TDMP2 Calculation of Dynamic Multipole Polarizabilities and Dispersion Coefficients of the Noble Gases Ar, Kr, Xe, and Rn

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Using the recently developed time-dependent second-order Møller−Plesset perturbation theory (TDMP2), we have calculated correlated frequency-dependent multipole polarizabilities for the noble gases argon through radon. To get accurate results, i.e., near the TDMP2 basis set limit, we considered large one-particle basis sets, optimized for polarizability calculations. With the exception of argon, where we assumed relativistic effects to be neglegible, we employed the spin-free Hamiltonian obtained by means of a Douglas−Kroll transformation to treat relativistic and correlation effects on equal footing. Where reference data are available, the results for the static values and for the first Cauchy moments of all polarizabilities considered are in good agreement with the best theoretical and experimental data. Utilizing these results, we have calculated improved dispersion coefficients for interactions involving the rare gas atoms Ar through Rn, which are estimated to be accurate within a few percent.

I. Introduction

The frequency-dependent polarizability is one of the central molecular properties. Experimentally it is related to typical linear optical properties such as the dispersion of the refractive index, the dielectric constant, the Verdet constant, and the Rayleigh scattering cross section as well as the Rayleigh depolarization ratio. Another important application of polarizabilities is the calculation of the long-range asymptotic part of the weak interaction potential of van der Waals complexes.

While the asymptotic induction energy can be calculated from the static multipole polarizabilities and the multipole moments, the dispersion energy is most commonly described in terms of dispersion coefficients, which are related to the dynamic multipole polarizabilities at imaginary frequencies via the Casimir−Polder formula.

The usefulness of dispersion coefficients, thus employing a $1/R$ expansion of the second-order dispersion energy, for the construction of interaction potentials for van der Waals complexes has been shown by several impressive applications.[1−4] However, the ab initio calculation of frequency-dependent response properties is a problem far from standard, if one has to account for the contributions of the electron correlation. Accurate correlated calculations of dispersion coefficients exist only for van der Waals complexes of a few small molecules such as H_2,[5−7] N_2,[2,8−10] H_2O,[1] NH_3,[1] and CO.[2]

In the series of the noble gas atoms very accurate explicitly correlated calculations are available for helium.[6,7] Multiconfigurational self-consistent-field linear response (MCSCF-LR) calculations in extended basis sets have been performed for He and Ne.[11] A MCSCF calculation of frequency-dependent response properties of argon has been published very recently by Jaszuński et al.[12] Employing the many-body perturbation theory method developed by Wormer and co-workers,[1,9] which includes contributions of single, double and triple excitations, SDT-MBPT(2), Thakkar et al. have calculated dispersion coefficients for the dimers of the atoms neon through xenon.[2] The authors point out, however, that due to basis set deficiencies and the neglect of relativistic effects, their results are not very accurate for the heavier atoms krypton and xenon, and they stress the need for calculations that treat accurately the relativistic contributions to the dynamic multipole polarizabilities. The uncertainity about the relativistic effects is also one of the major contributions to the estimated errors of a benchmark calculation for the static dipole polarizabilities of krypton and xenon by Rice et al.,[13] using second-order Møller−Plesset perturbation theory (MP2) and the single- and double-excitation coupled-cluster method with a perturbational estimate of connected triple excitations (CCSD(T)). Very recently Nicklass et al.[14] calculated static dipole and quadrupole polarizabilities of the atoms neon through xenon using relativistic and nonrelativistic effective core potentials and MP2 as well as CCSD(T).

For the polarizability of the heaviest rare gas atom, radon, to our knowledge, up to now no ab initio calculation has been published.

Recently, we have developed and implemented a time-dependent second-order Møller−Plesset (TDMP2) method for the calculation of dynamic linear response properties.[15] Within this method the frequency-dependent polarizability is calculated as the second derivative of the MP2 energy with respect to the strengths of two external fields, oscillating with the same frequency. In the static limit this approach becomes equivalent to MP2 finite-field calculations, which has the advantage that the TDMP2 correlations corrections, i.e., the difference from the time-dependent Hartree−Fock (TDHF) values, can be well compared with MP*n* contributions to the static polarizabilities. In contrast to a similar method of Rice and Handy,[13] the TDMP2 method conserves the symmetry of the polarizability tensors and the second-order pole structure corresponding to the double excitations.

The purpose of the present paper is to investigate the accuracy of the TDMP2 method for the calculation of frequency-dependent polarizabilities for systems that are suitable for a perturbational treatment of the correlation effects. A second intention of the present communication is to provide accurate relativistic ab initio calculations for the polarizabilities and the dispersion coefficients of the heavier noble gases. Therefore, we employed the spin-free no-pair Hamiltonian H_+^{sf1}, which is obtained through a Douglas−Kroll transformation of the no-pair Hamiltonian,[16−20] correct to second order in the potential

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generated by the nucleus. The important approximations made in this ansatz for the relativistic Hamiltonian are the use of the unmodified nonrelativistic potentials for the electron−electron interaction and the interaction with the external electric fields. H_+^{sf1} averages over the fine-structure components; thus, a one-component formalism is obtained. Due to these approximations, only a modification of the one-electron integrals is required, so that H_+^{sf1} can easily be combined with the TDMP2 method to obtain the relativistic contributions to the frequency-dependent polarizabilities at the correlated level.

