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Dipole polarizability of the fluoride ion with many-body methods

Stanislaw A. Kucharski,* Yoon S. Lee, George D. Purvis III, and Rodney J. Bartlett
Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611
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The dipole polarizability of F^- and the electron affinity of F are studied using full fourth-order many-body perturbation theory (MBPT) and the infinite-order coupled-cluster single- and double-excitation model (CCSD). It is shown that the fourth-order correlation corrections for the polarizability of F^- are larger than second-order, raising questions about the suitability of finite-order methods for including electron correlation effects on the polarizability of this system. MBPT-CC results in a variety of basis sets suggest that the experimentally unknown polarizability of F^- is ~ 18—20 a.u., of which a large percentage is due to the inclusion of triple-excitation effects.

I. INTRODUCTION

Use of the many-body perturbation theory (MBPT) in the calculation of second-order properties goes back to the work of Kelly.[1] The method proposed there is often referred to as a double perturbation theory, since the Hamiltonian contains an external field and a correlation operator which are treated as perturbations, while the unperturbed problem is the Hartree-Fock solution in the absence of the external field. Such an approach suffers from the fact that single-particle excitation effects are very important for one-particle perturbations and these are often inadequately included in lower orders of a double perturbation expansion.

Considerable efficiency may be gained by assuming as an unperturbed problem the Hartree-Fock solution in the presence of the external field. As shown by Bartlett and Purvis,[2] this can be done by the so-called coupled Hartree-Fock (CHF) method which requires the solution of the Hartree-Fock equations in the presence of the field, for finite field strengths, taking numerical derivatives with respect to the field strength to obtain moments and polarizabilities. This has been shown[3–5] to be equivalent to the summation to infinite order of some classes of diagrams, properly called "relaxation terms,"[2,6] since these terms account for the change in the orbitals in the presence of the external field perturbation. The "true" correlation contributions may be found by performing ordinary MBPT calculations subject to using the CHF finite-field, field-dependent orbitals, followed by numerical differentiation of the correlated energy.

The correlation contributions to electric properties are usually the most time consuming part of the calculation. In most cases, these corrections are only about 10% of the total value.[7] However, the electric dipole polarizabilities of the negative ions are rather exceptional in this respect. For instance, it has been shown[8] that the CHF value of the dipole polarizability of H^- is equal to 93.0 a.u., while the total correlated result is 206.4 a.u., with the correlation contribution more than doubling the CHF result. Obviously, in order to achieve an acceptable accuracy for the theoretical results, one has to take into account a substantial part of the correlation effects, which in the present paper are calculated by using full fourth-order MBPT and coupled-cluster theory.[9–14]

The fluoride ion F^- is a particularly interesting case. There is no reliable experimental value available for its dipole polarizability. Also, any theoretical calculation will suffer from the difficulty in properly describing the extreme electronegativity of F and highly important effects of electron correlation in F^-.

There are several papers devoted to the evaluation of the dipole polarizability of the fluoride ion.[15–28] Numerical CHF calculations[15–17] which exclude the true correlation effects have provided a value of 10.66 a.u. for the dipole polarizability. However, other works that have included the effects of electron correlation[21–28] suggest a value almost twice as large as the CHF results. The correlated results obtained by these authors point to the rather slow convergence of the perturbation series, which raises pertinent questions about higher-order correlation effects.

In the present paper we investigate higher-order correlation contributions using the coupled-cluster (CC) theory for the dipole polarizability of negative ions. One can anticipate that CC values, being a result of the infinite summation of certain classes of diagrams, would provide more reliable values than finite-order perturbation theory. In particular, we have recently extended the CC theory to include all contributions of T_1 and T_2 in the CC single- and double-excitation (CCSD) wave function $\exp(T_1$

$+T_2)\,|\,\Phi_0\rangle$,[9] thus the CCSD model contains the residual single-excitation effects (i.e., those remaining after a CHF calculation) that have been found to be significant in other property calculations.[2] The present results are the first report of CC results for properties.

In addition, the previous correlated calculations were limited to fourth-order correlation effects arising from only single and double excitations. Consequently, since triple-excitation effects could be expected to significantly affect the correlation correction for one-electron second-order properties, we report the full fourth-order MBPT result to the F^- polarizability. By combining CCSD results with the fourth-order triple-excitation diagram contribution, the primary correction to the CCSD model, much information about higher-order correlation corrections for the polarizabilities and electron affinity of F^- is obtained, suggesting a theoretical value for the experimentally uncertain polarizability of F^-.

Section II of the paper presents a short theoretical description of the applicable approaches, while Sec. III reviews the theoretical results for the dipole polarizability of the fluoride ion. Sections IV and V discuss the present results.

