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Correlated Polarization Propagator Calculations of Static Polarizabilities

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Abstract

We present a systematic comparison of the correlation contribution at the level of the second-order polarization propagator approximation (SOPPA) and MP2 to the static dipole polarizability of (1) Be, BeH⁺, BH, CH⁺, MgH⁺, AlH, SiH⁺, and GeH⁺; (2) BH₃, CH₄, NH₃, H₂O, HF, BF, and F₂; and (3) N₂, CO, CN[−], HCN, C₂H₂, and HCHO. Fairly extended basis sets were used in the calculations. We find that the agreement with experimental values is improved in SOPPA and MP2 over the results at the SCF level. The signs and magnitudes of the correlation contribution in SOPPA are similar to those obtained in analytical derivative MP2 calculations. However, it is not possible to say, in general, which method gives the largest correlation contribution or the best agreement with experiment, nor is it possible to make a priori prediction of the sign of the correlation contribution. For the first group of molecules, which have a quasi-degenerate ground state, additional CCDPPA and CCSDPPA calculations were performed and compared with polarizabilities obtained as analytical/numerical derivatives of the CCD and CCSD energies. The CCSDPPA results were found to be in better agreement with other calculations than were the SOPPA results, demonstrating the necessity of using methods based on infinite-order perturbation theory for these systems. © 1994 John Wiley & Sons, Inc.

I. Introduction

The calculation of molecular dipole polarizabilities has been an active area of theoretical chemistry for years.[†] One of the main reasons for that is that the dipole polarizability plays an important role in many areas of physical chemistry like molecular interactions and light scattering. Another reason is that the calculation of dipole polarizabilities often is the first step toward the study of hyperpolarizabilities, which govern the nonlinear optical effects.^{††}

Historically, the most widely used approach to the calculation of dipole polarizabilities is the finite field method [3], in which a small external field is added as a perturbation to the Hamiltonian and the dipole polarizability is then obtained as the numerical first derivative of the calculated perturbed dipole moment or the numerical second derivative of the total perturbed energy. In a related approach, the external field is simulated by an array of distant point charges [4]. Both methods have the advantage that they can be applied to any kind of correlated method for which an energy can be calculated or a dipole moment can be defined.

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[†]For a review of the calculations of electric properties, see, e.g., [1].

^{††}For a review of the calculations of nonlinear properties, see, e.g., [2].

However, only for methods fulfilling the Hellmann–Feynman theorem like SCF or MCSCF, will the polarizabilities calculated as first derivatives of the dipole moment and calculated as a second derivatives of the energy be identical.

The second type of methods, which have taken over the field in recent years, are based on analytical derivatives of the energy with respect to the external electric field. These methods make use of know-how from the geometrical derivative techniques. At the SCF/RPA level, analytical higher-order derivatives can be obtained [5, 6]. Analytical first- and second-order derivatives are now routinely calculated at the MP2 level [7, 8] and first and second derivatives are also available for various coupled cluster and higher-order MBPT methods [9].

Another methodology for the calculation of second- as well as higher-order molecular properties is provided by the response or propagator theory [10, 11]. Electron correlation may be introduced into these methods via the Møller–Plesset perturbation theory or multiconfigurational approaches. As the molecular second- and higher-order properties (e.g., polarizabilities and hyperpolarizabilities) are obtained as the response of first-order properties (e.g., dipole moments) to external or internal perturbations, the results are identical only to the results of energy-derivative calculations in the case of methods fulfilling the Hellmann–Feynman theorem.

The perturbative polarization propagator method that is consistent through second order in the fluctuation potential has been coined the second-order polarization propagator approximation (SOPPA) [12]. This method has been applied to the calculation of a range of second-order properties including indirect nuclear spin–spin coupling constants [13], magnetizabilities [14–16], and nuclear magnetic shielding constants [16, 17]. Polarizability calculations using the SOPPA method have been performed on He [18, 19], Be [18], H₂ [19, 20], HF [18, 20], HCl [21], CO [12, 18, 21], N₂ [21, 22], and Cl₂ [21, 23]. In the present work, we have extended the range of application to several other molecules in order to compare the performance of SOPPA with the MP2 analytical derivative technique for the calculation of the static polarizability. We have considered four different types of atoms or molecules: (1) systems with four or six valence electrons and quasi-degenerate ground states like Be or BH; (2) other first-row hydrides AH_n; (3) the single-bonded molecules BF and F₂; and (4) multiple-bonded molecules like N₂ or HCN. For the systems in group (1), we have also performed calculations at the level of the coupled cluster polarization propagator approximations (CCDPPA/CCSDPPA) [24] as well as comparative calculations using analytical or numerical derivatives of the CCD and CCSD energies. Large basis sets, which were previously tested in the calculation of magnetic properties [15, 16] of these systems, have been used. Even though polarization propagator methods compute static and frequency-dependent polarizabilities with equal ease and the latter are the quantities that are most directly comparable with experiments, we have here reported only static polarizabilities. The reason for that is that the main purpose of this article was to compare the SOPPA method with MP2 or other correlated methods and the latter methods nearly always report only static polarizability tensors. In a forthcoming publication [25], we will discuss the frequency dependence of the same quantities at the SOPPA level of approximation.

In the following section, a brief review of the perturbative polarization propagator methods are given. In Section III, the details of the calculation are described, and in the last sections, we discuss our results.

