite-field results deviate from those of the DID model and where minor discrepancies appear in the results obtained at the SCF, MBPT2, and CCSD(T) levels.

by the corresponding limiting values $\alpha_{\parallel,\perp}(R \to \infty) = 2\alpha$. A striking feature of such scaled results, shown in Fig. 3, is that the curves obtained from the finite-field SCF, MBPT2, CCSD, and CCSD(T) calculations practically coincide with each other. In other words, the way the electron correlations are taken into account, although affecting the absolute values of the dimer and atomic polarizabilities, has no noticeable influence on the ratios $\alpha_\perp(R)/(2\alpha)$ and $\alpha_\parallel(R)/(2\alpha)$. The curves according to the DID model expressions (3) are shown in Fig. 3 for the experimental value 27.29 of the atomic Xe polarizability [3]. As the figure reveals, the scaled *ab initio* dimer polarizabilities coincide with those of the DID model for internuclear distances exceeding the value ≈4.5 Å. The latter value turns out to be a good estimate of the equilibrium internuclear separation for the Xe dimer. This fact, known from the literature, is also confirmed by our computations of the interaction energy for the dimer. The energy curves are obtained with the BSSE corrections included and shown in Fig. 4. As is common for van der Waals clusters, the SCF interaction energy does not exhibit a minimum as a function of R, while the energy curves obtained taking account of the electron correlations have the local minima corresponding to attractive interaction between the atoms. For distances smaller than ≈4.5 Å, the DID model overestimates the longitudinal and underestimates the transverse dimer polarizabilities. In addition, $\alpha_\parallel(R)$ in the DID model becomes negative for distances smaller than $(2\alpha)^{1/3} \approx 2.01$ Å, thereby exhibiting an unphysical behavior (not included in the curve in the figure). Also seen for small distances are minor deviations between the *ab initio* scaled curves (the inset in the figure). The overall impact of Fig. 3 is worth reiterating: the relativistic *ab initio* calculations with our original basis set yield scaled polarizabilities that are rather insensitive to the level of included electron correlations, and, in addition, for internuclear distances around and exceeding the equilibrium distance for the dimer, these scaled values are in perfect agreement with the DID model.

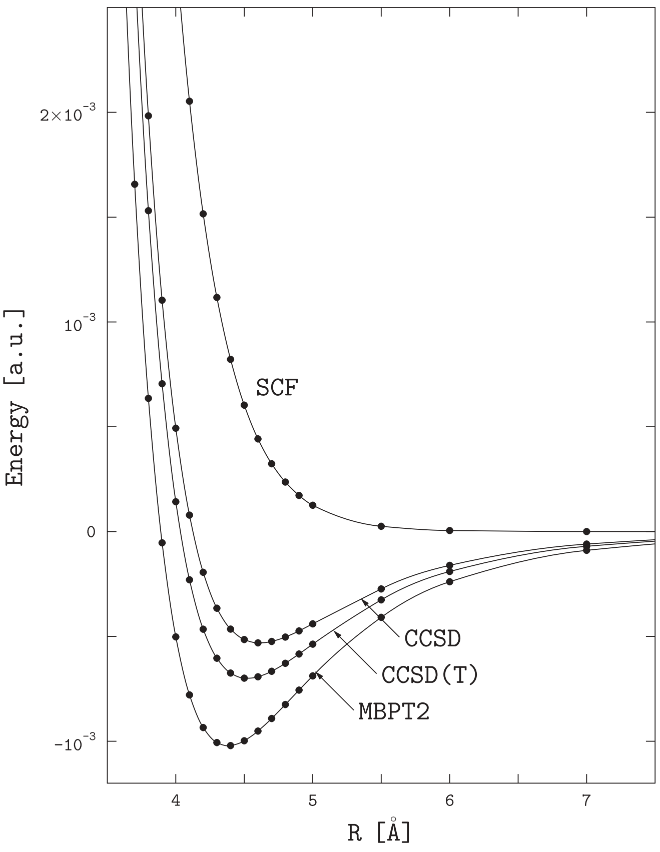

FIG. 4. Dimer interaction energy.

With the CCSD(T) values of the dimer polarizabilities, the anisotropy $\Delta\alpha$ for the internuclear distance 4.5 Å is 7.28. This theoretical result agrees well with the experimentally measured anisotropy 8.77 ± 2.02 reported in Ref. [19].