II. SUMMARY OF THE THEORY

Here we present only a brief summary of the theoretical background underlying MBPT and CC methods in connection with finite-field perturbation theory. The more detailed description is given elsewhere.[2,6]

The total molecular energy E can be expanded in a series with respect to the external electric field $\vec{F}$:

$$E = E(0) - \mu_i F_i - \tfrac{1}{2}\alpha_{ij} F_i F_j - \frac{1}{3!}\beta_{ijk} F_i F_j F_k - \cdots \;, \tag{1}$$

where summation over repeated indices is implied. Thus, being able to determine E as a function of the field strength F, both the dipole moment μ and the polarizabilities $\alpha, \beta, \gamma, \ldots$ can be obtained by numerical differentiation.

To find the total molecular energy E as a function of some perturbational parameter λ we have to solve a λ-dependent Schrödinger equation

$$H(\lambda)\psi(\lambda) = E(\lambda)\psi(\lambda) \;. \tag{2}$$

Within the MBPT scheme we solve this equation perturbatively. The total Hamiltonian $H(\lambda)$ is split in a standard way:

$$H(\lambda) = H_{\mathrm{HF}}(\lambda) + V(\lambda) \;, \tag{3}$$

$$V(\lambda) = \sum_{\substack{i<j \\ i,j}} r_{ij}^{-1} - \sum_i U_i(\lambda) \;, \tag{4}$$

where $U_i(\lambda)$ is a Hartree-Fock effective potential, determined in a self-consistent way in the presence of the external perturbation.

The unperturbed—with respect to V—problem is set up within the HF model:

$$H_{\mathrm{HF}}(\lambda)\Phi_{\mathrm{HF}}(\lambda) = E_0(\lambda)\Phi_{\mathrm{HF}}(\lambda) \;, \tag{5}$$

where

$$H_{\mathrm{HF}}(\lambda) = H^0_{\mathrm{HF}} + \lambda H^1 = \sum_i h_i(\lambda) \;, \tag{6}$$

$$H^0_{\mathrm{HF}} = \sum_i h_i + \sum_i U_i(\lambda) \;, \tag{7}$$

$$\lambda H^1 = \sum_i \vec{F}\cdot\vec{r}_i \;. \tag{8}$$

The set of one-particle λ-dependent states is generated by solving the one-electron HF equations

$$h_i(\lambda)\phi_i(\lambda) = \epsilon_i(\lambda)\phi_i(\lambda) \;. \tag{9}$$

All of these equations may be solved using either finite-field techniques, where $\vec{F}$ is fixed at some small value, or by prior expansion in λ, from which the CPHF (coupled perturbed Hartree-Fock) equations may be obtained.[3] Because it is easy to use finite-field techniques in computer programs written to calculate the energy we take this option in the following. Hence the CHF energy and orbitals are actually λ dependent, so the corresponding values are obtained by solving Eq. (9) for several values of λ and then by taking derivatives evaluated at the point $\lambda = 0$. Any possible differences between finite-field CHF and CPHF results are caused by the inaccuracies of the numerical differentiation.[4] The one-electron states resulting from Eq. (9) form the basis for the MBPT-CC calculations.

Within the finite-field MBPT scheme we find the correlation contribution to the wave function and energy using the Goldstone linked diagram formula[10]

$$\psi_{\mathrm{MBPT}}(\lambda) = \Phi_{\mathrm{HF}} + \sum_{k=1}^{\infty} \{[E_0(\lambda) - H_{\mathrm{HF}}(\lambda)]^{-1} V(\lambda)\}^k \,|\, \Phi_{\mathrm{HF}}(\lambda)\rangle_L \;, \tag{10}$$

$$E_n(\lambda) = \langle \Phi_{\mathrm{HF}} \,|\, H \,|\, \psi_{\mathrm{MBPT}} \rangle = E_{\mathrm{HF}}(\lambda) + \sum_{k=1}^{n-1} \langle \Phi_{\mathrm{HF}}(\lambda) \,|\, V(\lambda) \{[E_0(\lambda) - H_{\mathrm{HF}}(\lambda)]^{-1} V(\lambda)\}^k \,|\, \Phi_{\mathrm{HF}}(\lambda)\rangle_L \;, \tag{11}$$

where $E_n(\lambda)$ is a total energy up to the nth order and the subscript L indicates that only linked terms should be taken into account. Of course, differentiation relative to λ is required to obtain the correlation corrections for properties. The energy diagrams through fourth order are shown in Fig. 1. For reference, these are conveniently separated into different classes of contributions by the excitation level at the middle vertex.