II. Theory

In the presence of an external static electric field, the components of the electric dipole moment μ of a molecule or atom can be written as [26]

$$\mu_i(F) = \mu_i^{(0)} + \sum_j \alpha_{ij} F_j + \frac{1}{2} \sum_{jk} \beta_{ijk} F_j F_k + \frac{1}{6} \sum_{jkl} \gamma_{ijkl} F_j F_k F_l + \dots, \quad (1)$$

where $\mu^{(0)}$ is the permanent electric dipole moment and α , β , and γ are the static dipole polarizability and the static first and second hyperpolarizability tensors, respectively. The isotropic polarizability α and the polarizability anisotropy $\Delta\alpha$ are defined as

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \sqrt{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}. \quad (3)$$

From Eq. (1) we see that the dipole polarizability is the linear response of the molecular dipole moment to an external electric field and the β and γ hyperpolarizabilities are the quadratic and cubic responses, respectively. The static dipole polarizability is thus given as the zero-frequency limit of the linear response function [11] or polarization propagator [27, 28]:

$$\alpha_{ij} = -\langle\langle r_i; r_j \rangle\rangle_{\omega=0}, \quad (4)$$

where r_i is the i -th component of the electric dipole operator in the second quantized notation and in atomic units. Approximations to the polarization propagator can be obtained from the equation of motion:

$$\langle\langle r_i; r_j \rangle\rangle_{\omega} = (r_i^+ | \tilde{h}) (\hbar | \omega \hat{I} - \hat{H}_0 | \tilde{h})^{-1} (\hbar | r_j) \quad (5)$$

A complete operator manifold \hbar , consisting of all possible particle conserving excitation operators, has been introduced in the preceding equation and we have applied the superoperator formalism [29] in which the binary product of two operators A and B is defined as

$$(A | B) = \langle 0 | [A^+, B] | 0 \rangle \quad (6)$$

and the superoperator Hamiltonian \hat{H}_0 and superoperator identity operator are

$$\hat{H}_0 A = [H, A] \quad (7)$$

$$\hat{I} A = A. \quad (8)$$

The operator manifold forms a column vector and \tilde{h} labels the transposed row vector. Different approximate polarization propagator schemes can be devised by choosing an approximation to the, in principle, exact reference state $|0\rangle$ in the operator binary product (6) and by truncating the complete set of operators \hbar . In the perturbative polarization propagator approximations, one chooses a Møller–Plesset perturbation expansion of the reference state:

$$|0\rangle = N(|HF\rangle + |0^{(1)}\rangle + |0^{(2)}\rangle + \dots) \quad (9)$$

and uses (single, double, ...) excitation and de-excitation operators with respect to the Hartree–Fock state as the operator set \hbar . The n -th order approximation to the polarization

propagator is then obtained by keeping all terms in the three binary products in Eq. (5) up to and including order n in the fluctuation potential. The first-order approximation is the random-phase approximation (RPA), which for static properties is equivalent to coupled Hartree–Fock. For the second-order polarization propagator approximation (SOPPA), it turns out [12] to be necessary to include the first-order correction to the wave function $|0^{(1)}\rangle$ and the term in the second-order correction to the wave function, which originates from single excitations together with all particle–hole $\{q^+, q\}$ and two particle–two hole $\{q^+q^+, qq\}$ excitation and de-excitation operators in the operator manifold \mathbf{h} . The static polarizability can then be calculated from the polarization propagator in SOPPA as [12, 28]

$$\begin{aligned}\alpha_{ij} &= -(W_{2,\omega=0})_{ij} - (W_{4,\omega=0})_{ij} \\ &= -(T_{\omega=0})_i(P_{\omega=0})^{-1}(\tilde{T}_{\omega=0})_j - (W_{4,\omega=0})_{ij}\end{aligned}\quad (10)$$

$$\begin{aligned}&= -2((r_i^+ | \tilde{q}^+) - (r_i^+ | \tilde{q}^+ \tilde{q}^+)D^{-1}C)(-A+B+\tilde{C}D^{-1}C)^{-1}((q^+ | r_j) - (q^+q^+ | r_j)D^{-1}C) \\ &\quad + 2(r_i^+ | \tilde{q}^+ \tilde{q}^+)D^{-1}(q^+q^+ | r_j).\end{aligned}$$

The W_4 term is negative, whereas the correlation contribution to the W_2 term may be positive or negative. The complete SOPPA static polarizabilities are therefore always larger than the results of calculations, where the W_4 term is omitted.

The actual expressions for the matrices in terms of two-electron integrals and orbital energies can be found in Appendix C of [28] (for a correction to the W_4 term, see [19]). The W_4 term is a second-order term, whereas the three terms T , P , and \tilde{T} , which are all evaluated to second order, contain terms of order 0, 1, and 2. Consequently, the W_2 term also contains contributions of higher than second order. By expanding the inverse P matrix in orders of perturbation theory for analysis purposes, we can see that the polarization propagator expression in Eq. (10) gives rise to sums of terms to infinite order. Thus, several series of diagrams are included in SOPPA summed to infinite order. These terms, sometimes referred to as collective excitation effects [30], have no direct counterpart in analytical derivative perturbation theory calculations, as they are primarily caused by the requirement that the poles of the polarization propagator, and therefore the excitation energies, are correct to second order [27, 28]. In actual calculations, the complete inverse propagator, and not its expanded counterpart, is applied using the reduced linear equation technique as implemented in the RPAC 9.0 program package [31, 32].

The coupled cluster doubles (CCDPPA) and coupled cluster singles and doubles (CCSDPPA) polarization propagator approximations [24] are generalizations of SOPPA and are obtained by replacing the perturbation theory double excitation correlation coefficients by coupled cluster doubles amplitudes t_2 in the matrices A , B , $(r_i^+ | q^+)$ and $(r_i^+ | q^+q^+)$ and the single-excitation correlation coefficients by the coupled cluster singles amplitudes t_1 in $(r_i^+ | q^+)$. The latter holds for CCSDPPA only. This implies that we obtain SOPPA when we use the first iteration coupled cluster amplitudes in CCDPPA. Although CCDPPA/CCSDPPA includes additional higher-order terms, which implicitly sum selected classes of self-energy diagrams originating from single and double excitations to infinite order, it is still only consistent through second order, since we have not included, e.g., all third-order terms.

III. Computational Details

All propagator calculations have been performed with the Odense version [15,16] of the RPAC 9.0 program package [31]. The atomic integrals, molecular orbital energies, and coupled cluster amplitudes were obtained from the Gaussian 92 program system [8], which was interfaced with the RPAC program. The MP2, CCD, and CCSD static polarizabilities were calculated as analytical second derivatives (MP2), combined numerical and analytical second derivatives (CCD), and as pure numerical second derivatives (CCSD) of the corresponding energies using the Gaussian 92 program system. We use spherical Gaussian basis functions. The calculations were performed at the geometries given in [15] for BeH^- , BH, CH^+ , MgH^- , AlH, SiH^+ , and GeH^+ ; in [16a] for N_2 , CO, CN^- , HCN, and C_2H_2 ; and in [16b] for BH_3 , CH_4 , NH_3 , H_2O , HF, BF, and F_2 . The geometry for HCHO was taken from [33].