IV. DISCUSSION AND CONCLUDING REMARKS

In this paper, we have studied the electric-dipole polarizabilities of the Xe dimer. Although addressing these properties is by far not a new subject, in contrast to previous studies our calculations rely on a fully relativistic all-electron approach, allowing us to refer to our results as benchmark ones. The finite-field *ab initio* polarizability calculations have been performed with a specially designed extended set of basis GTOs by application of the SCF procedure followed by an accounting for the electron correlations within the MBPT2, CCSD, and CCSD(T) methods. The atomic polarizability has been thoroughly compared with the available theoretical and experimental data, and the dimer polarizabilities have been determined with account for the BSSE corrections in a broad range of internuclear separations. Special care was taken to analyze the effects of the nonadditivity and anisotropy of the dimer polarizability. In particular, for the internuclear distance of 4.5 Å corresponding to the minimum of the CCSD(T) interaction energy, the value of the anisotropy $\Delta\alpha$ was found to agree with the experimentally measured value from Ref. [19]. Another finding, which we consider to be quite remarkable, concerns the relative polarizabilities obtained as the ratios of dimer polarizabilities to the sum of the independent atomic polarizabilities determined at the same level of the *ab initio* description. Such scaled polarizabilities, determined with the SCF, MBPT2, CCSD, and CCSD(T) methods turn out to be close to each other with very high accuracy. Only minor deviations in the relative values obtained with different methods can be observed at small (smaller than 4.5 Å) displacements between the atoms. It is also remarkable that the scaled polarizabilities of the dimer for displacements exceeding 4.5 Å perfectly agree with the results of the simple DID model. On the grounds of these observations, in order to determine accurate theoretical values of the dimer polarizabilities it is sufficient to invest the computational efforts in obtaining reliable polarizability of the single Xe atom, and then to use the scaling relations (3) of the DID model. We expect this approach to be applicable to larger Xe clusters and will address this issue in our studies currently in progress.

To this end, we will discuss the anionic states formed by attaching an extra electron to the dimer in the presence of an external magnetic field. A theoretical description of the ground bound state of the attached electron requires a full multielectron treatment of the anion thereby formed. We will not address the ground state for now but discuss the *excited* magnetically induced states, where the influence of the underlying neutral core on the excess electron can be reduced to a central potential acting on this electron. This is the polarization potential (1). The simplest meaningful approximation to the qualitative analysis of the binding assumes the extra electron to occupy the zero-point Landau orbitals. These orbitals can be specified by the discrete values of the projection of the angular momentum of the electron onto the direction of the magnetic field, labeled by the integer quantum number s. For an isotropic central potential, s is a good quantum number, enumerating therefore the states of the bound electron. In order to estimate the corresponding binding energies ε_s, one needs to average the central potential with the two-dimensional (for motion transverse to the magnetic field) electron density for the Landau orbitals and integrate it over the remaining (longitudinal) coordinate (see Ref. [8] for the details). For the central potential from an isotropic polarizability of 2α (α is the atomic polarizability), the procedure gives the closed-form results

$$\varepsilon_s(2\alpha) = 0.12(2\alpha)^2 B^3 \delta_s^2, \tag{6}$$

where B is the magnetic field strength in atomic units (i.e., in units of 2.3554×10^5 T), $s = 1,2,\ldots$, $\delta_1 = 1$, and $\delta_s = [1 - (1.5/s)]\delta_{s-1}$. For anisotropic polarizability, the number s is no longer a good quantum number, and care should be taken when the above-described procedure is applied. We will assume the effects of the anisotropy of the dimer polarizability on the magnetically induced anionic states to be small enough that we can neglect the coupling between the Landau orbitals with different s. The estimates of the binding energies then appear to deviate from these given by Eq. (6) as follows:

$$\begin{gathered}\varepsilon_s\,(\alpha_\perp,\alpha_\parallel) = \xi_1^2 \xi_2^2 \varepsilon_s(2\alpha),\\ \xi_1 = \frac{\bar{\alpha}}{2\alpha}, \quad \xi_2 = 1 + \frac{1 - 3\cos^2\vartheta}{24}\,\frac{\Delta\alpha}{\bar{\alpha}},\end{gathered} \tag{7}$$

where $\bar{\alpha} = (2\alpha_\perp + \alpha_\parallel)/3$ is the average value of the dimer polarizability and ϑ is the angle between the dimer axis and the magnetic field direction. For the equilibrium internuclear separation of 4.5 Å, the CCSD(T) values of the polarizabilities yield $\xi_1 = 1.003$ and the parameter ξ_2 varying between 0.99 and 1.0055, depending on the orientation of the dimer with respect to the magnetic field. This means that the effects of the nonadditivity and anisotropy of the dimer polarizability influence the magnetically induced binding to a minor extent; in particular, the corresponding binding energies change by less than 2.6% of the values (6) devised assuming additive contributions of the individual atomic polarizabilities. For smaller internuclear separations, even though the anisotropy $\Delta\alpha$ becomes larger, the binding energies of the magnetically induced states still remain not much influenced: for a displacement of 4.0 Å the anisotropy-induced changes in binding energies are less than 3.3%, and for a displacement of 3.5 Å the changes are less than 4.2%.