In the next section we will briefly sketch the definition of the frequency-dependent polarizabilities and the theory of the TDMP2 method, which has been introduced in ref 15. The technical details, especially the construction of the one-particle basis sets, are discussed in section III. In section IV we present and discuss the results of our calculations.

II. Theory

Traditionally, the frequency-dependent polarizability $\alpha_{QW}(-\omega;\omega)$ is defined as the linear response of the expectation value $\langle\hat{Q}\rangle$ to a field described by the operator $\hat{W}$, which oscillates with frequency ω. As has been pointed out in refs 15 and 21, $\alpha_{QW}(-\omega;\omega)$ can alternatively be defined as the second derivative of the energy with respect to the strength of two external fields that oscillate with frequencies of the same absolute value, but with opposite signs. Hence, if the Hamiltonian is given by

$$\hat{H}(t) = \hat{H}^{(0)} + \hat{h}_Q^{(1)}(-\omega,t) + \hat{h}_W^{(1)}(\omega,t) \tag{1}$$

where $\hat{h}_W^{(1)}(\omega,t)$ is defined as

$$\hat{h}_W^{(1)}(\omega,t) = [f_W(\omega)\mathrm{e}^{+i\omega t} + f_W(\omega)^*\mathrm{e}^{-i\omega^* t}]\hat{W} \tag{2}$$

and a similiar definition holds for $\hat{h}_Q^{(1)}(-\omega,t)$. Then $\alpha_{QW}(-\omega;\omega)$ can be calculated from the energy as

$$\alpha_{QW}(-\omega;\omega) = -\left.\frac{\partial^2 E}{\partial f_Q(-\omega)\partial f_W(\omega)}\right|_0 \tag{3}$$

Using this definition, a correlated correction to the TDHF frequency-dependent polarizability can be obtained in the framework of Møller−Plesset perturbation theory as the second derivative of the time-dependent MP2 energy:

$$\alpha_{QW}(-\omega;\omega) = \alpha_{QW}^{\mathrm{TDHF}}(-\omega;\omega) + \Delta\alpha_{QW}^{\mathrm{TDMP2}}(-\omega;\omega)$$

$$\Delta\alpha_{QW}^{\mathrm{TDMP2}}(-\omega;\omega) = -\left.\frac{\partial^2(\Delta E_{\mathrm{MP2}})}{\partial f_Q(-\omega)\partial f_W(\omega)}\right|_0$$

with

$$\Delta E_{\mathrm{MP2}} = \frac{1}{2}(\langle\tilde{\Psi}_0^{(1)}(t)|\hat{V}|\tilde{0}\rangle + \langle\tilde{0}|\hat{V}|\tilde{\Psi}_0^{(1)}(t)\rangle) \tag{4}$$

In the last equation $|\tilde{0}\rangle$ is the TDHF wave function, which is used as the reference state for the time-dependent Møller−Plesset perturbation theory, and $|\tilde{\Psi}_0^{(1)}(t)\rangle$ is the first-order Møller−Plesset correction for the wave function. $\hat{V}$ is the electron fluctuation potential.

To evaluate the second derivatives of ΔE_{MP2}, we have made extensive use of the machinery developed in the context of geometrical derivative techniques;[22−24] in particular, we have used the Lagrangian formulation[25] to obtain numerical stable expressions for the correlation correction to the frequency-dependent polarizability that do not reference the second-order TDHF parameters.

If $\hat{Q}$ and $\hat{W}$ are electric multipole operators, then for real or pure imaginary frequencies $\alpha_{QW}(-\omega;\omega)$ is a real quantity. Below the first transition frequency, $\alpha_{QW}(-\omega;\omega)$ can be expanded in a series of Cauchy moments,

$$\alpha_{QW}(-\omega;\omega) = \sum_{k=0}^{\infty}\omega^{2k}S_{QW}(-2k-2) \tag{5}$$

where the moments $S_{QW}(k)$ are defined by a sum over states expression

$$S_{QW}(k) = \sum_{n\neq 0}2\langle 0|\hat{Q}|n\rangle\langle n|\hat{W}|0\rangle(E_n - E_0)^{k+1} \tag{6}$$

or in terms of oscillator strengths and transition energies

$$S_{QW}(k) = \sum_{n\neq 0}f_{n0}(\Delta E_{n0})^k \tag{7}$$

Equation 5 is a Taylor expansion of $\alpha_{QW}(-\omega;\omega)$ in ω. Therefore, one could expect that the Cauchy moments can be obtained as numerical derivatives of the frequency-dependent polarizabilities, in case they are not available as analytical derivatives. But, as it has been remarked by several authors,[26,27] as a consequence of the singularities of $\alpha_{QW}(-\omega;\omega)$ at the transition frequencies, this leads to instable results.