IV. Results for Systems with Quasi-degenerate Ground State

The beryllium atom, BH, CH^+ , and AlH are difficult cases for any method based on perturbation theory because of their quasi-degenerate ground states. However, previous CCSDPPA calculations of the excitation energies and oscillator strengths [34–36] gave very good agreement with experiment and MC-RPA calculations [37]. In our study of the magnetizability of these systems [15], we also found that deficiencies of SOPPA could be alleviated by using the CCDPPA or CCSDPPA methods. We thus decided to investigate the behavior of SOPPA vs. the CC-based perturbative propagator methods, also for the calculation of static polarizabilities of these systems.

In our previous study [15], we systematically optimized basis sets for the calculation of the magnetizability of these systems. The final basis sets were fairly large and we would expect them to give good results also for polarizabilities. In Table I we report the Thomas–Reiche–Kuhn (TRK) sum rule $S(0)$ and the isotropic static polarizability in the length, mixed, and velocity representation. At the RPA level and in the limit of a complete basis set, the three representations are equivalent and thus give the same results for the polarizability and for the TRK sum rule, which in this limit is equal to the number of electrons. The overall fulfillment of the TRK sum rule in all three representations is good as is the internal agreement between the three representations. However, we can see that it is better for the first-row systems than for the molecules containing second-row atoms and better for the neutral and positively charged systems than for the negative ions. The largest disagreement is consequently found for MgH^- . A similar statement can be made about the agreement between the length, mixed, and velocity formulation of the polarizability, and it illustrates the difficulties associated with a proper description of fluxional molecules. The basis sets for GeH^+ are not of the same quality, as Ge has occupied *d*-orbitals and the basis sets should therefore, in principle, include *g*-functions. However, even for this molecule, the agreement between the different representations of the polarizability and TRK sum rule is quite good, showing that the basis sets are balanced, although the absolute value of the TRK sum rule is too small.

In Tables II and III, the isotropic polarizability and polarizability anisotropy at various correlated levels are shown for some of the basis sets from [15]. The CCDPPA and CCSDPPA results for the isotropic polarizability (Table II) are lower than the RPA results for all atoms and molecules (between ~4% for CH^+ and ~28% for MgH^-), whereas SOPPA predicts a small increase for BH and CH^+ (~0.5%) and a much larger positive (~15%) correlation correction

TABLE I. Energies, TRK sum rule, and static polarizability at the RPA level of Be, BeH⁻, BH, CH⁺, MgH⁻, AlH, SiH⁺, and GeH⁺.^a

	Basis set ^b	No. CGTOs	E_{SCF}	Δ_{MP2}	$S_{\text{RPA}}^L(0)$	$S_{\text{RPA}}^M(0)$	$S_{\text{RPA}}^V(0)$	$\alpha^L(0)$	$\alpha^M(0)$	$\alpha^V(0)$
Be	[11s6p4d4f]	77	-14.572873	-0.661080	4.0124	3.9796	3.9481	44.937	44.724	44.515
BeH ⁻	[11s6p4d4f/9s8p1d]	115	-15.134369	-0.098487	6.0016	5.9792	5.9605	326.91	327.02	327.28
BH	[9s8p5d3f/6s5p1d]	105	-25.130132	-0.120556	6.0010	5.9977	5.9946	22.789	22.795	22.801
CH ⁺	[9s7p6d3f/5s4p1d]	103	-37.909457	-0.137940	6.0015	5.9977	5.9943	7.7543	7.7576	7.7610
MgH ⁻	[11s8p5d3f/9s8p1d]	119	-200.142216	-0.323205	13.728	13.559	13.415	347.12	346.63	346.50
AlH	[9s8p6d2f/6s6p1d]	106	-242.447075	-0.372626	13.917	13.909	13.904	48.792	48.765	48.740
SiH ⁺	[9s7p6d3f/5s4p1d]	103	-289.147784	-0.392760	13.929	13.918	13.910	21.071	21.028	20.985
GeH ⁺	[10s7p6d4f/5s4p2d]	116	-2075.566761	-0.812749	24.830	24.386	24.001	22.298	22.266	22.234

^a E_{SCF} is the Hartree-Fock SCF total energy and Δ_{MP2} is the Δ_{MP2} correlation energy; $S_{\text{RPA}}^L(0)$, $S_{\text{RPA}}^M(0)$, and $S_{\text{RPA}}^V(0)$ are the RPA values of the Thomas-Reiche-Kuhn sum rule in the length, mixed, and velocity representations; $\alpha^L(0)$, $\alpha^M(0)$, and $\alpha^V(0)$ are the static polarizabilities at the RPA level in the length, mixed, and velocity representations. All are expressed in atomic units: 1 au of $E = E_h \approx 4.35975 \times 10^{-18}$ J; 1 au of $\alpha = 4\pi\epsilon_0 a_0^3 \approx 1.64878 \times 10^{-41}$ J⁻¹ C² m².

^bFor a detailed description of the basis set and geometries, see [15].

for BeH^- . For the other systems, SOPPA reduces the isotropic polarizability between $\sim 2\%$ for SiH^+ and $\sim 8\%$ for MgH^- . This behavior is slightly different from the trend that we found for the paramagnetic contribution to the magnetizability [15] where SOPPA gave a different sign of the correlation contribution than did CCDPPA or CCSDPPA for all these molecules but GeH^+ .

The correlation contribution at the MP2 level is always larger than at the SOPPA level with the exception of the calculation for MgH^- with the largest basis set. Contrary to SOPPA, MP2 predicts a decrease of the polarizability of BH and CH^+ , in agreement with the higher-order correlated methods. The differences between the various coupled cluster methods are, in general, smaller than between SOPPA and MP2. It is interesting to note that the correlation correction at the CCDPPA level is always smaller than at the CCSDPPA level, whereas the derivative-derived CCD correction is either very close to the CCSD correction or, in the case of Be and AlH , even larger.