The all-electron relativistic studies presented in this paper allow us to conclude that the finite-field polarizability calculations with the basis set we developed provide reliable benchmark results for both the single Xe atom and the Xe dimer. As in the previous investigations, we find the electron correlations to have an essential impact on the values of the polarizability. On the other hand, for realistic, not-too-small internuclear distances, the scaled polarizabilities as functions of the internuclear distance exhibit a high similarity of the results obtained from the classical DID model to the *ab initio* results of the SCF, MBPT2, CCSD, and CCSD(T) theoretical treatments. Therefore, reliable polarizability values for the dimer can be deduced from an accurate *ab initio* atomic polarizability by application of the DID scaling relations. The efficiency of this approach will be examined in the course of further studies of larger Xe clusters.

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[1] K. D. Bonin and V. V. Kresin, *Electric-Dipole Polarizabilities of Atoms, Molecules, and Clusters* (World Scientific, Singapore, 1997).

[2] P. Stampfli, Phys. Rep. **255**, 1 (1995).

[3] T. M. Miller and B. Benderson, Adv. At. Mol. Phys. **13**, 1 (1977).

[4] R. H. Orcutt and R. H. Cole, J. Chem. Phys. **46**, 697 (1967).

[5] V. G. Bezchastnov, P. Schmelcher, and L. S. Cederbaum, Phys. Rev. A **61**, 052512 (2000).

[6] V. G. Bezchastnov, P. Schmelcher, and L. S. Cederbaum, Phys. Chem. Chem. Phys. **5**, 4981 (2003).

[7] V. G. Bezchastnov, P. Schmelcher, and L. S. Cederbaum, Phys. Rev. Lett. **95**, 113002 (2005).

[8] V. G. Bezchastnov, P. Schmelcher, and L. S. Cederbaum, Phys. Rev. A **75**, 052507 (2007).

[9] L. Silberstein, London Edinburgh Dublin Philos. Mag. J. Sci. **33**, 521 (1917).

[10] J. Applequist, J. R. Carl, and K.-K. Fung, J. Am. Chem. Soc. **94**, 2952 (1972).

[11] C. Domene, P. W. Fowler, P. Jemmer, and P. A. Madden, Mol. Phys. **98**, 1391 (2000).

[12] J. Ciao and B. J. Berne, J. Chem. Phys. **97**, 8628 (1992).

[13] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[14] P. D. Dacre, Mol. Phys. **47**, 193 (1982).

[15] G. Maroulis, A. Haskopoulos, and D. Xenides, Chem. Phys. Lett. **396**, 59 (2004).

[16] P. J. Leonard, At. Data Nucl. Data Tables **14**, 21 (1974).

[17] D. P. Shelton, Phys. Rev. A **42**, 2578 (1990).

[18] U. Hohm and U. Trümper, Chem. Phys. **189**, 443 (1994).

[19] S. Minemoto, H. Tanji, and H. Sakai, J. Chem. Phys. **119**, 7737 (2003).

[20] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[21] A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).

[22] A. Kumar and W. J. Meath, Can. J. Chem. **63**, 1616 (1985).

[23] U. Hohm and K. Kerl, Mol. Phys. **69**, 803 (1990).

[24] J. Andzelm, S. Huzinaga, M. Klobukowski, and E. Radzio, Mol. Phys. **52**, 1495 (1984).

[25] M. Douglas and N. M. Kroll, Ann. Phys. (NY) **82**, 89 (1974).

[26] B. A. Hess, Phys. Rev. A **32**, 756 (1985); **33**, 3742 (1986).

[27] K. Andersson *et al.*, computer code MOLCAS Version 7, University of Lund, Sweden.

[28] K. D. Dyall, I. P. Grant, F. A. Parpia, and E. P. Plummer, Comput. Phys. Commun. **55**, 425 (1989).

[29] K. G. Dyall and K. Fægri Jr., Theor. Chim. Acta **94**, 39 (1996).