A way to get around these problems is to fit an effective spectrum to the dynamic polarizabilities:

$$\alpha_{QW}(-\omega;\omega) = \sum_m \tilde{f}_{QW,m}/(\widetilde{\Delta E}_{QW,m}^2 - \omega^2) \tag{8}$$

From these pseudo oscillator strength distributions accurate Cauchy moments for negative k values can be obtained via eq 7. Such effective spectra can also be used to solve the Casimir−Polder integral, which appears in the definition of the dispersion coefficients.

Alternatively, the dispersion coefficients can be calculated directly from the frequency-dependent multipole polarizabilities by numerical, e.g., Gauss−Chebyshev or Gauss−Legendre, integration. We adopted the following definitions for the isotropic dispersion coefficients:[28]

$$C_6^{\mathrm{AB}} = \frac{3\hbar}{\pi}\int_0^{\infty}\alpha_1^{\mathrm{A}}(i\omega)\,\alpha_1^{\mathrm{B}}(i\omega)\,\mathrm{d}\omega \tag{9}$$

$$C_8^{\mathrm{AB}} = \frac{15\hbar}{2\pi}\int_0^{\infty}\alpha_1^{\mathrm{A}}(i\omega)\,\alpha_2^{\mathrm{B}}(i\omega) + \alpha_2^{\mathrm{A}}(i\omega)\,\alpha_1^{\mathrm{B}}(i\omega)\,\mathrm{d}\omega \tag{10}$$

$$C_{10}^{\mathrm{AB}} = \frac{14\hbar}{\pi}\int_0^{\infty}\alpha_1^{\mathrm{A}}(i\omega)\,\alpha_3^{\mathrm{B}}(i\omega) + \alpha_3^{\mathrm{A}}(i\omega)\,\alpha_1^{\mathrm{B}}(i\omega)\,\mathrm{d}\omega + \frac{35\hbar}{\pi}\int_0^{\infty}\alpha_2^{\mathrm{A}}(i\omega)\,\alpha_2^{\mathrm{B}}(i\omega)\,\mathrm{d}\omega \tag{11}$$

where α_1, α_2, and α_3 are the isotropic dipole, quadrupole, and octupole polarizabilities, respectively.

III. Technical Details

For polarizability calculations it is extremely important that one takes some care in the construction of the one-particle basis sets. To get the contributions from electrons in orbitals with an angular momentum l to the linear response to a multipolar electric field $Q_{l'}$, a considerable number of polarization functions must be included in the range $l \otimes l' = |l - l'|, ..., |l + l'|$. The mean contribution to the polarizability of the noble gas atoms

TABLE 1: Static Dipole, Quadrupole, and Octupole Polarizabilities and Cauchy Moments for Argon (in au)

	TDHF	TDMP2	lit.	expt
α_1	10.759	11.15	11.062[c]	11.07[f]
	10.757[b]		11.17 ± 0.05[d]	11.08[g]
	10.758[q]		11.16,[h] 11.17[l]	11.074[i]
	10.76[a]		11.23,[e] 11.12[o]	11.08[j]
			11.032[p]	
α_2	50.210	52.78	51.862[c]	
	50.21[a]		53.58[e]	
			52.09[p]	
α_3	530.2	553.1	536.38[c]	
	531.3[a]			
$S_1(0)$	17.81	17.81	16.70[k]	18.00[m]
$S_1(-1)$	8.658	8.775	8.638[k]	8.768 ± 0.09[g]
$S_1(-3)$	15.85	16.95	15.78[k]	16.788 ± 0.17[g]
$S_1(-4)$	25.45	28.28	25.27[k]	27.91 ± 0.28[g]
			28.32[l]	27.98[n]
$S_2(0)$	50.98	52.48		
$S_2(-1)$	45.25	46.35		
$S_2(-3)$	65.20	70.70		
$S_2(-4)$	95.53	107.0		
$S_3(0)$	433.6	483.8		
$S_3(-1)$	428.0	442.5		
$S_3(-3)$	765.6	812.2		
$S_3(-4)$	1214	1312		

[a] Numerical coupled Hartree−Fock, ref 30. [b] Coupled Hartree−Fock, ref 33. [c] Diagrammatic SDT-MBPT(2), ref 2. [d] Finite field CCSD(T), ref 35. [e] Finite field MP4(SDTQ), ref 36. [f] Experiment, ref 37. [g] Constrained dipole oscillator strength distribution (DOSD), ref 34. [h] Finite field MP2, ref 35. [i] Reference 38. [j] Reference 39. [k] TDHF, ref 2. [l] MCSCF-LR, ref 12. [m] Exact value corresponding to the Thomas−Reiche−Kuhn sum rule. [n] Reference 40. [o] CCSD(T), ref 29. [p] MP2 with pseudopotential, ref 14. [q] Numerical Hartree−Fock, ref 41.

comes from the electrons in the valence s and p shells. Hence, one needs at least d polarization functions for the dipole polarizability and f polarization functions for the quadrupole polarizability. To get reasonable octupole polarizabilities, one must even include a set of g functions.