Correlation at the CCSDPPA level increases the polarizability anisotropy (Table III) of the neutral and positively charged molecules and reduces it in case of the anions. The correlation corrections at the CCDPPA level have the same sign as at the CCSDPPA level, but are with the exception of one calculation on MgH^- smaller in magnitude. However, the anisotropy, and to a smaller extent also the isotropic polarizability, of MgH^- are still very much basis-set-dependent, showing again that the basis set for MgH^- is not as converged as are the basis sets for the other systems. SOPPA shows a similar but less pronounced trend with the exception of BeH^- and BH , where the SOPPA correlation correction has the opposite sign. As was the case for the isotropic polarizability, the correlation correction at the MP2 level is always larger than that of SOPPA and it has a different sign for BH .

Compared with previous [18, 37, 38] calculations on Be (see footnotes of Table II), we find that our uncorrelated value is $\sim 2\%$ lower. Taking this into account, our CCSDPPA or CCD result is in close agreement with the MC-RPA value of Graham and Yeager [37] and the finite point charges CCD result of Thakkar [38]. For BH and CH^+ , our RPA results for the isotropic and anisotropic polarizability are almost identical to the uncorrelated results of Bishop et al. [39]. However, using MC-SCF wave functions, they predicted a larger reduction of the isotropic polarizability ($\sim 10\%$ for BH and $\sim 7\%$ for CH^+) than we obtain at the CCSDPPA or CCSD level ($\sim 7\%$ for BH and $\sim 4\%$ for CH^+). In our study of the magnetizability [15], we observed the same relation between MC-RPA and CCSDPPA. The differences between our CCSDPPA and the MC-SCF results of Bishop et al. [39] are smaller in the case of the polarizability anisotropy. The MBPT(4) study of Diercksen and Hernandez [40] shows trends similar to our calculation, but is not directly comparable as their basis set is much smaller than ours. The agreement with the MBPT calculation of Diercksen and Sadlej on AlH [41] is good at the uncorrelated level, but there are small differences between the correlated results, the MBPT(4) result being very close to our CCSD result. Diercksen and Sadlej [41] obtained a larger anisotropy at the SCF level than we did, but CCSDPPA gives a correlation correction close to their MBPT(4) result.

V. Results for First-row Hydrides and Other Singly Bonded Molecules

For the remaining first-row hydrides as well as the singly and multiple-bonded systems studied, we used the basis sets that were optimized for the calculation of nuclear magnetic shieldings and magnetizabilities [16] ($[9s9p5d2f]$ basis set on the nonhydrogen atoms and $[5s4p1d]$ on hydrogen). The basis sets are well balanced as can be seen from the good

TABLE II. Static isotropic polarizability $\alpha^L(0)$ of Be, BeH⁻, BH, CH⁺, MgH⁻, AlH, SiH⁺, and GeH⁺ at several levels of approximation.^a

Basis set ^b	No.	SOPPA			CCDPPA			CCSDPPA			MP2	CCD	CCSD
		CGTOs	RPA	W ₂	W ₂ + W ₄	W ₂	W ₂ + W ₄	W ₂	W ₂ + W ₄	W ₂			
Be ^c		77	44.937	42.307	42.614	37.932	38.714	36.258	37.017	36.258	41.420	36.989	37.541
BeH ⁻		101	327.72	378.29	381.84	305.79	311.74	270.95	276.12	270.95	418.44		
		115	326.91	370.80	374.37	302.53	308.44				416.37		
BH ^d		105	22.789	22.694	22.848	21.198	21.559	20.839	21.201	20.839	22.460	21.543	21.531
CH ⁺ ^e		103	7.7543	7.7351	7.7807	7.3401	7.4581	7.3285	7.4492	7.3285	7.6551	7.4322	7.4357
MgH ⁻		107	300.981	278.562	281.284	248.270	253.112	213.405	217.394	213.405	277.09		
		119	347.120	315.482	318.539	279.645	284.873				320.12		
AlH ^f		106	48.792	47.055	47.428	44.548	45.237	43.683	44.363	43.683	46.076	45.508	45.670
SiH ⁺		103	21.071	20.520	20.670	19.649	19.925	19.538	19.817	19.538	20.194	20.012	20.034
GeH ⁺		104	22.284	21.728	21.889	21.081	21.335	20.924	21.180	20.924	21.039	21.057	
		116	22.299	21.495	21.656	20.980	21.223				20.822		

^a $\alpha^L(0)$ is the isotropic static polarizability [Eq. (2)] in the length representation expressed in atomic units: 1 au of $\alpha = 4\pi\epsilon_0 a_0^3 \approx 1.64878 \times 10^{-41} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$.^bSee footnote b of Table I.^cCf. the RPA (45.88) and SOPPA (43.54) result of Jørgensen et al. [18] (50 STOs); the SCF (45.608), MBPT(2) (42.114), MBPT(3) (40.151), MBPT(4) (38.851), and CCD (37.205) result of Thakkar [38] ([9s9p6d2f]); the RPA (45.64) and MC-RPA (37.64) result of Graham and Yeager [37] ([9s9p5d]).^dCf. the SCF (22.7) and MC-SCF (20.3) result of Bishop et al. [39] ([7s5p2d/4s3p]).^eCf. the SCF (7.74) and MC-SCF (7.18) result of Bishop et al. [39] ([7s5p2d/4s3p]); the SCF (7.60) and MBPT(4) (7.33) result of Diercksen and Hernandez [40] ([5s3p2d/3s2p]).^fCf. the SCF (48.90), MBPT(2) (46.37), MBPT(3) (45.80), and MBPT(4) (45.62) Diercksen and Sadlej [41] ([12s7p4d1f/8s4p2d]).