Within the coupled-cluster method we solve Eq. (2) by observing that the exact wave function ψ_{MBPT} can be expressed in the form[12,13]

$$\psi_{\mathrm{CC}}(\lambda) = e^{T(\lambda)}\Phi_{\mathrm{HF}}(\lambda) \;, \tag{12}$$

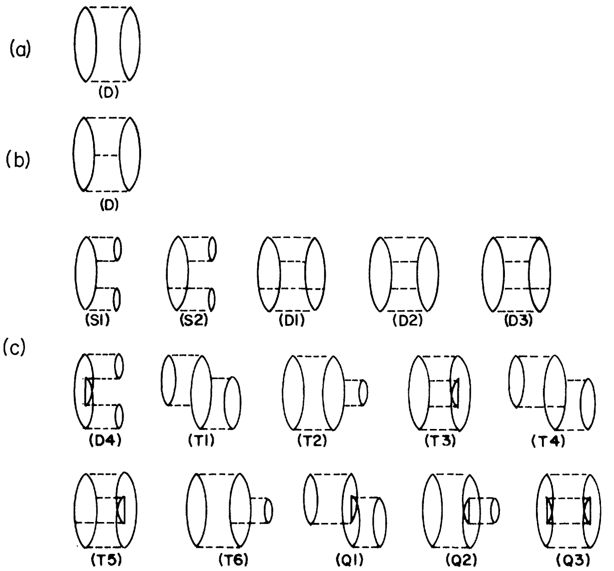

FIG. 1. Arrowless antisymmetrized Goldstone diagrams for the (a) second- (b) third- and (c) fourth-order MBPT energy. By providing arrows for each nonsymmetric loop, the full set of antisymmetrized diagrams is obtained (Ref. 10).

where the operator $T(\lambda)$ is a cluster operator that sums all of the connected wave-function contributions in Ψ_{MBPT}. The exponential expansion of $\exp[T(\lambda)]$ includes all other linked but disconnected wave-function contributions to Ψ_{MBPT}. Hence, coupled-cluster theory is a natural infinite-order generalization of finite-order MBPT methods. The cluster operator may be separated into one-body, two-body, etc., parts,

$$T(\lambda)=T_1(\lambda)+T_2(\lambda)+\cdots \;, \tag{13}$$

$$T_n(\lambda)=(n!)^{-2}\sum_{a,b,c,\ldots} t_{ijk\ldots}^{abc\ldots}\, a^\dagger b^\dagger c^\dagger \cdots kji \tag{14}$$

and the energy is obtained from

$$E=\langle \Phi_{\mathrm{HF}}\,|\,H\,|\,\Psi_{\mathrm{CC}}\rangle \;. \tag{15}$$

Substituting expansion (13) into (12), multiplying from the left by $e^{-T(\lambda)}$, and projecting onto a subspace of single, double, etc., excitations we obtain sets of nonlinear equations which give the coefficients $t_{ijk\ldots}^{abc\ldots}$. The important feature of Eq. (12) is that the energy arises always as a sum of linked diagrams independently of the approximations introduced into $T(\lambda)$ in Eq. (13).

There are two types of approximations made in practical applications of the CC equations. One arises when we truncate the series of Eq. (13), for example, to $T_1(\lambda)+T_2(\lambda)$. We assume this approximation here which defines the CCSD model.[9] Other approximations are often introduced into the resulting amplitude, $\{t_i^a\}$, $\{t_{ij}^{ab}\}$, equations such as truncating the expressions to include only selected linear contributions in the amplitudes. The latter, however, violates the spirit and much of the advantages of the CC technique, so we make no such approximation here. Instead, we properly include all nonlinear terms that arise, such as quartic T_1 terms and quadratic and cubic T_1 and T_2 cross terms.[9]

Since T_1 and T_2 occur in the exponential operator, the final result for the wave function includes an infinite summation of all single and double excitations in a configuration-interaction (CI) sense, plus a part of the triple, quadruple, and higher excitations that can arise from the various products involving T_1 and T_2. This accounts for all terms in the fourth-order energy except those arising from the T_3 operator, i.e., diagrams $T1$–$T6$ in Fig. 1. Thus to include the principal correction term to CCSD we include the fourth-order T_3 contribution. This level of calculation is denoted throughout the paper as CCSD + $T(4)$.

III. REVIEW OF THE PREVIOUS CALCULATIONS

The early studies of the fluoride polarizability which go back to the 1960s were limited to the CHF level,[15–17] and in one case, to a small CI.[18] The results obtained there range from 8.1 a.u. (Ref. 18) to about 12.2 a.u. (Ref. 17), although the numerical CHF result is 10.66 a.u. (Ref. 16), which should be the CHF limit. The experimental value available at that time was considerably lower, i.e., about 6.4 a.u. (Ref. 19). The more recent empirical and semiempirical estimates made by Coker[19] suggest the value of the fluoride-ion polarizability to be greater than 10 a.u., superficially close to the above "best" CHF values.

