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Electric dipole polarizabilities of atomic valence states

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The second-order perturbation method for single-state multireference wave functions generated in complete-active-space self-consistent-field (CASSCF) calculations has been employed for computing electric dipole polarizabilities of different valence-electronic states of the first- (C,N,O,F) and second-row (Si,P,S,Cl) atoms. The results of calculations with polarized basis functions provide a uniform set of accurate polarizability data for those systems. Also, atomic quadrupole moment values obtained by using the CASSCF method are presented.

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I. INTRODUCTION

The majority of interactions and resulting processes is governed by electric forces between interacting species. The electron density of an atom embedded in some source of electric field responds to this perturbation [1]. The corresponding lowest-order response to the homogeneous external electric field brings about the notion of the electric dipole polarizability [1]. A considerable part of the atomic scattering data is interpreted in terms of simple interaction potentials whose leading ingredients involve atomic dipole polarizabilities [2,3]. This makes the dipole polarizability of an atom a useful and interesting property [4,5].

The electric ground-state dipole polarizabilities of light atoms are usually known with reasonable accuracy [5,6]. Most of the corresponding data follow from theoretical calculations [5–8]. Much less is known for atomic polarizabilities in excited electronic states [5]. On the other hand, those data are needed for the interpretation of scattering processes involving excited-state channels. In this paper we report on calculations of dipole polarizabilities in valence-electronic states of the first- (C, N, O, and F) and second-row (Si, P, S, and Cl) atoms.

The present calculations of atomic dipole polarizabilities in different valence-electronic states derive from the following two recent developments. A perturbation method for the treatment of the electron-correlation contribution for arbitrary nondegenerate reference states has been devised [9,10] and has proven to give highly accurate wave functions with a relatively small computational effort. The second development consists of the standardization of the methodology for accurate calculations of dipole polarizabilities with truncated sets of Gaussian-type orbitals (GTO's) and contracted GTO's (CGTO's) [11]. Both the theory underlying our calculations and certain computational aspects of this study are surveyed in Sec. II. Different factors affecting the accuracy of the calculated atomic dipole polarizabilities are analyzed in Sec. III. According to this analysis the most trustworthy results are summarized in Sec. IV. In that section some results obtained in this study for atomic quadrupole moments are also presented.

II. THEORY AND COMPUTATIONAL METHODOLOGY

A. Second-order perturbation treatment of the electron correlation with a complete-active-space self-consistent-field reference function

The method used in this paper for the determination of the electron-correlation contribution to atomic dipole polarizabilities follows from a two-step consideration of the electron-correlation problem. In the first step the electron-correlation effects are accounted for by the so-called complete-active-space self-consistent-field method (CASSCF) [13,14]. This approach gives a full configuration-interaction (CI) wave function for a certain number of electrons that are distributed among the given number of (active) orbitals. All orbitals are self-consistently optimized. In addition to the active orbital space a certain number of orbitals can be assumed to be always doubly occupied, leading to what is termed the frozen (no optimization involved) or inactive (optimized) orbital subspaces.

The size of the active orbital subspace and the number of electrons therein determine the length of the corresponding full CI expansion. To avoid prohibitively long CI vectors, the electron-correlation effects beyond those that are taken into account by the given CASSCF CI wave function, can be studied perturbationally. In the second-order perturbation treatment, hereafter referred to as the CASPT2 approach, one anticipates that the major part of the near-degeneracy effects is being accounted for within the CASSCF approximation [9,10]. The perturbation treatment with a single-state multiconfiguration CASSCF function is aimed primarily at recovering what is known as the dynamic correlation contribution [14]. This is a natural extension of the single-state single-configuration approach [15] in perturbation theories of the electron correlation.

There is obviously a certain ambiguity with respect to the partition of the electron-correlation effects between the CASSCF and the CASPT2 approximations. It is expected that with the increasing number of active orbitals used to build the CASSCF wave function the importance of the corresponding perturbation correction will diminish. Thus, for large enough active spaces the second-order perturbation treatment should become sufficient for accurate calculations of the electron-correlation energy. This anticipated feature of the CASPT2 method can only be substantiated by a study of different active spaces and reference functions. Of additional practical importance is that the given CASSCF reference function must be well balanced, i.e., the choice of the active orbital subspace must avoid accidental overweighting of certain configurations.