A. Argon. The basis set for argon was constructed by starting from the correlation-consistent aug-cc-pV5Z basis of Woon and Dunning.[29] From this basis we took the (21s13p)/[8s7p] subset and augmented it with two diffuse s and p functions ($\zeta_s = 0.0194, 0.0070$ and $\zeta_p = 0.0147, 0.0054$), further adding successively d, f, and g orbitals, with exponents taken from the p orbitals, until the CHF results for the static dipole, quadrupole, and octupole polarizabilities were converged to within 0.1%. To improve the treatment of the core correlation effects, we also added two steep d functions ($\zeta_d = 15.73, 35.53$). The resulting (23s15p9d7f5g)/[10s9p9d7f5g] basis gives CHF dipole and quadrupole polarizabilities that differ less than 0.1% from the numerical values (see Table 1). The static octupole polarizability is ca. 0.2% lower than the numerical reference value.[30]

B. Krypton. For the krypton atom we started with the Gaussian primitive (26s20p14d) WTF basis from Huzinaga and Klobukowski.[31] In the WTF basis sets the same exponents are used for all angular momenta. We contracted the primitives to a [13s11p7d] set, using a generalized contraction scheme with SCF orbital coefficients. The outermost nine s, eight p, and six d functions were left uncontracted. For numerical reasons we removed the innermost primitive s function. We augmented this basis by extrapolating with even-tempered series with four s, four p, and added six d functions, where we used the exponents of the outermost p functions. Finally, we included successively seven f and six g functions (the exponents were again taken form the WTF set of exponents: $\zeta_{f1-f7} = \zeta_{s20-s26}$ and $\zeta_{g1-g6} = \zeta_{s21-s26}$), until the CHF results for the polarizabilities α_1, α_2, and α_3 were converged within 0.1%. The seven f and six g functions have been collated in a (1222) and a (222) contraction, respectively, where the contraction coefficients were determined by a scheme first used by Sadlej for polarizability basis sets.[32] In this scheme the contraction coefficients of polarization functions, having common exponents with the highest occupied atomic orbital, are calculated from the SCF coefficients of this orbital by scaling them with $\alpha_i^{\Delta l/2}$, where α_i is the exponent of the primitive Gaussian function and Δl the difference in the angular momenta of the highest occupied orbital and the polarization function. With the resulting [16s14p12d4f3g] basis we obtained (nonrelativistic) CHF polarizabilities that differ less than 0.1% from the reference values.

To obtain a balanced treatment of the relativistic effects, we constructed for the relativistic polarizability calculations a second basis, using the same exponents but contraction coefficients determined from a relativistic SCF calculation.

C. Xenon. For xenon we used again the WTF basis set, which in this case consists of a (28s23p17d) set, as a starting point. We reduced this basis, using again a generalized contraction scheme and SCF orbital coefficients, to a [5s4p2d]+(10s8p6d) set, where (10s8p6d) denotes the outermost primitive functions which have been left uncontracted. To this basis we added two s and two p functions with exponents determined by extrapolating the most diffuse WTF exponents with an even-tempered series and three d ($\zeta_{d18-d20} = \zeta_{s26-s28}$) and seven f functions ($\zeta_{f1-f7} = \zeta_{s22-s28}$). We collated the seven f functions to a (2221) contraction, again using Sadlej's scaling scheme to determine the coefficients.

Due to technical limitations, we could not amend this basis by a sufficient number of g functions needed to calculate accurate octupole polarizabilities. Because of that, we do not give results for $\alpha_3(\omega)$ and C_{10} for xenon. As for krypton, we constructed also for xenon an analogous second basis set with contraction coefficients determined from a relativistic SCF calculation.

D. Radon. For the heaviest rare gas atom we also started from the WTF basis set of Huzinaga and Klobukowski.[31] In the case of radon we contracted this (28s24p18d11f) primitive set to a [6s5p3d1f]+(7s5p3d) basis, which we augmented by one s and one p function ($\zeta_s = \zeta_p = 0.025\,611\,783$) and four d functions ($\zeta_{d19-d22} = \zeta_{s26-s29}$) as well as four primitive f functions ($\zeta_{f12-f15} = \zeta_{s22-s25}$). Because an accurate determination of the quadrupole polarizability of radon would demand even more f-type polarization functions, we give for radon only the results for the dipole polarizability and C_6 dispersion coefficients.

For all atoms we calculated the considered polarizabilities at the grid points $\phi_j = [(2j - 1)/4N]\pi$ of an N-point Gauss−Chebyshev integration,

$$\frac{1}{2\pi}\int_0^\infty \alpha^A(i\omega)\,\alpha^B(i\omega)\,d\omega = \frac{1}{4N}\sum_{j=1}^{N}\frac{\alpha^A(i\cot(\phi_j))\,\alpha^B(i\cot(\phi_j))}{\sin^2(\phi_j)} \tag{12}$$

with $N = 10$, 15, and 20. Comparison of the dispersion coefficients obtained by numerical integration with these grid points showed that the numerical integration is converged within an accuracy of four digits.