A thorough analysis of the quality of the theoretical and empirical data on fluoride-ion dipole polarizability given by Sadlej[21] led to the conclusion that the experimental value given in Ref. 20 is still too low. The reason for that is the large and positive correlation correction to the polarizabilities of the negative ions. Similar situations are found in the case of other negative ions, e.g., Cl^-.[16,22] These conclusions found a confirmation in the several papers by Sadlej and others[23–28] devoted to the determination of the F^- dipole polarizability with the inclusion of some portions of the correlation energy.

In Table I we present a summary of the previous correlated calculations of the dipole polarizability of the fluoride ion. Two groups of basis sets were employed there: the first one based on the paper by Kistenmacher *et al.*[29] includes sets denoted as *A*, *B*, and *C* while the second basis was developed starting from Huzinaga's ($11s\,7p$) uncontracted atomic basis and includes sets *D*, *E*, *F*, and *G*. The basis sets within each group differ by a number of additional diffuse *s*, *p*, *d*, and *f* functions and, in the case of the second group, also by the contraction scheme (see footnotes to Table I).

For relatively small basis sets the CHF values of the polarizability are rather sensitive to the addition of the diffuse functions; see the upper values for the basis *A*,*B*,*C*. For the larger basis, however, they practically remain the same as the CHF values for the *E*, *F*, and *G* sets, and equal to 10.7 a.u.,[25,26] which is near the Hartree-Fock limit.[16] The lower row values for the *A*, *B*, and *C* sets refer to calculations with field-dependent basis functions [electric field variant (EFV)] which introduces extra flexibility into a small basis set. These show significant improvement over the standard basis sets.

The correlation corrections limited to single- and double-excitation effects show a similar type of basis-set dependence as do the CHF values. For the *A*, *B*, and *C* basis sets they increase with basis-set size, or when extend-

TABLE I. Summary of previous results on the F^- polarizability (a.u.).

Basis set	Contraction	α_{CHF}	α_2	α_3	α_4^{SD}	α_{tot}
A	$(13s\,8p\,1d/7s\,4p\,1d)^{a,b}$	3.25	0.79	−0.31		3.73
		9.23	3.35	−1.58		11.00
B	$(14s\,9p\,1d/8s\,5p\,1d)^{c,b}$	4.65	2.91	−1.78		5.78
		10.57	6.27	−3.91		12.93
C^d	$(14s\,9p\,2d/8s\,5p\,2d)^{c,d}$	6.05	2.74	−1.76		7.03
		10.62	5.92	−3.98		12.56
D	$(12s\,8p\,4d/12s\,8p\,4d)^{e,f}$	10.33	5.13	−3.21	3.55	15.80
E^g	$(15s\,10p\,5d/12s\,8p\,5d)^{h,f}$	10.67	6.13	−4.06	4.96	17.70
F	$(15s\,10p\,5d\,1f/12s\,8p\,5d\,1f)^{h,f}$	10.67	6.22	−4.10	5.04	17.82
G	$(13s\,9p\,5d/13s\,9p\,5d)^{e,i}$	10.68	6.32	−4.19	5.08	17.89

[a] Taken from Kistenmacher *et al.* (Ref. 29).

[b] Upper row values are obtained from the field-independent basis sets (Refs. 21, 23, and 24), while the lower row values result from electric field variant (EFV) calculations (Ref. 21).

[c] Augmented basis set *A*.

[d] Employed in the present calculations and hereafter denoted as I.

[e] Taken from Huzinaga (Ref. 30) and augmented.

[f] Dipole polarizability values are obtained in Ref. 25.

[g] Employed in the present calculations and hereafter denoted as III.

[h] Taken from Huzinaga (Ref. 30), contracted and augmented.

[i] Dipole polarizability values are obtained in Ref. 26.

ed via the EFV approach, whereas for the larger basis sets *E*, *F*, and *G* they remain rather stable.

The correlation correction calculated for the basis sets *D*, *E*, *F*, and *G* show rather large fourth-order contributions ranging from 3.55 a.u. for the smallest basis set *D* up to 5.08 for the set *G*, although only part of the total fourth-order correlation was taken into account. However, with a HF starting point, fourth order is the first time that the residual single-excitation effects (i.e., those not included in the finite-field CHF result) can contribute, and these still are important for a one-particle operator.[2] However, to be thorough, two questions should be raised. First, what is the size of the fourth-order triple and quadruple contributions? Second, what is the behavior of the correlation contributions while summing higher-order correlation diagrams to infinite order by techniques of coupled-cluster theory? We address these two questions in the next sections.