The details of both the CASSCF method [14] and the CASPT2 approach [9,10] can be found elsewhere. For the present purpose one should only mention the strategy assumed in our calculations. The initial choice of the active orbital space for all atoms studied in this paper was always the valence *np* subspace. This gives in all cases a single-configuration open-shell (CAS) SCF reference function. By applying the CASPT2 method one obtains as a by-product an approximate density matrix [10] whose eigenvalues (occupation numbers for approximate natural orbitals) have then been used to determine the most convenient large active space. For both the first- and second-row atoms this large active space has been found to comprise the valence and next-to-valence orbital subspaces. The final and presumably most accurate results have been obtained by using the CASPT2 method with the CASSCF wave function for all valence electrons generated in the large active orbital space. It is worth mentioning that such a CASPT2 treatment also permits orbital substitutions involving the inactive orbitals. Hence the core-polarization and core-correlation effects can be accounted for through the second order in the respective electron-correlation perturbations [9,10].

Finally, let us mention that the form of the CASPT2 method depends on the choice of the Fock operator for the given set of CASSCF orbitals. In the early version of the method, the Fock operator was chosen to be fully diagonal [9]. This approximation has several computational advantages, though it may suffer from instabilities [9,10]. The results obtained in the diagonal approximation for the Fock operator will be hereafter referred to by the symbol CASPT2D. More recently, an extension [10] of the earlier version of the CASPT2 method [9] was proposed and it amounts to a uniform treatment of the diagonal and nondiagonal elements of the Fock operator [10]. The results of the corresponding calculation will be referred to by the symbol CASPT2F. The CASPT2F formalism is computationally more demanding than CASPT2D calculations and the mutual comparison of their results might be useful. In this context one should mention that the perturbation method explored recently by Wolinski and co-workers [16] is a particular case (two electrons in two active orbitals) of the CASPT2F scheme [10] used in this paper.

B. Calculations of atomic dipole polarizabilities

Since the CASSCF wave function optimized for the given state satisfies the Hellmann-Feynman theorem [13,14], the dipole polarizability $\alpha(M_L)$ for the given M_L value can be obtained either from the induced dipole moment or from the field-dependent total energy [17,18], the two routes being completely equivalent. This equivalence is lost for the CASPT2 wave function and the only legitimate method [17] for computing $\alpha(M_L)$ is based on the second derivative of the field-dependent energy.

The calculation of dipole polarizabilities by the CASPT2 method can be easily accomplished by using the finite-field numerical perturbation approach [19]. This technique has been followed in the present study. Based on our earlier experiences in SCF and many-body perturbation theory calculations of atomic and molecular polarizabilities [11,12], the numerical value of the external electric field strength has been chosen as equal to $+0.001$ a.u. This provides sufficiently high numerical stability of the calculated second derivatives of field-dependent energies in both CASSCF and CASPT2 approximations. Useful information concerning the choice of the numerical field strength parameter can be obtained at the level of the CASSCF approximation by comparing the dipole moment and energy derivatives. Such a comparison approximately determines the number of significant decimals in the polarizability values presented in this paper.

As mentioned in Sec. I the CASSCF quadrupole moments of different atomic states have also been calculated within the present study. According to the Hellmann-Feynman theorem those results correspond simply to the expectation value of the quadrupole moment operator over the given CASSCF wave function. All calculations reported in this paper have been carried out with the MOLCAS system of quantum chemistry programs developed in the laboratory [20].

C. Basis sets

The calculation of atomic dipole polarizabilities reported in this paper has been carried out with GTO/CGTO basis sets developed recently for the purpose of accurate high-level studies of atomic and molecular electric dipole properties [11,12]. Those so-called (first-order) polarized GTO/CGTO sets are of a rather moderate size ([10.6.4/5.3.2] for C through F and [13.10.4/7.5.2] for Si through Cl) and their high performance is already well established. By the method of their derivation they are capable of correctly representing the field-induced polarization of atomic valence shells [11]. Their recent application in calculations of molecular quadrupole moments [21] indicates that the atomic quadrupole moments computed in this paper should also be fairly accurate.

The polarized basis sets employed in this study constitute a part of the basis set library of the MOLCAS system of programs [20]. The details of their generation and documentation of their performance can be found in Refs. [11] and [12] [22].