To the relativistic results for the static polarizabilities and the dynamic polarizabilities at these 45 grid points, we fitted effective spectra that reproduce the calculated frequency-dependent polarizabilities with errors less than 10^{-5} au. The effective oscillator strength distributions are given in Tables 6−8. From the effective sprectra we calculated correlated (TDMP2) Cauchy moments $S(k)$ for $k = 0, -1, -3, -4$, while

TABLE 2: Static Dipole, Quadrupole, and Octupole Polarizabilities and Cauchy Moments for Krypton (in au)[m]

	TDHF (Δ_{rel})	TDMP2 (Δ_{rel})	lit.	expt
α_1	16.438 (−0.037)	16.85 (−0.01)	17.214[d]	16.79[g]
	16.477[b]		17.0 ± 0.2[e]	16.74[i]
	16.476[l]		16.89,[h] 17.08[f]	
	16.47[c]		16.966 (−0.01)[l]	
α_2	93.846 (−1.673)	96.75 (−1.55)	99.296[d]	
	95.55[a]		99.86[f]	
	94.25[c]		97.14 (−1.57)[l]	
α_3	1238 (−21.5)	1241 (−17.8)	1272.64[d]	
	1260[a]			
$S_1(0)$	28.79 (−0.17)	28.79	20.57[k]	36.00[j]
$S_1(-1)$	12.01 (−0.01)	12.13	11.51[k]	12.33 ± 0.12[g]
$S_1(-3)$	28.01 (+0.01)	29.42	28.26[k]	29.23 ± 0.29[g]
$S_1(-4)$	52.50 (+0.32)	56.78	52.51[k]	56.32 ± 0.56[g]
$S_2(0)$	71.40 (−0.88)	71.72		
$S_2(-1)$	72.45 (−1.23)	73.36		
$S_2(-3)$	141.2 (−2.1)	148.6		
$S_2(-4)$	237.5(−2.6)	255.4		
$S_3(0)$	716.0 (−12.5)	740.4		
$S_3(-1)$	844.1 (−15.1)	845.9		
$S_3(-3)$	2098 (−37)	2113		
$S_3(-4)$	3876 (−70)	3931		

[a] Numerical coupled Hartree−Fock, ref 30. [b] Coupled Hartree−Fock, ref 33. [c] Relativistic random phase approximation (RRPA) ref 42. [d] Diagrammatic SDT-MBPT(2), ref 2. [e] Finite-field CCSD(T), ref 35. [f] Finite-field MP4, ref 43. [g] Constrained dipole oscillator strength distribution (DOSD), ref 34. [h] Finite-field MP2, ref 35. [i] Reference 44. [j] Exact value corresponding to the Thomas−Reiche−Kuhn sum rule. [k] TDHF, ref 2. [l] Numerical Hartree−Fock, ref 41. [m] Shown are the relativistic TDHF and TDMP2 results; the relativistic corrections $\Delta_{rel} = X_{rel} - X_{non\text{-}rel}$, if available, are given in parentheses.

TABLE 3: Static Dipole and Quadrupole Polarizabilities and Cauchy Moments for Xenon (in au)[a]

	TDHF (Δ_{rel})	TDMP2 (Δ_{rel})	lit.	expt
α_1	26.75 (−0.35)	27.17 (−0.22)	28.233[d]	27.16[g]
	27.100[b]		27.4 ± 0.8[e]	27.29[h]
	26.97[c]		27.76,[f] 27.40[i]	
			27.417 (−0.206)[l]	
α_2	201.32 (−10.8)	202.8 (−9.64)	223.29[d]	
	212.60[b]		216.5[f]	
	204.3[c]		207.30 (−9.42)[l]	
$S_1(0)$	35.05 (−0.27)	35.05	24.09[j]	54.00[k]
$S_1(-1)$	17.25 (−0.04)	17.41	15.37[j]	17.31 ± 0.17[g]
$S_1(-3)$	54.25 (−0.78)	56.11	54.95[j]	56.39 ± 0.56[g]
$S_1(-4)$	121.0 (−1.0)	128.3	121.1[j]	129.6 ± 1.30[g]
$S_2(0)$	103.4 (−3.1)	104.8		
$S_2(-1)$	127.9 (−5.9)	128.2		
$S_2(-3)$	360.1 (−19)	367.9		
$S_2(-4)$	709.3 (−35)	739.1		

[a] Listed are the relativistic TDHF and TDMP2 results. The relativistic corrections $\Delta_{rel} = X_{rel} - X_{non\text{-}rel}$, if available, are given in parentheses. [b] Coupled Hartree−Fock, ref 33. [c] Relativistic random phase approximation (RRPA), ref 42. [d] Diagrammatic MBPT, ref 2. [e] Finite-field CCSD(T), ref 35. [f] Finite-field MP4(SDTQ), ref 43. [g] Constrained dipole oscillator strength distribution (DOSD), ref 34. [h] Reference 44. [i] Finite-field MP2, ref 35. [j] TDHF, ref 2. [k] Exact value corresponding to the Thomas−Reiche−Kuhn sum rule. [l] MP2 with pseudopotentials, ref 14.