IV. RESULTS AND DISCUSSION

Three basis sets were employed in the present calculations. The first, denoted as I, is taken from the paper by Wilson and Sadlej.[23] Basis II is that used by Bartlett and Purvis,[5] and the third one, denoted as III, was developed by Diercksen and Sadlej.[25] The basis sets I and III, containing 35 and 66 basis functions, were previously employed for F^- and are denoted in Table I as *C* and *E*, respectively. The reasons for choosing these two sets from the eight used by Sadlej and others[21–27] are as follows. It was mentioned in Sec. III that the basis sets come from two sources, Kistenmacher *et al.*[29] and Huzinaga,[30] so it is reasonable to use one representative of each group. Because the sets belonging to the first group (*A*, *B*, and *C* in Table I) are rather moderate in size, we selected the largest, believing it to be the best for this group. The basis sets derived from Huzinaga's set[30] are more sizable. To make our calculations economical, we selected the basis set which gives correct results, but is still reasonable in size. It can be seen from Table I that the addition of a set of *f* functions to the basis *E* has only a slight effect on the results, so from among four basis sets *D*, *E*, *F*, and *G* we decided to use basis set *E*. Details of these basis sets are described in Ref. 23 for I and in Ref. 25 for III.

The third basis set employed here, containing 46 functions and denoted in this paper as II, was used in the calculation of the hyperpolarizabilities for the HF molecule, and its description is given in Ref. 2. Because all the basis-set parameters were transferred without any change from the HF molecule to the F^- ion, its quality with respect to an F^- calculation might be poorer than the other two. However, this basis has the advantage that it was able to reproduce numerical HF results for the HF molecule and it is intermediate in size between I and III.

The dipole polarizabilities were obtained by performing two calculations for each basis set employed: one in the absence of the electric field and the other with an electric field equal to 0.005 a.u., and by then taking the numerical derivative of the energy with respect to the field. The correlation calculations for the basis set III were carried out by excluding the two highest-lying virtual orbitals. Their energies are equal to 266.7 and 1144.3 a.u. and because of their high values, the contribution to the correlation is expected to be negligible (check footnote to Tables III and IV). The coupled-cluster iterations were carried to a convergence of 10^{-6} a.u. in energy. This was achieved after 10 or 11 iterations.

The results presented in Tables II–V include the SCF values and the correlation contributions to the energy and electron affinity of the fluorine atom, as well as those for the energy and dipole polarizability of the fluoride ion.

For all the basis sets considered, the correlation components of the energy of the fluorine atom, see Table II,

TABLE II. Correlations contributions to the energy and electron affinity of the fluorine atom. SCF stands for self-consistent field, Hartree-Fock basis set calculation.

Contribution	Basis set I Energy (a.u.)	Aff.[a] (eV)	Basis set II Energy (a.u.)	Aff.[a] (eV)	Basis set III Energy (a.u.)	Aff.[a] (eV)
E_{SCF}	−99.413 850	1.218	−99.403 390	1.222	−99.413 189	0.944
E_2^{D}	−0.206 696	2.297	−0.204 438	2.349	−0.219 176	2.275
E_3^{D}	−0.009 221	−0.577	−0.008 943	−0.607	−0.009 318	−0.607
E_4^{S}	−0.001 015	0.119	−0.001 163	+0.133	−0.001 112	0.131
E_4^{D}	−0.002 078	0.104	−0.002 069	+0.113	−0.002 131	0.114
E_4^{T}	−0.003 200	0.213	−0.003 458	+0.252	−0.003 612	0.255
E_4^{Q}	0.001 699	−0.005	+0.001 652	−0.012	+0.001 715	−0.017
E_4^{SDQ}	−0.001 394	0.218	−0.001 448	+0.234	−0.001 389	0.231
$E_4^{\mathrm{SDTQ}}(E_4)$	−0.004 594	0.431	−0.004 906	0.486	−0.005 001	0.486
$E_2+E_3+E_4^{\mathrm{SDQ}}$	−0.217 311	1.938	−0.214 830	1.976	−0.229 884	1.899
$E_2+E_3+E_4$	−0.220 511	2.151	−0.218 287	2.228	−0.233 496	2.154
E_{CCSD}	−0.217 592	1.844	−0.215 123	1.874		
$E_{\mathrm{tot}}^{\mathrm{MBPT(4)}}$	−99.634 361	3.369	−99.621 678	3.450	−99.646 685	3.098
$E_{\mathrm{tot}}^{\mathrm{CCSD}+T(4)}$	−99.634 642	3.275	−99.621 971	3.348		

[a] Experimental value of the electron affinity of the fluorine atom is equal to 3.4 eV (Ref. 43).

exhibit similar structure. The order-by-order contributions show satisfactory convergence: the second-order value being ≈20 millihartree, the third order ≈9 millihartree, and the total fourth-order component ≈5 millihartree. All contributions are negative.