TABLE III. Static polarizability anisotropy $\Delta\alpha^L(0)$ of BeH^- , BH , CH^+ , MgH^- , AlH , SiH^+ , and GeH^+ at several levels of approximation.^a

	Basis set ^b	No. CGTOs	RPA	SOPPA $W_2 + W_4$	CCDPPA $W_2 + W_4$	CCSDPPA $W_2 + W_4$	MP2	CCD	CCSD
BeH^-	[11s6p4d2f/9s8p1d]	101	128.09	150.83	107.50	94.520	164.86		
	[11s6p4d4f/9s8p1d]	115	131.41	150.25	108.78		167.93		
BH^c	[9s8p5d3f/6s5p1d]	105	0.3437	0.1935	1.5115	1.6770	0.6353	2.1191	2.0787
$\text{CH}^+{}^d$	[9s7p6d3f/5s4p1d]	103	0.3754	0.5851	0.9959	1.0860	0.7246	1.3218	1.3265
MgH^-	[11s8p5d2f/9s8p1]	107	17.336	1.3995	6.0563	8.0662	11.727		
	[11s8p5d3f/9s8p1d]	119	85.084	58.499	41.900		51.477		
AlH^e	[9s8p6d2f/6s6p1d]	106	1.4317	3.9153	4.8535	5.0780	4.5508	4.4661	4.2806
SiH^+	[9s7p6d3f/5s4p1d]	103	2.2271	3.0761	3.2914	3.3927	3.2376	3.1379	3.1012
GeH^+	[10s7p5d3f/5s4p2d]	104	4.9721	6.2399	6.1808	6.4411	6.4721	6.2246	
	[10s7p6d4f/5s4p2d]	116	4.9600	6.5611	6.4255		6.8378		

^a $\Delta\alpha^L(0)$ is the static polarizability anisotropy [Eq. (3)] in the length representation expressed in atomic units: 1 au of $\Delta\alpha = 4\pi\epsilon_0 a_0^3 \approx 1.64878 \times 10^{-41} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$.

^bSee footnote b of Table I.

^cCf. the SCF (0.3) and MC-SCF (1.5) result of Bishop et al. [39] ([7s5p2d/4s3p]).

^dCf. the SCF (0.37) and MC-SCF (1.19) result of Bishop et al. [39] ([7s5p2d/4s3p]); the SCF (0.42) and MBPT(4) (1.40) result of Diercksen and Hernandez [40] ([5s3p2d/3s2p]).

^eCf. the SCF (1.61), MBPT(2) (5.06), MBPT(3) (5.27), and MBPT(4) (5.27) Diercksen and Sadlej [41] ([12s7p4d1f/8s4p2d]).

agreement among the length, mixed, and velocity representations of the static polarizability at the RPA level and the fulfillment of the TRK sum rule in Table IV. However, they are not as diffuse as, e.g., the basis sets used by Diercksen et al. [42–45] and we therefore do not expect to reach the SCF limit for the polarizability.

We see from Table V that the correlation correction to the isotropic polarizability is larger at the SOPPA level than at the MP2 level (with the exception of F_2 and CH_4) contrary to what we found for the nuclear magnetic shielding constants of the singly bonded molecules [16b] and for the polarizabilities of the quasi-degenerate molecules (see Section IV). The differences are particularly spectacular for F_2 , where SOPPA gave a large correlation correction to the nuclear magnetic shielding constant and a comparable MP2 calculation [46] predicted it to be negligible, whereas the present calculation shows the reversed trend for the polarizability. The differences between the SOPPA and MP2 results are, however, always smaller than the differences between RPA and either of the correlated methods, again with the exception of F_2 . In the case of the anisotropy, SOPPA gives a larger correction than does MP2 only for BH_3 and BF . For the HF molecule, SOPPA and MP2 predict a different sign of the correlation correction to the anisotropy.

The agreement with experimental results [47–53] (see Table V) is generally improved at the SOPPA level. In particular, the agreement is good for the isotropic polarizability of F_2 and CH_4 , if one takes into account the estimated vibrational correction [48] for CH_4 , and for the isotropic polarizability and anisotropy of HF. In comparison with MP2, better agreement is obtained at the SOPPA level for the isotropic polarizability of NH_3 , H_2O , HF, and F_2 and for the anisotropy of HF.

Compared with other calculations [42–45, 54–58] (see footnotes of Table V), we observe that our RPA results are 1–4% too low. The differences between our MP2 results and the results of previous MBPT(2) [42–45, 54, 57, 58] calculations are even larger. This shows that our basis sets optimized for magnetizability and nuclear magnetic shielding constants are not as good for polarizabilities. In particular, the hydrogen basis set does not contain as many diffuse functions as in some of the other calculations. However, we are concerned mainly with a direct comparison with MP2 using the same basis sets, and the absolute values are therefore not of primary importance.

TABLE IV. Energies, TRK sum rule, and static polarizability at the RPA level of BH_3 , CH_4 , NH_3 , H_2O , HF, BF, and F_2 .^{a, b}

	E_{SCF}	ΔE_{MP2}	$S_{RPA}^L(0)$	$S_{RPA}^M(0)$	$S_{RPA}^V(0)$	$\alpha^L(0)$	$\alpha^M(0)$	$\alpha^V(0)$
BH_3	-26.402240	-0.162729	8.0241	7.9942	7.9755	16.286	16.230	16.177
CH_4	-40.216499	-0.254858	10.0160	9.9962	9.9835	15.896	15.875	15.855
NH_3	-56.223936	-0.298855	10.0056	9.9967	9.9934	12.586	12.636	12.691
H_2O	-76.066200	-0.332326	10.0070	9.9960	9.9924	8.2075	8.2471	8.2943
HF	-100.069451	-0.350180	10.0130	9.9971	9.9887	4.7229	4.7217	4.7234
BF	-124.167220	-0.446529	14.0093	13.9981	13.9886	19.318	19.307	19.297
F_2	-198.770975	-0.675943	18.0162	17.9973	17.9828	8.4703	8.4451	8.4204

^aSee footnote a of Table I.

^bUsing a [9s9p5d2f] basis set on the heavy atoms and a [5s4p1d] basis set on hydrogen. For the detailed description of the basis set and geometries, see [16].