TABLE 4: Static Dipole Polarizability and Cauchy Moments for Radon (in au)[a]

	TDHF (Δ_{rel})	TDMP2 (Δ_{rel})
α_1	32.75 (−1.38)	33.16 (−0.83)
$S_1(0)$	30.81	30.81
$S_1(-1)$	20.20	20.39
$S_1(-3)$	71.85	73.73
$S_1(-4)$	176.8 (−4.49)	185.2

[a] Listed are the relativistic TDHF and TDMP2 results. The relativistic correction $\Delta_{rel} = X_{rel} - X_{non\text{-}rel}$, if available, are given in parentheses.

the TDHF values for the Cauchy moments were calculated directly from the TDHF spectra.

IV. Results and Discussion

The static polarizabilities and the Cauchy moments for the atoms argon through radon are summarized in Tables 1−4. Our nonrelativistic results for the static dipole polarizabilities of argon, krypton, and xenon are in very good agreement with the MP2 results of Rice et al.[35] and a MCSCF-LR calculation of Jaszuński et al.[12] Also the differences from the CCSD(T) results of Rice et al.[35] are small. This indicates that both basis sets are sufficiently converged and second-order Møller−Plesset perturbation theory is appropiate to describe the correlation effects on the polarizabilities of the rare gases. The differences of the SDT-MBPT(2) results of Thakkar et al.[2] are small for argon, but for krypton and xenon our results are 2−5% smaller, which is probably mainly due to remaining basis set deficiencies in ref 2.

While our nonrelativistic TDHF values coincide with the reference data of Bishop and Cybulski,[33] our relativistic TDHF results, which we obtained using the no-pair operator $\hat{H}_+^{sf1}$, are slightly smaller than the numerical relativistic random phase approximation (RRPA) values of Kolb et al. Probably these differences arise due to the neglect of higher order relativistic contributions to the electron−electron and to the electron−external field interaction. On the other hand, the relativistic

TABLE 5: Dispersion Coefficients for Rare Gas−Rare Gas Interactions, Obtained from the Relativistic TDHF and TDMP2 Results[e]

	C_6				C_8			C_{10}		
	TDHF	TDMP2	lit.[a]	expt[b]	TDHF	TDMP2	lit.[a]	TDHF	TDMP2	lit.[a]
He−He	1.375	1.430	1.460 977 8[c]	1.458	13.12	13.76	14.117 855[c]	168.4	178.0	183.69125[c]
He−Ne	2.727	3.041	3.0712[d]	3.029	31.36	36.12	36.175[d]	453.5	548.9	545.08[d]
He−Ar	9.091	9.475	9.5667[d]	9.538	158.1	166.8	167.47[d]	3505	3713	3701.1[d]
He−Kr	12.83 (−0.03)	13.28 (−0.02)	13.652[d]	13.40	258.0 (−3.8)	268.8 (−3.6)	279.99[d]	6752 (−113)	6968 (102)	7256.6[d]
He−Xe	18.88 (−0.15)	19.46 (−0.10)	19.916[d]	19.54	467.5 (−20.0)	480.1 (−18.6)	524.99[d]			16674[d]
He−Rn	22.31 (−0.60)	22.99 (−0.42)								
Ne−Ne	5.514	6.543	6.553	6.383	73.46	91.79	90.34	1177	1589	1535
Ne−Ar	17.66	19.85	19.753	19.50	344.4	396.5	390.12	8145	9618	9335.2
Ne−Kr	24.80 (−0.05)	27.74 (−0.03)	28.009	27.30	550.8 (−7.4)	627.0 (−7.5)	638.14	15 170 (−250)	17 680 (250)	17 658
Ne−Xe	36.34 (−0.26)	40.54 (−0.20)	40.518	39.66	973.1 (−38.5)	1094 (−38.9)	1162.3			38 978
Ne−Rn	42.93 (−1.06)	47.91 (−0.81)								
Ar−Ar	62.01	64.80	64.543	64.30	1553	1644	1623.2	47 210	50 240	49 063
Ar−Kr	88.35 (−0.20)	91.66 (0.12)	93.161	91.13	2451 (−27)	2566 (−25)	2616.7	83 260 (−1170)	86 850 (−1080)	88 260
Ar−Xe	131.5 (−1.2)	135.7 (−0.8)	137.97	134.5	4260 (−150)	4403 (−137)	4669.4			
Ar−Rn	155.7 (−4.7)	160.6 (−3.3)								
Kr−Kr	126.3 (−0.6)	130.1 (−0.3)	135.08	129.6	3844 (−80)	3981 (−72)	4187.3	143 800 (−7100)	147 400 (−3400)	155 450
Kr−Xe	188.7 (−2.2)	193.2 (−1.5)	201.27	191.9	6623 (−283)	6774 (−254)	7389.1			
Kr−Rn	223.7 (−7.5)	229.0 (−5.1)								
Xe−Xe	283.4 (−5.4)	288.4 (−3.8)	302.29	285.9	11 260 (−700)	11 390 (−615)	12 807			
Xe−Rn	336.3 (−14.2)	342.1 (−9.7)								
Rn−Rn	399.4 (−26.3)	406.1 (−17.8)								