One of the more interesting questions pertain to the relative magnitude of the fourth-order energy coming from single, double, triple, and quadruple excitations. There are several papers dealing with this problem, which stresses the importance of the triple-excitation components.[31–42] It follows from the series of atoms and molecules discussed elsewhere,[31,32,35,36] that the relatively largest triple-excitation contributions occur in systems containing multiple bonds.[37,35] For the atoms, an increasing value of the triple component is observed when going from Li to Ne in the first row atoms.[31] The structure of the fourth-order contributions to the correlation energy of the fluorine atom obtained in this work supports the view of the important role of the triple-excitation contribution. The results collected in Table II show the E_4^{T} component as the prevailing one. It is equal to ≈ -3.5 millihartree as compared with ≈ -2.1 and -1.1 millihartree for the E_4^{D} and E_4^{S} contributions, respectively. The quadruple-excitation diagram component is here also large being equal to 1.7 millihartree, and its sign is positive. However, the effect of CI quadruple excitations is given by the sum of the linked and unlinked quadruples, and this value amounts to -17 millihartree, which is clearly the dom-

TABLE III. SDTQ-MBPT(4) and CCSD correlation contribution to the energy of the fluoride ion (a.u.).

Contribution	Basis set I	II	III
E_{SCF}	−99.458 608[a]	−99.448 313	−99.457 890[b]
E_2^{D}	−0.291 123[a]	−0.290 762	−0.302 793[c]
E_3	+0.011 991[a]	+0.013 367	+0.013 007[c]
E_4^{S}	−0.005 394	−0.006 040	−0.005 910
E_4^{D}	−0.005 902	−0.006 224	−0.006 306
E_4^{T}	−0.011 046	−0.012 712	−0.012 981
E_4^{Q}	+0.001 877	+0.002 221	+0.002 335
E_4^{SD}	−0.011 296	−0.012 273	−0.012 216[c]
E_4^{SDQ}	−0.009 419	−0.010 052	−0.009 881
E_4	−0.020 465	−0.022 764	−0.022 862
$E_2+E_3+E_4^{\mathrm{SDQ}}$	−0.288 551	−0.287 447	−0.299 667
$E_2+E_3+E_4$	−0.299 597	−0.290 159	−0.312 648
E_{CCSD}	−0.285 357	−0.283 998	−0.296 331
$E_{\mathrm{CCSD}}+E_4^{\mathrm{T}}$	−0.296 403	−0.296 710	−0.309 312

[a] Repetition of the results reported in Ref. 23.

[b] Repetition of the results reported in Ref. 25.

[c] The small difference as compared to the values given by Diercksen *et al.* (Ref. 25) originates from deleting the two highest-lying virtual orbitals in this calculation.

inant correction for a configuration-interaction single- and double-excitation (CISD) calculation. The net $E_4^{\mathrm{D}}+E_4^{\mathrm{Q}}$ contributions is here rather small, -0.4 millihartree, which is slightly different from what is reported in Ref. 31 where $E_4^{\mathrm{D}}+E_4^{\mathrm{Q}}=-1.0$. However, those differences may be assigned to the basis-set effect since the basis sets used here are rather large compared to the $DZ+P$ (double zeta plus polarization) set used in Ref. 31. The open-shell F atom is treated with an unrestricted Hartree-Fock reference function, but the CCSD multiplicity in basis I is 2.0002 so there is no appreciable spin contamination.

Going from the neutral F atom to the negative fluoride ion we observe substantial changes in the structure of the correlation contributions to the energy as in Table III. Because the total correlation energy is larger, the particular contributions also increase their value. In the third order there is a sign alternation with the E_3 value changed from -9 millihartree for the F atom to $+13$ millihartree for the fluoride ion. The total fourth-order term is negative, but larger than the third order, being equal to -23 millihartree (-20 for basis set I).

The structure of the fourth-order energy contributions is also modified. The dominant part of E_4 arises from the triple excitation: ≈ -13 millihartree (-11 for the basis set I), then come single and double contributions which are here nearly the same, ≈ -6 millihartree, and the smallest part is due to the quadruple-excitation diagrams, $\approx +2$ millihartree. Comparing those values with corresponding ones for the fluorine atom we observe the largest increase in the single components, a factor of 5, then, in the triple one, a factor of 4, and the double contribution is 3 times greater, while the E_4^{Q} is affected only slightly. Thus for the negative ion there is no useful cancellation of the quadruple term against the rest of the fourth order. The fact that the fourth-order energy is larger than the third order, with the positive sign of the third order, leads to the supposition that the fifth-order energy might come with a positive sign, cancelling part of the fourth-order contribution.

The pattern of the correlation contributions for the F^- energy also affects the electron affinity of the fluorine atoms, see Table II. The correlation part accounts for nearly two-thirds of the total value of the electron affinity. Most of it in the second-order component, ≈ 2.3 eV. The third-order contribution occurs with negative sign and its value is ≈ -0.6 eV. Total fourth-order component amounts to about 0.5 eV (0.4 for basis set I) and practically cancels most of the third-order increment. The fourth-order structure is the same as for F^-, i.e., $E_4^{\mathrm{T}} \cong E_4^{\mathrm{S}}+E_4^{\mathrm{D}}$, and all are positive, whereas $E_4^{\mathrm{Q}} \sim 0$, and is negative. Again, CI quadruples amount to a larger contribution of ~ 0.3 eV.