TABLE V. Static polarizability $\alpha^L(0)$ and anisotropy $\Delta\alpha^L(0)$ of BH_3 , CH_4 , NH_3 , H_2O , HF , BF , and F_2 .^a

	$\alpha(0)$					$\Delta\alpha(0)$				
	SOPPA					SOPPA				
	RPA	W_2	$W_2 + W_4$	MP2	Exp.	RPA	$W_2 + W_4$	MP2	Exp.	
BH_3	16.286	16.498	16.594	16.549		4.2252	4.2705	4.2483		
CH_4 ^b	15.896	16.184	16.312	16.361	16.59 [48]	0.0000	0.0000	0.0000		
NH_3 ^c	12.586	13.478	13.615	13.563	14.82 [47]	0.0936	0.9764	1.0478	1.94 [49]	
H_2O ^d	8.2075	9.1833	9.2889	9.0658	9.45 [50]	1.3655	0.9949	0.8953	0.45 [50]	
HF ^e	4.7236	5.4019	5.4631	5.2779	5.60 [51]	1.3657	1.4020	1.2659	1.48 \pm 0.14 [52]	
BF	19.318	19.878	20.062	19.821		4.0265	1.8735	2.3806		
F_2 ^f	8.4703	8.2751	8.3812	7.893	8.38 [53]	9.0636	6.3201	5.0860		

^aSee footnote a of Tables II and III.

^bCf. the SCF (α : 15.97), MBPT(2) (α : 16.53), MBPT(3) (α : 16.39), and SD-MBPT(4) (α : 16.44) result of Diercksen and Sadlej [42] ($[\text{6s4p3d}/4\text{s2p}]$).

^cCf. the SCF (α : 12.92/ $\Delta\alpha$: 0.56) and MP2 (α : 14.27/ $\Delta\alpha$: 1.92) result of Rice and Handy [54] ($(4+1\text{s } 3+1\text{p } 2+1\text{d}/3+1\text{s } 2+1\text{p}) + (1\text{s}1\text{p}1\text{d}/1\text{s}1\text{p})$ ANO); the SCF (α : 12.95/ $\Delta\alpha$: 0.56), MBPT(2) (α : 14.40/ $\Delta\alpha$: 1.99), MBPT(3) (α : 13.87/ $\Delta\alpha$: 1.47), and MBPT(4) (α : 14.37/ $\Delta\alpha$: 1.93) result of Diercksen and Sadlej [43] ($[\text{8s5p3d1f}/4\text{s2p1d}]$); the SCF (α : 12.96/ $\Delta\alpha$: 0.58), MBPT(2) (α : 14.46/ $\Delta\alpha$: 2.06), CCSD (α : 14.13/ $\Delta\alpha$: 1.81), and CCSD(T) (α : 14.38/ $\Delta\alpha$: 2.01) of Sekino and Bartlett [58] ($[\text{5s3p2d}/3\text{s2p1d}] + 2\text{ s and p lone-pair functions}$).

^dCf. the RPA (α : 8.54/ $\Delta\alpha$: 1.12) and MC-RPA [CAS (4220) (α : 9.50/ $\Delta\alpha$: 0.43); CAS (6331) (α : 9.35/ $\Delta\alpha$: 0.44)] result of Luo et al. [55] ($[\text{8s5p3d1f}/4\text{s2p1d}]$); the SCF (α : 8.53/ $\Delta\alpha$: 1.09), MBPT(2) (α : 9.81/ $\Delta\alpha$: 0.33), MBPT(3) (α : 9.28/ $\Delta\alpha$: 0.65), and MBPT(4) (α : 9.82/ $\Delta\alpha$: 0.45) result of Diercksen et al. [44] ($[\text{8s5p3d1f}/4\text{s2p1d}]$); the SCF (α : 8.55/ $\Delta\alpha$: 1.05), MBPT(2) (α : 9.87/ $\Delta\alpha$: 0.25), CCSD (α : 9.61/ $\Delta\alpha$: 0.41), and CCSD(T) (α : 9.79/ $\Delta\alpha$: 0.34) of Sekino and Bartlett [58] ($[\text{5s3p2d}/3\text{s2p1d}] + 2\text{ s and p lone-pair functions}$).

^eCf. the RPA (α : 4.58/ $\Delta\alpha$: 1.36) and SOPPA (α : 4.75/ $\Delta\alpha$: 1.33) result of Jørgensen et al. [18] (45 STOs); the RPA (α : 4.896/ $\Delta\alpha$: 1.279) and MC-RPA (α : 5.461/ $\Delta\alpha$: 1.105) result of Jaszuński et al. [56] ($[\text{8s6p4d3f}/5\text{s3p2d}]$); the SCF (α : 4.90/ $\Delta\alpha$: 1.26), MBPT(2) (α : 5.69/ $\Delta\alpha$: 1.07), MBPT(3) (α : 5.38/ $\Delta\alpha$: 1.19), and MBPT(4) (α : 5.77/ $\Delta\alpha$: 1.10) result of Diercksen et al. [45] ($[\text{8s5p3d1f}/4\text{s2p1d}]$); the SCF (α : 4.93/ $\Delta\alpha$: 1.25), MBPT(2) (α : 5.74/ $\Delta\alpha$: 1.04), CCSD (α : 5.61/ $\Delta\alpha$: 1.11), and CCSD(T) (α : 5.71/ $\Delta\alpha$: 1.19) of Sekino and Bartlett [58] ($[\text{5s3p2d}/3\text{s2p1d}] + 2\text{ s and p lone-pair functions}$).

^fCf. the SCF (α : 8.590/ $\Delta\alpha$: 9.213), MBPT(2) (α : 8.292/ $\Delta\alpha$: 5.160), MBPT(3) (α : 8.028/ $\Delta\alpha$: 5.365), and SDQ-MBPT(4) (α : 8.485/ $\Delta\alpha$: 5.964) result of Maroulis and Thakkar [57] ($[\text{6s4p3d1f}]$).

VI. Results for Multiple-bonded Systems

The fulfillment of the TRK sum rule in length, mixed, and velocity representations (Table VI) is excellent for all the molecules. Similarly, there is almost no difference between the static polarizability in the three representations. As for the other molecules, the polarizabilities and anisotropies at the SOPPA level may both be larger or smaller than in SCF. Also, the agreement with experimental values [47, 49, 59, 60] is improved at the SOPPA level for most molecules.