[a] Diagrammatic MBPT, ref 2. [b] Constrained dipole oscillator strength distribution (DOSD), ref 34. [c] Explicitly electron-correlated wave functions, ref 7. [d] He polarizabilities from explicitly correlated calculations, ref 45, combined with SDT-MBPT(2) polarizabilities, ref 2. [e] The relativistic corrections $\Delta_{rel} = X_{rel} - X_{non\text{-}rel}$, if available, are given in parentheses.

TABLE 6: Effective Spectra for the Dynamic Dipole polarizabilities of the Rare Gas Atoms Argon, Krypton, Xenon, and Radon[a]

	argon	krypton	xenon	radon
f_1	5.258 775(−2)	5.077 264(−1)	5.967 541(−1)	6.697 943(−1)
ϵ_1	3.934 488(−1)	3.833 601(−1)	3.292 296(−1)	2.976 378(−1)
f_2	7.102 176(−1)	1.926 559	2.275 850	2.734 009
ϵ_2	4.779 406(−1)	5.325 379(−1)	4.461 459(−1)	4.306 781(−1)
f_3	2.779 239	3.008 410	3.341 749	3.466 641
ϵ_3	7.118 201(−1)	7.739 638(−1)	6.502 047(−1)	6.506 601(−1)
f_4	2.610 211	1.864 500	1.599 387	1.433 909
ϵ_4	1.123 188	1.193 541	1.054 208	1.119 581
f_5	6.512 723(−1)	4.584 903(−1)	3.140 273	6.583 299
ϵ_5	2.868 816	2.432 923	2.882 557	2.620 869
f_6	1.383 960	2.735 953	7.780 914	1.042 036(+1)
ϵ_6	6.293 535	5.215 679	4.513 715	4.334 533
f_7	5.158 529	7.686 506	4.718 534	3.082 151
ϵ_7	1.352 548(+1)	9.350 942	6.364 469	5.126 991(+1)
f_8	3.326 653	2.639 744	4.034 865(−1)	2.419 501
ϵ_8	6.558 974(+1)	2.300 833(+1)	8.762 114	1.189 087(+1)
f_9	1.106 431	3.262 793(−1)	2.712 681	
ϵ_9	2.508 799(+1)	3.150 360(+1)	2.102 459(+1)	
f_{10}	2.662 884(−2)	7.635 370	8.482 693	
ϵ_{10}	6.293 292	9.443 989(+1)	7.966 707(+1)	

[a] Powers of 10 are indicated in parentheses.

effects that we obtained agree perfectly with the relativistic effects calculated very recently by Nicklass et al.[14] using energy-adjusted ab initio pseudopotentials and the Wood−Boring equation to account for relativity. There are some common trends for the relativistic effects on the polarizabilities of the noble gases. As one would expect, the absolute value of the relativistic contributions rises with the charge of the nucleus. For the noble gas atoms relativity lowers the polarizabilities; thereby, the effect is always smaller on the correlated, i.e. the TDMP2, results than on the TDHF values. The nonadditivity of the relativistic and the correlation contribution $(\Delta_{rel}(\text{TDMP2}) - \Delta_{rel}(\text{TDHF}))/\alpha^{\text{TDMP2}}$ varies for the atoms Kr, Xe, and Rn, and the multipole components considered between 0.1% for the dipole polarizability of krypton and 1.7% for the dipole polarizability of radon. This indicates that for heavy atoms it is important to treat correlation and relativistic effects on the same footing.

TABLE 7: Effective Spectra for the Dynamic Quadrupole Polarizabilities of the Rare Gas Atoms Argon, Krypton, and Xenon[a]

	argon	krypton	xenon
f_1	2.620 977	3.593 950	5.634 619
ϵ_1	4.861 862(−1)	4.288 470(−1)	3.694 177(−1)
f_2	4.183 020	1.465 240(+1)	2.089 752(+1)
ϵ_2	6.133 922(−1)	5.953 293(−1)	5.015 610(−1)
f_3	1.635 972(+1)	7.075 968	4.918 438(+1)
ϵ_3	8.902 472(−1)	8.482 164(−1)	8.327 371(−1)
f_4	3.734 259	3.317 477(+1)	1.015 244(+1)
ϵ_4	1.222 714	1.154 952	1.266 036
f_5	1.758 387(+1)	5.395 276	7.891 146
ϵ_5	1.585 548	2.295 183	2.813 741
f_6	4.244 805	3.328 343	6.839 896
ϵ_6	3.218 605	5.518 951	6.447 328
f_7	1.211 432	3.836 676	3.314 335
ϵ_7	7.400 566	1.196 136(+1)	1.054 455(+1)
f_8	2.544 003	6.585 183(−1)	8.863 809(−1)
ϵ_8	1.851 198(+1)	2.584 800(+1)	3.659 547(+1)

[a] Powers of 10 are indicated in parentheses.