It should be stressed that the pattern of the correlation contributions to the energy and electron affinity is retained for all three basis sets employed, which points to a comparative basis-set independence.

For the smaller basis sets, i.e., I and II, the CCSD calculations were performed to estimate the correlated energy. The calculations show that E_{CCSD} is very close to the E_4^{SDQ} value, cf. $-0.217\,311$ for E_4^{SDQ} vs $-0.217\,592$ for E_{CCSD}, and similarly for the basis set II. This means that in the case of the fluorine atom, the inclusion of higher-order diagrams does not substantially modify the fourth-order value.

The comparison of the theoretical value of the electron affinity with the available experimental estimate[43] shows excellent agreement for the smaller basis sets used, but poorer results for the largest basis, so there is no convergence with size. Basis f orbitals are also likely to play an important role in this property.[44] Fourth-order perturbation theory seems to overestimate the affinity as shown by comparison with the infinite-order CCSD results in basis I and II. The CC results given for the electron affinity have values 3.062 and 3.096 eV for the basis sets I and II, respectively. The correction coming from fourth-order triples increase these by 0.213 and 0.252 eV, respectively, which gives—especially for the basis set II—a value very close to the experimental one, compare 3.348 vs 3.4 eV.[43] However, we see no real convergence with basis sets, since the affinity computed in basis III at the MBPT(4) level is much smaller than in the smaller basis sets. A study of the electron affinity of F as a function of basis set has been published by Roos *et al.*[44]

The results for the dipole polarizability, presented in Table IV, show the basis set III to be considerably superior to basis set I for this property, and somewhat superior to II. (For the *exact* unperturbed wave function, a second-order property satisfies a variational bound, which is approximately true even for an inexact unperturbed wave function.)[45] However, the trends among the different correlation contributions are the same for all the

TABLE IV. SDTQ-MBPT(4) and CCSD correlation contribution to the dipole polarizability of the fluoride ion (a.u.).

Contribution[a]	Basis set I	 II	 III
α_{CHF}	6.05[b]	10.39	10.67[c]
		Correlation corrections	
α_2^{D}	2.74[b]	5.34	6.14[d]
α_3^{D}	-1.76[b]	-3.38	-4.07[d]
α_4^{S}	1.38	2.46	3.25
α_4^{D}	0.72	1.39	1.72
α_4^{T}	1.36	2.75	3.36
α_4^{Q}	-0.10	-0.19	-0.24
α_4^{SD}	2.10	3.85	4.97[d]
α_4^{SDQ}	2.00	3.66	4.73
α_4^{SDTQ} $(\equiv\alpha_4)$	3.36	6.41	8.09
$\alpha_2+\alpha_3+\alpha_4^{\mathrm{SDQ}}$	2.98	5.61	6.80
$\alpha_2+\alpha_3+\alpha_4$	4.34	8.36	10.16
α_{CCSD}	2.17	3.81	4.96
$\alpha_{\mathrm{CCSD}}+\alpha_4^{\mathrm{T}}$	3.53	6.56	8.32

[a] Total polarizability is $\alpha_{\mathrm{CHF}}+\alpha_M$ for MBPT and $\alpha_{\mathrm{CHF}}+\alpha_{\mathrm{CCSD}}$ for CC theory.

[b] Repetition of the results reported in Ref. 23. Numerical CHF value is 10.66 (Refs. 15—17).

[c] Repetition of the results reported in Ref. 25.

[d] The small difference as compared to the values given by Diercksen *et al.* (Ref. 25) originates from deleting the two highest-lying virtual orbitals in this calculation.

basis sets considered, so the analysis of the structure of the correlation corrections is common to the three calculations. The value of the dipole polarizability seems, however, to be most reliable for the basis set III and we will refer to these results in the further parts of the discussion.

At first sight, the proportions of the different correlation components of the dipole polarizability resemble those of the F^- energy and of the electron affinity of the fluoride atom. There is a negative and large third-order contribution and also large but positive fourth-order one. The perturbational series seems to be, in this case, more divergent than in the case of the energy and the electron affinity. The fourth-order component, which is $+8.1$ a.u. for the basis set III, is larger than the second-order one, $+6.1$ a.u., and even more so compared to the third-order, -4.1 a.u. To our knowledge, this is one of the few times fourth-order correlation corrections have exceeded second order,[10] although it is common for the fourth-order energy to be larger than the third order.[36]

Within the fourth order the most important contributions come from the triple and single excitations, both being nearly the same value: 3.4 and 3.3 a.u., respectively. The double-excitation part is about half that much, and the quadruple part is, as usual, of the opposite sign, and negligibly small, -0.2 a.u. Comparing different approximation schemes, we observe that because of the large α_3^T value, none of the approximations SD-MBPT(4) and SDQ-MBPT(4) seem to work well, whereas both yield very similar results.