SOPPA gives a larger correlation contribution than does MP2 for the isotropic polarizability of N_2 , CO , C_2H_2 , and CH_2O , and a smaller for HCN and CH^- , whereas the correlation correction to the anisotropy at the MP2 level is larger than in SOPPA with the exception of CO and CH_2O . In the case of CH_2O , SOPPA and MP2 even predict a different sign of the correlation correction to the anisotropy. As for the hydrides in Section V, the differences between the isotropic

TABLE VI. Energies, TRK sum rule, and static polarizability at the RPA level of N_2 , CO, CN^- , HCN, C_2H_2 , and CH_2O .^{a,b}

	E_{SCF}	ΔE_{MP2}	$S_{RPA}^L(0)$	$S_{RPA}^M(0)$	$S_{RPA}^V(0)$	$\alpha^L(0)$	$\alpha^M(0)$	$\alpha^V(0)$
N_2	-108.992336	-0.495335	14.0091	13.9977	13.9883	11.483	11.469	11.456
CO	-112.789373	-0.477372	14.0076	13.9981	13.9901	12.313	12.312	12.310
CN^-	-92.347176	-0.461195	14.0080	13.9973	13.9925	25.261	25.259	25.264
HCN	-92.914292	-0.462389	14.0064	13.9981	13.9909	16.745	16.747	16.749
C_2H_2	-76.854576	-0.418465	14.0064	13.9966	13.9882	23.325	23.320	23.315
CH_2O	-113.920562	-0.517142	16.0204	15.9951	15.9779	16.827	16.797	16.770

^aSee footnote a of Table I.^bFor the detailed description of the basis set and geometries, see [16].

polarizabilities at the SOPPA and MP2 levels are smaller than their correlation correction to the RPA results. This is, on the other hand, not, in general, the case for the anisotropy. Comparison with the available experimental results shows that MP2 gives better agreement than does SOPPA for CO and the isotropic polarizability of C_2H_2 . However, for the isotropic polarizability of N_2 and HCN, the uncorrelated calculations are closest to the experimental values.

Our RPA results are in good agreement with the results of other uncorrelated calculations [54, 58, 59, 61–64] (see footnotes of Table VII), confirming that the incompleteness of the hydrogen basis set is the reason for the differences that we observed for the hydrides in Section V. The sign of the correlation correction to the isotropic polarizability of N_2 seems to be rather basis-set-dependent. The MP2 calculation of Rice and Handy [54], the MBPT(3) calculation of Cernusak et al. [65], and the MC-RPA calculation of Jaszuński et al. [61] predict a reduction like in the present and the earlier SOPPA calculation [21], which, however, is in contrast to another, even though not as complete, SOPPA calculation [22], the MC-RPA calculation of Luo et al. [62], and the MBPT calculations of Maroulis and Thakkar [59] and Sekino and Bartlett [58], which all give a positive correlation contribution. However, the anisotropy is reduced at the correlated level in all calculations.

For CO, we find good agreement between our MP2 and earlier [58, 63] MBPT(2) results. In the case of CN^- and HCN, we can only compare with the MBPT calculations of Fowler and Dierksen [66], which were performed in the smaller, but optimized Sadlej [67] basis set. Our RPA and MP2 results for CN^- are smaller, whereas for HCN, we obtained slightly larger results. Our computed reduction of the isotropic polarizability of C_2H_2 at the MP2 level is larger than the one obtained in the MBPT calculations of Maroulis and Thakkar [64]. For the anisotropy, the situation is reversed. Finally, for formaldehyde, Rice and Handy [54], obtained a smaller value at the RPA and MP2 levels than we did. Their correlation correction is, however, slightly larger than ours.

VII. Conclusions

We have compared correlated calculations of the static dipole polarizability of three groups of molecules with different electronic structures using the second-order polarization propagator approximation (SOPPA) and the analytical energy derivative technique at the MP2 level. In addition, for systems where previous experience tells us that SOPPA is insufficient, we have also

TABLE VII. Static isotropic polarizability $\alpha^L(0)$ and anisotropy $\Delta\alpha^L(0)$ of N_2 , CO , CN^- , HCN , C_2H_2 , and CH_2O .^a

	$\alpha(0)$					$\Delta\alpha(0)$			
	SOPPA					SOPPA			
	RPA	W_2	$W_2 + W_4$	MP2	Exp.	RPA	$W_2 + W_4$	MP2	Exp.
N_2 ^b	11.483	11.148	11.309	11.367	11.74 ± 0.06 [59]	5.1796	4.2341	4.1913	4.45 [60]
CO ^c	12.313	13.062	13.255	13.080	13.08 [47]	3.1856	4.5613	3.6434	3.53 [49]
CN^- ^d	25.261	26.439	26.845	27.000		7.4495	7.3100	7.0258	
HCN ^e	16.745	16.286	16.529	16.441	16.74 [47]	8.6256	8.3097	8.0028	
C_2H_2 ^f	23.325	22.011	22.307	22.449	22.67 ± 0.23 [60]	12.127	11.926	11.607	11.81 ± 0.35 [60]
CH_2O ^g	16.827	18.157	18.387	17.630		7.6667	5.1262	7.9232	

^aSee footnote a of Table II.

^bCf. the RPA (α : 11.36/ $\Delta\alpha$: 4.86) and SOPPA (α : 11.29/ $\Delta\alpha$: 4.07) result of Oddershede and Svendsen [21] (50 STOs); the RPA (α : 11.37) and SOPPA (α : 11.57/ $\Delta\alpha$: 4.16) result of Stroyer-Hansen and Svendsen [22] ([5s3p2d]); the RPA (α : 11.559/ $\Delta\alpha$: 5.202) and MC-RPA (α : 11.062/ $\Delta\alpha$: 4.328) result of Jaszuński et al. [61] ([11s8p4d1f]); the RPA (α : 11.560/ $\Delta\alpha$: 5.196) and MC-RPA (α : 11.606/ $\Delta\alpha$: 4.341) result of Luo et al. [62] ([8s6p4d3f]); the SCF (α : 10.91/ $\Delta\alpha$: 5.76), MBPT(2) (α : 10.88/ $\Delta\alpha$: 4.74), MBPT(3) (α : 10.92/ $\Delta\alpha$: 5.21), and MBPT(4) (α : 11.09/ $\Delta\alpha$: 5.25) result of Cernusak et al. [65] ([8s5p2d1f]); the SCF (α : 11.512/ $\Delta\alpha$: 5.172), MBPT(2) (α : 11.562/ $\Delta\alpha$: 4.161), MBPT(3) (α : 11.600/ $\Delta\alpha$: 4.607), and SDQ-MBPT(4) (α : 11.675/ $\Delta\alpha$: 4.648) result of Maroulis and Thakkar [59] ([6s4p3d1f]); the SCF (α : 11.46/ $\Delta\alpha$: 5.24) and MP2 (α : 11.40/ $\Delta\alpha$: 4.29) result of Rice and Handy [54] ([4+1s 3+1p 2+1d] + [1s1p1d] ANO); the SCF (α : 11.422/ $\Delta\alpha$: 5.372), MBPT(2) (α : 11.455/ $\Delta\alpha$: 4.439), CCSD (α : 11.609/ $\Delta\alpha$: 4.826), and CCSD(T) (α : 11.752/ $\Delta\alpha$: 4.869) of Sekino and Bartlett [58] ([5s3p2d]).