For the Cauchy moments, reference data are only available for the dipole components $S_1(k)$. Comparison of the TDMP2 results for $S_1(k)$ with $k = -1$, -3, and -4 with the pseudo dipole oscillator strength (DOSD) data of Kumar and Meath[34] shows that the TDMP2 method reproduces the frequency dependence of the dipole polarizability of the atoms argon through xenon quite accurately. With the exception of $S_1(-4)$ of Ar, which deviates by 1.3% from the DOSD result, all TDMP2 values of these moments are within the error ranges of the pseudo-DOSD data, which are estimated by the authors to be about ±1%.[34]

According to the Thomas−Reiche−Kuhn sum rule the exact value for the Cauchy moment $S_1(0)$ is identical with the number of electrons in the atom. For light atoms, this sum rule is often used as a criterion for the completeness of the basis set with respect to the description of dipole excitations. To fulfill the TRK sum rule for heavier atoms, one would need a large number of very compact polarization functions to account for the contributions of even the innermost core electrons, which would raise the dipole polarizability only by a

TABLE 8: Effective Spectra for the Dynamic Octupole Polarizabilities of the Rare Gas Atoms Argon and Krypton[a]

	argon	krypton
f_1	7.294 399(+1)	1.069 065(+2)
ϵ_1	5.293 888(−1)	4.567 263(−1)
f_2	4.652 621(+1)	6.868 507(+1)
ϵ_2	6.704 095(−1)	5.444 208(−1)
f_3	1.442 586(+2)	1.626 148(+2)
ϵ_3	1.008 614	7.242 058(−1)
f_4	1.172 850(+2)	3.231 807(+2)
ϵ_4	1.749 459	1.339 451
f_5	4.672 486(+1)	4.464 042(+1)
ϵ_5	2.376 782	2.706 793
f_6	1.981 838(+1)	1.312 286(+1)
ϵ_6	4.731 728	4.762 424
f_7	1.080 376(+1)	6.372 558
ϵ_7	1.505 720(+1)	1.318 681(+1)
f_8	2.539 131(+1)	1.491 295(+1)
ϵ_8	3.503 470(+1)	1.155 448(+2)

[a] Powers of 10 are indicated in parentheses.

marginal amount. Therefore, as has been pointed out previously by Thakkar et al.,[2] the fulfillment of the TRK sum rule is for heavier atoms not a suitable criterion for the basis set quality for polarizability calculations. For argon, krypton, xenon, and radon our results violate the TRK sum rule $S_1(0)$ by 0.19, 7.21, 18.95, and 49.19, respectively, although the dipole polarizabilities and the Cauchy moments are very close to the reference data.

From the accuracy of the results we obtained for the dynamic dipole polarizabilities of Ar, Kr, and Xe, we conclude that a conservative estimate for the error of our results for the quadrupole and octupole polarizabilities of these atoms and for the dipole polarizability of Rn will be about ±2%, accounting for the probably slightly larger basis set deficiency errors for these properties.

In Table 5 we have listed the results for the dispersion coefficients C_6, C_8, and C_{10} for rare gas−rare gas interactions, involving the atoms He through Rn. For helium and neon we used the TDMP2 results for the dynamic polarizabilities from ref 15 to calculate the dispersion coefficients.

For the interactions between the atoms Ar, Kr, and Xe the TDMP2 results for the C_6 coefficients are within the error ranges (±1%) of the pseudo-DOSD values. According to the accuracy we obtained for the polarizabilities, we estimate the TDMP2 values for the C_8 and C_{10} coefficients for these interactions to be accurate within 2% and 3%, respectively. For the interactions involving a helium or a neon atom the errors of the TDMP2 dispersion coefficients are probably slightly larger because for these atoms we used smaller basis sets for the polarizability calculations, not that close to the TDMP2 basis set limit as for the atoms Ar through Rn.

As one could expect, the relativistic effects on the dispersion coefficients follow closely the same trends found for the polarizabilities. In all cases relativity lowers the dispersion coefficients and the magnitude of the relativistic effect rises with the nuclear charges of the atoms considered. As for the polarizabilities, the absolute values of the relativistic contributions are always somewhat smaller on the TDMP2 level than on the TDHF results. Also the differences of the dispersion coefficients of ref 2 follow mainly the differences found for the static polarizabilities, varying between 0.2% for the C_6 coefficient for $(Ne)_2$ and 12% for the C_8 coefficient of $(Xe)_2$. But for complexes, containing only the atoms He through Ar, the overall difference is small.

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