This is in general agreement with already reported studies on the fourth-order contributions to the electric properties of molecules.[37–42] The values of the fourth-order contributions to the dipole polarizability of the FH and H_2O molecules[37,40] show the same mutual proportions, i.e, $\alpha_4^T \geq \alpha_4^S \cong 2\alpha_4^D$ while α_4^Q is negligible. There is a different structure exhibited by the fourth-order correction to the dipole polarizability of the beryllium atom.[40] In this case, α_4^D becomes the dominant part. There is not, however, such a regular pattern for other electric properties such as the dipole and quadruple moment.[38]

The total fourth-order polarizability of F^- is as large as 20.8 a.u., see Table V. This value, however, seems to be exaggerated because of the aforementioned sign alteration property of the MBPT series. Some estimates of the extent of the cancellation by the higher-order terms can be made on the basis of the coupled-cluster results. The CCSD correlation contribution α_{CCSD} is equal to 5.0 a.u., while the same diagrams summed only to fourth order, i.e., $\alpha_2+\alpha_3+\alpha_4^{\mathrm{SDQ}}$ gives the value 6.8 a.u.

If the total fourth-order results $\alpha_2+\alpha_3+\alpha_4$ would be corrected by the infinite summation in the same proportion, we would obtain the final value of the dipole polarizability of F^- equal to ≈ 18 a.u.

V. CONCLUSIONS

From the viewpoint of accurate correlated calculations, the fluoride ion represents an interesting study. The correlation contributions to the energy and the dipole polarizability are quite large. Moreover, the first terms of the MBPT series show very slow convergence and even inclusion of all fourth-order terms does not give results of chemical accuracy (i.e., within 1 millihartree). Because of the occurring sign alteration, the fourth-order results seem to overshoot.

TABLE V. Summary of the dipole polarizability calculation. Total dipole polarizability values (a.u.).

Method	Basis set I	 II	 III
CHF	6.05[a]	10.39	10.67[b]
SD-MBPT(4)	9.13	16.20	17.71[c]
SDQ-MBPT(4)	9.03	16.00	17.47
SDTQ-MBPT(4)	10.39	18.75	20.83
CCSD	8.22	14.20	15.63
CCSD + $T(4)$	9.58	16.95	18.99

[a] Repetition of the results reported in Ref. 23.

[b] Repetition of the results reported in Ref. 25. Numerical CHF value is 10.66 (Refs. 15—17).

[c] The small difference as compared to the values given by Diercksen *et al.* (Ref. 25) originates from deleting the two highest-lying virtual orbitals in this calculation.

A reasonable estimate of the quality of the fourth-order results can be obtained by performing coupled-cluster-type calculations, i.e., summing to infinity all diagrams that derive from T_1 and T_2 and their couplings. The CCSD energy for F^- is ~ 3 millihartree above its fourth-order equivalent, i.e., $E_2+E_3+E_4^{\mathrm{SDQ}}$, while the polarizability in the large basis set is ~ 2 a.u. less.

Assuming also that the fourth-order triple contribution would be partially canceled by higher orders, we may estimate the total dipole polarizability to be about 18 a.u., however, basis-set expansion could introduce a correction in the other direction. Hence our best estimate for the dipole polarizability of F^- is ~ 18—20 a.u. which is substantially larger than the available empirical estimates[20] and slightly larger than the theoretical estimates made so far.[23] It is also clear that more standard methods for electron correlation effects like single-reference CISD are not likely to account for difficult problems like F^- or, in general, negative ions due to the neglect of higher-order excitations.

The structure of the fourth-order contribution points to the importance of the triple-excitation terms in energy calculations, which in the case of F^- account for more than half of the fourth-order component. However, it is still important in such assessments to distinguish the value of quadruple-excitation diagrams from CI quadruple-excitation effects, which causes the largest single energy correction to CISD. In the dipole polarizability calculations, triple-excitation terms are equally important as the single-excitation contribution, both measured relative to field-dependent orbitals which supports a previous supposition[2] and the conclusion of Diercksen *et al.*[41,42]

For systems like the fluorine atom and fluoride ion, even more reliable results could be obtained by developing more advanced tools for approaching the correlation problem. This may be accomplished within the MBPT scheme by including fifth-order terms, or within the CC approach by also taking into account connected triple-excitation terms, as has recently been accomplished.[46] Some kinds of complex correlation corrections will also require multi-reference-function MBPT-CC methods for very high accuracy results (see Ref. 10 for a review).

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[*] Permanent address: Department of Chemistry, Silesian University, Szkolna 9, PL-40-006 Katowice, Poland.

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