III. CASSCF AND CASPT2 CALCULATIONS OF ATOMIC DIPOLE POLARIZABILITIES: THE CHOICE OF THE REFERENCE FUNCTION AND THE PERFORMANCE OF DIFFERENT APPROXIMATIONS

The efficiency of the second-order CASPT2 method is expected to depend on the choice of the CASSCF reference function. This dependence can be analyzed by repeating calculations with different reference functions of increasing size and complexity. In due course of the present study, a simple systematic procedure for the generation of a suitable reference function has been developed following the ideas employed in single-configuration methods [23]. As already explained in Sec. II A, for each atom the initial CASPT2 calculations have been carried out with the smallest valence active space. The reference function was thus equivalent to the corresponding open-shell restricted Hartree-Fock (RHF) result. The approximate CASPT2 natural orbitals for such a reference function and the corresponding occupation numbers have been used to devise a suitable large active space for final CASSCF calculations [10].

For all atoms and all their valence states the initial active space has been chosen to comprise only the valence *p*-type orbitals; the valence *s* shell being considered as inactive [14]. The extended active space has been assumed to retain the shell structure and to comprise orbitals with distinctly large occupation numbers. For the first-row atoms the corresponding active space is built from $2s$, $2p$, $3s$, $3p$, and $3d$ orbitals. For the second-row atoms the active orbital space has been determined as built from $3s$, $3p$, $3d$, $4s$, and $4p$ orbitals.

The approximate selection of the large active space has been afterward validated by comparing the CASPT2 occupation numbers from the initial calculations with those obtained from the large-active-space CASSCF wave functions. It has also been found that the approximate natural orbitals that follow from the initial CASPT2 calculations provide a very good approximation to the final CASSCF natural orbitals in the extended active space. This method is advocated as a useful computational tool for initializing CASSCF calculations with a large number of weakly occupied active orbitals using as input approximate natural orbitals determined in small-active-space CASSCF calculations.

The dependence of the CASPT2 dipole polarizability data on the reference function is illustrated in Table I by

TABLE I. CASSCF and CASPT2 calculations of the dipole polarizability of the carbon and silicon atoms in different approximations. For the purpose of identifying small differences two decimals are shown. The last one is significant only in comparisons of different methods for the same M_L component of the given state of the same atom. All results in a.u. (1 a.u. of dipole polarizability $\simeq 0.148\,18$ Å^3).

				Active orbital space			Active orbital space	
State	M_L	Method[a]	Atom	$2p$[b,c]	$2s2p3s3p3d$[b]	Atom	$3p$[d,e]	$3s3p3d4s4p$[d]
^3P	0	CASSCF	C	9.80	9.82	Si	32.42	30.46
		CASPT2D		10.16	9.96		31.30	30.70
		CASPT2F		10.14	9.94		31.24	30.74
	±1	CASSCF		12.68	11.92		41.36	38.88
		CASPT2D		12.16	12.10		40.22	39.40
		CASPT2F		12.32	12.12		40.16	39.44
^1D	0	CASSCF		13.50	14.75		50.51	49.47
		CASPT2D		14.77	15.15		51.07	50.49
		CASPT2F		14.85	15.18		50.98	50.63
	±1	CASSCF		12.76	13.74		46.64	45.42
		CASPT2D		13.84	14.08		46.84	46.28
		CASPT2F		13.90	14.10		46.76	46.40
	±2	CASSCF		10.54	10.70		35.02	33.26
		CASPT2D		11.04	10.86		34.14	33.66
		CASPT2F		11.06	10.86		34.10	33.72
^1S	0	CASSCF		14.06	15.28		50.10	49.40
		CASPT2D		17.74	16.06		54.22	50.72
		CASPT2F		17.84	16.18		54.14	51.10

[a] See Sec. II A for an explanation of abbreviations.

[b] In the CASSCF and CASPT2 calculations the $1s$ orbital is frozen in its form determined in small-active-space CASSCF calculations where it was optimized.

[c] The $2s$ orbital is inactive in the CASSCF and CASPT2 calculations.

[d] The K and L shell orbitals are frozen. They are determined in small-active-space CASSCF calculations, where they were optimized.

[e] The $3s$ orbital is inactive in the CASSCF and CASPT2 calculations.

the results obtained for different valence states of two representative systems: the carbon and silicon atoms. Virtually the same pattern has been observed for the other atoms studied in this paper.