^cCf. the RPA (α : 10.54/ $\Delta\alpha$: 3.32) and SOPPA (α : 10.62/ $\Delta\alpha$: 3.20) result of Jørgensen et al. [18] (46 STOs); the RPA (α : 11.56/ $\Delta\alpha$: 2.94) and SOPPA (α : 12.45/ $\Delta\alpha$: 4.45) result of Oddershede et al. [12, 21] (48 STOs); the SCF (α : 12.34/ $\Delta\alpha$: 3.17), MBPT(2) (α : 13.28/ $\Delta\alpha$: 3.65), MBPT(3) (α : 12.94/ $\Delta\alpha$: 3.56), and MBPT(4) (α : 13.21/ $\Delta\alpha$: 3.57) result of Diercksen and Sadlej [63] ([8s5p3d1f]); the SCF (α : 12.23/ $\Delta\alpha$: 3.37), MBPT(2) (α : 13.09/ $\Delta\alpha$: 3.91), CCSD (α : 12.692/ $\Delta\alpha$: 3.97), and CCSD(T) (α : 13.04/ $\Delta\alpha$: 3.92) of Sekino and Bartlett [58] ([5s3p2d]).

^dCf. the SCF (α : 27.137/ $\Delta\alpha$: 8.158), MBPT(2) (α : 30.845/ $\Delta\alpha$: 8.466), MBPT(3) (α : 29.661/ $\Delta\alpha$: 8.715), MBPT(4) (α : 31.485/ $\Delta\alpha$: 9.424), and CCSD (α : 31.123/ $\Delta\alpha$: 9.301) result of Fowler and Diercksen [66] ([5s3p2d]).

^eCf. the SCF (α : 16.566/ $\Delta\alpha$: 8.852), MBPT(2) (α : 16.538/ $\Delta\alpha$: 8.430), MBPT(3) (α : 16.496/ $\Delta\alpha$: 8.600), MBPT(4) (α : 16.691/ $\Delta\alpha$: 9.045), and CCSD (α : 16.511/ $\Delta\alpha$: 8.719) result of Fowler and Diercksen [66] ([5s3p2d]).

^fCf. the SCF (α : 23.32/ $\Delta\alpha$: 12.11), MBPT(2) (α : 22.81/ $\Delta\alpha$: 11.42), MBPT(3) (α : 22.79/ $\Delta\alpha$: 11.61), DQ-MBPT(4) (α : 22.55/ $\Delta\alpha$: 11.65), and CCD (α : 22.52/ $\Delta\alpha$: 11.58) result of Maroulis and Thakkar [64] ([4s3p3d1f/3s2p1d]).

^gCf. the SCF (α : 16.59/ $\Delta\alpha$: 7.61) and MP2 (α : 17.55/ $\Delta\alpha$: 7.90) result of Rice and Handy [54] ([4+1s 3+1p 2+1d/3+1s 2+1p] + [1s1p1d/1s1p] ANO).

reported polarizabilities calculated using the coupled cluster-based second-order polarization propagator approximations (CCDPPA/CCSDPPA) as well as analytical and numerical derivatives of the energy at the CCD and CCSD level. We applied fairly large basis sets that were not tailored for polarizability calculation, but, instead, optimized for the calculation of magnetic properties of the same systems. Comparison with other calculations at the uncorrelated level and the fulfillment of certain sum rules showed that with the exception of the hydrogen basis for some of the hydrides the basis sets are flexible enough to give a good description of the polarization induced in the systems also by an electric field.

The comparison between SOPPA and MP2 showed that the correlation contribution provided by the two second-order methods to static dipole polarizabilities are similar in sign and magnitude. Exceptions are the isotropic polarizability of BH and CH^+ and the anisotropy of BH, HF, and

CH₂O, for which the SOPPA and MP2 correlation contribution had different signs, and the isotropic polarizability of AlH, SiH⁺, GeH⁺, and F₂ as well as the anisotropy of CO, CN⁻, and C₂H₂, for which the differences between the SOPPA and MP2 results were larger than the difference between either of them and the uncorrelated SCF/RPA result. However, it is not possible to state in general or a priori which method gives the larger correlation contribution to the polarizability or the better agreement with experimental results.

For the systems with quasi-degenerate ground states like Be, BH, or CH⁺, we found large differences between SOPPA and CCSDPPA results. The latter are in much better agreement with other correlated calculations. CCSDPPA overcomes, therefore, also for the polarizability, as for other similar molecular properties, the deficiencies of low-order perturbative methods like SOPPA. As in our previous study on the magnetizability of these molecules, we observed, however, that multiconfigurational methods give larger correlation contributions, which most likely is due to a combination of the lack of dynamic correlation in MC-RPA calculations with too small active spaces and the lack of nondynamical correlation in the present approach.

It is also characteristic of this and other correlated calculations of polarizability tensor components that the correlation correction may have either sign and that it is difficult a priori to predict which sign to expect. That makes it difficult to use SCF/RPA polarizabilities for predictive purposes. However, within a given class of molecules, we often find the same sign of the correlation contribution. For instance, the correlation correction at the SOPPA level to the isotropic polarizability is positive for all the neutral hydrides (Table V), and at the CCPPA level, negative for all the quasi-degenerate molecules (Table II).

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