In the same table the performance of the CASPT2D approximation as compared to the CASPT2F results is exemplified. As shown by the corresponding data both methods give almost the same results. Although the CASPT2D method based on the diagonal approximation for the Fock operator [9] might be sensitive to small perturbations, its computationally less demanding character is of practical importance.

One of the interesting features of the results shown in Table I is the relatively small dependence of the CASPT2 data on the choice of the CASSCF reference function. With the single-configuration reference the perturbation treatment usually overshoots the value of the dynamical correlation correction to the dipole polarizability. A part of this contribution, including the effects beyond the second-order treatment, is automatically accounted for by the large-active-space CASSCF wave function. Most of the remaining dynamical correlation contribution fol-

TABLE II. Dipole polarizabilities of valence-electronic states of the first-row atoms. All values in a.u.

					Reference results		
			This work		Theoretical		
Atom	State	M_L	RHF[a]	CASPT2[b]	RHF	Other	Exptl.
C	^3P	0	9.8	9.9	10.10,[c] 9.75,[d] 10.000[g]	10.15,[e] 9.06,[f] 9.83[f]	
		±1	12.7	12.1	13.05,[c] 12.63,[d] 13.00[g]	12.69,[e] 11.22,[f] 12.24[f]	
	^1D	0	13.5	15.2			
		±1	12.8	14.1			
		±2	10.5	10.9			
	^1S	0	14.1	16.2			
N	^4S	0	7.3	7.3	7.365,[c] 7.436[g]	7.43[e]	7.63±0.4[h]
	^2D	0	7.3	8.3			
		±1	7.2	8.2			
		±2	7.2	7.7			
	^2P	0	7.5	8.1			
		±1	7.7	8.9			
O	^3P	0	5.1	6.1	5.143,[c] 5.03,[i] 5.066[g]	6.044,[e] 5.81,[j] 5.90[j]	5.2±0.4[h]
		±1	4.6	5.0	4.587,[c] 4.59,[i] 4.505[g]	5.096,[e] 4.93,[j] 5.01[j]	
	^1D	0	4.5	5.0			
		±1	4.6	5.2			
		±2	5.1	5.9			
	^1S	0	5.0	5.8			
F	^2P	0	3.1	3.4	3.092,[c] 3.117[g]	3.466[e]	
		±1	3.4	3.9	3.391,[c] 3.355[g]	3.905[e]	

[a] Results of CASSCF calculations with the following partition of the orbital space: inactive ($1s2s$), active $2p$. They are equivalent to open-shell RHF results.

[b] CASPT2F calculations with CASSCF reference functions determined by the following partition of the orbital space: frozen $1s$, active ($2s2p3s3p3d$). See footnote b to Table I.

[c] RHF results from Ref. [7].

[d] RHF results from Ref. [24].

[e] Correlated (CEPA) results from Ref. [7].

[f] Correlated (CEPA) results from Ref. [24].

[g] Numerical RHF calculations from Ref. [25].

[h] Experimental rotational average values as given in Refs. [7] and [25].

[i] RHF results from Ref. [26].

[j] Correlated (CEPA) results from Ref. [26].

lows from the subsequent CASPT2 treatment. However, its value is not necessarily smaller than that obtained in the single-configuration CASPT2 calculation. This shows that the partition of the final polarizability value into CASSCF and second-order CASPT2 contributions significantly depends on subtleties of the reference function.

As shown by the data of Table I, in most cases the single-configuration CASPT2 data are in good agreement with those obtained for CASSCF functions built of extended active spaces. This, however, indicates only that there are no important near-degeneracies involving electronic states from beyond the *np* valence active space.

The results obtained for other first- and second-row atoms studied in this paper show principally the same pattern as exemplified by the data of Table I. A further extension of the active orbital space, i.e., beyond $(2s2p3s3p3d)$ and $(3s3p3d4s4p)$ for the first- and second-row atoms, respectively, is for several reasons impractical. The CASPT2 method anticipates a relatively small CASSCF wave function whose size is capable of removing the near-degeneracy effects on the reference state. Once those are principally absent, the second-order treatment of the remaining electron-correlation contribution is assumed to be sufficient for obtaining accurate results. Moreover, the use of very large active spaces with a number of weakly occupied orbitals usually brings about serious convergence problems in CASSCF calculations. Some measure of the importance of a further extension of the reference function is given by the magnitude of the CASPT2 correction to CASSCF polarizabilities calculated with extended active orbital space. The analysis of the corresponding data indicates that the $(2s2p3s3p3d)$ and $(3s3p3d4s4p)$ active spaces for the first- and second-row atoms represent a suitable choice for reliable CASPT2 calculations. The final CASPT2 results of this paper will be therefore presented only for those extended active spaces.

A variety of different active spaces has been studied in several pilot calculations. Out of them one can conclude that the choice of active orbitals should be made according to their sequence of importance, which follows from the occupation number analysis. Moreover, active spaces that generate a poorly balanced set of configurations

TABLE III. Dipole polarizabilities of valence-electronic states of the second-row atoms. All values in a.u.

			This work		Theoretical[a] reference results	
Atom	State	M_L	RHF[b]	CASPT2[c]	RHF[d]	Other[e]
Si	^3P	0	32.4	30.7	38.83	36.70
		±1	41.4	39.4		
	^1D	0	50.5	50.6		
		±1	46.6	46.4		
		±2	35.0	33.7		
	^1S	0	50.1	51.1		
P	^4S	0	25.2	24.6	25.41	24.68
	^2D	0	28.2	28.9		
		±1	27.8	28.3		
		±2	26.6	26.6		
	^2P	0	27.7	27.6		
		±1	30.0	30.9		
S	^3P	0	21.4	22.6	19.17	19.60
		±1	17.9	18.1		
	^1D	0	17.9	18.1		
		±1	18.8	19.2		
		±2	21.5	22.4		
	^1S	0	20.8	21.3		
Cl	^2P	0	13.0	13.3	14.20	14.71
		±1	14.7	15.3		

[a] Only the corresponding rotationally averaged values are reported in Ref. [8].

[b] Results of CASSCF calculations with the following partition of the orbital space: inactive $(1s2s2p3s)$, active $3p$. They are equivalent to open-shell RHF results.

[c] CASPT2F calculations with CASSCF reference functions determined by the following partition of the orbital space: frozen $(1s2s2p)$, active $(3s3p3d4s4p)$. See footnote d to Table I. Moving the $(2s2p)$ shell to the inactive subspace has a negligible effect on the calculated data.

[d] RHF values from Ref. [8].

[e] Correlated (CEPA) values from Ref. [8] obtained in the valence approximation.

should be avoided. They usually lead to an unbalanced form of the CASSCF wave function that is difficult to repair by the second-order perturbation treatment. A good example is provided by calculations on C(^3P) with the active space comprising $2s$ and $2p$ orbitals, which lead to a two-configuration CASSCF wave function. A poor balance between those configurations results in a considerable deterioration of the CASSCF polarizability (11.36 a.u. for $M_L=0$). The deficiency of the reference function results in an overcorrected CASPT2 value of 5.90 a.u. On the other hand, both the small ($2p$) and the large ($2s2p3s3p3d$) active spaces exhibit a regular behavior and make the dynamic CASPT2 contribution relatively small. A similar pattern has also been observed in calculations for Si(^3P) with the active spaces built of either $3s$ and $3p$, or $3s$, $3p$, and $3d$ orbitals.

IV. RESULTS AND DISCUSSION

The M_L components of the dipole polarizability of the valence atomic states for the first- and second-row atoms calculated in this study are presented in Tables II and III, respectively. In addition to the CASPT2 (CASPT2F) results obtained with CASSCF reference functions determined in extended active spaces (see Sec. III), the CASSCF data for the valence np active space are given also. Since the latter are equivalent to the corresponding open-shell RHF results, their comparison with the CASPT2 values provides important information about the magnitude of the electron-correlation contribution to atomic polarizabilities.

The present results give a rather unique and reliable set of dipole polarizabilities for atomic valence states. Most of the available polarizability data refer to the ground electronic states. The comparative experimental values are scarce and rather inaccurate. No experimental data seem to be known for the second-row atoms.

The present results for the lowest valence-state polarizability of the first-row atoms compare well with the reference RHF and correlated data. Of particular importance is the agreement between the present RHF values and those computed by Voegel, Hinze, and Tobin [25] using a numerical RHF method. The correlated data of other authors [7,24,26] presented in Table II have been calculated in the coupled-electron-pair approximation (CEPA) [7,24,26] and depend to some extent on the method of their evaluation. The results that follow from the induced dipole moments may considerably differ [24] from those obtained as the energy derivatives. Nonetheless, in most cases the magnitude of CEPA correlation corrections to atomic dipole polarizabilities agrees well with the present data, i.e., with the corresponding differences between the CASPT2 and RHF CASSCF values of Table II.

The dipole polarizabilities and their anisotropies for the second-row atoms (Table III) are usually much larger than the corresponding values for the first-row atoms. This implies much larger anisotropy of interaction potentials for the second-row atoms. Moreover, the data of Table III show a considerable state dependence of the dipole polarizability that is much larger than that computed for the first-row atoms.

Only the rotational RHF and CEPA results seem to have been reported by Reinsch and Meyer [8] for the second-row atoms. The RHF (38.4, 25.2, 19.1, and 14.1 a.u. for Si, P, S, and Cl, respectively) and CASPT2 (36.5, 24.6 19.6, and 14.6 a.u.) rotational averages evaluated from the present data agree well with the respective results of Reinsch and Meyer [8]. This indirectly shows that the CASPT2 values for higher electronic states should also be quite reliable.

As a by-product of the CASSCF calculations we have obtained several quadrupole moment data for different valence-electronic states. No attempt has been made to further correct their values for dynamical correlation effects. However, the magnitude of the electron-correlation correction to atomic quadrupole moments can be estimated by a comparison of the RHF CASSCF and large-active-space CASSCF data of Table IV.

The present results for the ground electronic states of carbon and oxygen agree well with the recent calculations of Staemmler and co-workers [24,26]. This indicates that the electron-correlation contribution, which is not accounted for by our extended CASSCF calculations, should not considerably affect the present data. Since the quadrupole moment of an atom usually gives the leading terms of the long-range part of interaction potentials, the present data can be used to study different channels in scattering processes for a variety of atomic valence states.

In addition to the tabulation of dipole polarizabilities and quadrupole moments of valence-electronic states for the first- and second-row atoms, the present paper provides an additional illustration of the efficiency and high

TABLE IV. Quadrupole moments of atomic valence states. All results in a.u. The values reported in this table correspond to the parallel component of the quadrupole moment tensor for the $M_L=0$ component of the given state.

Atom	State	RHF[a]	CASSCF[b]
C	^3P	1.539[c]	1.420[c]
	^1D	−1.656	−1.614
N	^2D	−0.079	−0.120
	^2P	0.196	0.262
O	^3P	−0.968[d]	−1.021[d]
	^1D	0.884	0.891
F	^2P	0.701	0.726
Si	^3P	3.691	3.297
	^1D	−3.917	−3.594
P	^2D	−0.134	−0.174
	^2P	0.335	0.415
S	^3P	−2.341	−2.252
	^1D	2.207	2.075
Cl	^2P	1.779	1.702

[a] CASSCF calculations with np valence space of active orbitals.

[b] CASSCF calculations with extended active spaces. See Sec. III.

[c] RHF and CEPA results of Ref. [24] are 1.542 and 1.397 a.u., respectively.

[d] RHF and CEPA results of Ref. [26] are −0.918 and −0.969 a.u., respectively.

performance of the CASPT2 method [9,10]. This method has been recently used in very successful studies of the ozone molecule [27(a),27(b)], excitation energies in the nickel atom [27(c)], and excited states of the benzene molecule [27(d)] and the related azabenzenes [27(e)]. In its present application to the calculation of atomic dipole polarizabilities both the approximate (CASPT2D) [9] and complete (CASPT2F) formulations have been shown to be equally successful. Once the primary correlation effects are accounted for by the reference function, the second-order treatment of the remaining electron-correlation contribution is sufficient for accurate calculations of a variety of atomic and molecular properties [9,10,27].

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[22] In the tabulated basis set data of Ref. [11] a misprint has been found in the basis set for the hydrogen atom: the *s*-type GTO exponent of 33.865 014 should read 33.685 014. The same misprint occurs in Table 5 of Ref. [12]. Additionally, in Ref. [12] the *p*-type orbital exponent for Cl (47.795) should read 44.795. Correct values of all orbital exponents are used in the basis set library of MOLCAS.

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