Theoret. Chim. Acta (Berl.) 60, 19–39 (1981)

THEORETICA CHIMICA ACTA
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Finite-Field Many-Body Perturbation Theory. Calculations of the Dipole Polarizability of the Fluoride Ion Using Electric-Field-Variant Gaussian-Type Orbitals

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The dipole polarizability of the fluoride ion, F^-, is calculated using finite-field many-body perturbation theory. The use of electric-field-variant basis sets in such calculations is investigated. Scaling of the zero-order Hamiltonian and the formation of Padé approximants are considered. Empirical and theoretical estimates of the polarizability of F^- are compared.

Key words: Many-body perturbation theory – Finite-field method – Dipole polarizability – Electric-field-variant basis set.

1. Introduction

During the past decade the diagrammatic many-body perturbation theory (MBPT) [1–3] has been developed into a convenient and computationally tractable scheme [4–6] for the calculation of electron correlation energies which compares favourably with other methods currently in use [7–18]. Within the algebraic approximation [5] the MBPT approach provides a very efficient and highly systematic method for the study of the electron correlation problem in many-electron systems and offers certain advantages in comparison with more

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0040-5744/81/0060/0019/$04.20

standard treatments [7, 10, 15, 18]. Moreover, the interpretation of correlation effects by using the hole-particle formalism and Feynman diagrams [1–3, 18–20] is very instructive and appealing.

Virtually the same approach can be employed for many-electron systems in the presence of some external perturbation [1]. This results [1, 21, 22] in the diagrammatic MBPT scheme for the interpretation and calculation of correlation contributions to the properties of many-electron systems, e.g. electric and magnetic moments and susceptibilities of atoms and molecules [23, 24]. However, in the case of externally perturbed systems the choice of the appropriate single-particle states becomes less obvious than for the unperturbed problem. One can use either the single-particle states determined from the Hartree–Fock (HF) treatment of the unperturbed system [1, 21, 25–31] or the perturbation-adapted single-particle states [21, 22, 31–36]. In the latter case, the HF problem must be solved for the perturbed system prior to the consideration of correlation effects. Both these cases have recently been given a detailed diagrammatic analysis [21, 31] which clearly indicates the preference of the MBPT treatment of the correlation effects for atomic and molecular properties based on the perturbed HF orbitals obtained from the coupled Hartree–Fock (CHF) [37–39] perturbation theory.

The most convenient way of performing diagrammatic MBPT calculations of correlation corrections to properties is to use the so-called finite-field perturbation approach [40–42]. This technique has already been successfully utilized in several other studies of correlation contributions to atomic [43, 44] and molecular [45–49] properties and appears to be the most efficient computational method for the electric field perturbation. Within the diagrammatic MBPT approach, the finite-field perturbation scheme leads to the field-dependent correlation energy diagrams [50] whose differentiation with respect to the field strength gives directly the correlation corrections under consideration. Recent applications of the finite-field diagrammatic MBPT [21, 22, 31–36] appear to be very promising and this method is also employed in the present calculations.

The present paper is aimed at a systematic study of correlation contributions to the electric dipole polarizability of the fluoride ion. The negative ions are special in that the correlation contribution to their polarizabilities can be very large [51]. Recent preliminary MBPT calculations of the polarizability of the fluoride ion [33] have led to the conclusion that the corresponding second-order correlation correction is also exceptionally large. This obviously raises the question of the higher-order correlation contributions to the fluoride ion polarizability. In comparison with the second-order effects they should be smaller but not necessarily negligible. In this paper, the corresponding diagrammatic MBPT calculations are carried out through the third-order in the correlation perturbation, the scaling procedure is used and appropriate Padé approximants are constructed [52, 53, 67, 68, 70].

Accurate calculation of atomic and molecular polarizabilities imposes certain specific requirements with regard to the form and character of the basis set

[43, 45]. In the standard fixed-basis set approach one has to use a number of polarization and diffuse functions [43–45, 54, 55] and, when investigating the correlation effects, a given basis set must account for both the external field perturbation and the electron correlation [21, 22, 33–36]. Even for relatively small systems this may lead to basis sets of prohibitively large size. To overcome these problems it has been proposed [56] to use the Gaussian-type orbitals with explicit dependence on the electric field strength. These electric-field-variant (EFV) GTO bases [56, 57] have been found very efficient in the CHF calculations of atomic and molecular polarizabilities [56–61]. More recently they have been also successfully utilized for the calculation of correlation corrections to polarizabilities [21, 22, 32, 33, 62]. Several useful features of the EFV GTO bases make them certainly very appropriate for the present purposes. It should be pointed out that in the case of negatively charged species the basis set problem may become even more acute than for neutral systems [51, 63].

A brief survey of the theory and methods employed in the present study is given in the next section. The corresponding computational aspects and some numerical details are described in Sect. 3. Both the correlation energy data and the polarizability results are presented in Sect. 4. In Sect. 5 our results are discussed in the light of the disagreement between the theroretical and empirical polarizability values of the fluoride ion. It is concluded that the third-order MBPT results for the free fluoride ion polarizability are more realistic than most of the so-called empirical values.

2. Theory and Methods

2.1. Diagrammatic Many-Body Perturbation Theory

A comprehensive description of the diagrammatic many-body formulation [19, 20] of the Rayleigh–Schrödinger perturbation theory for electron correlation energies in molecules has been given in a number of recent papers [1–3, 5, 7, 10, 18, 64]. Therefore, it is sufficient to give only a brief explanation of the notation used throughout this paper which is basically the same as that employed elsewhere [5, 7, 65].

Let us first consider a many-electron system in the absence of external perturbations. The total Hamiltonian H is split into the zero-order operator H_0 and the internal perturbation H_1. The level shift ΔE with respect to the lowest eigenvalue E_0 of the zero-order Hamiltonian H_0 can be given the following perturbation expansion

$$\Delta E = E_1 + E_2 + E_3 + \cdots \tag{1}$$

where E_n is the nth order perturbed energy with respect to the perturbation H_1 [5, 7, 65]. All these perturbed energies can be given a diagrammatic representation and it can be shown that only terms described by linked diagrams [19, 20] enter the perturbation series (1).

If H_0 is taken to be the HF Hamiltonian, then E_0+E_1 is the HF energy of a given system and the sum $E_2+E_3+\cdots$ is referred to as the total correlation energy E_{corr}. On using the algebraic approximation [5], the sum of the corresponding zero- and first-order energies is the self-consistent field (SCF) energy, E_{SCF}, and the correlation energy is taken with respect to it.

In practice we have only some truncated expansion for the total energy, E, and we try to obtain the best approximation to E by using a few terms, say $2N+1$, of the perturbation expansion

$$E=E_0+\Delta E=E_0+E_1+E_2+E_3+\cdots. \tag{2}$$

The most natural is to consider the usual truncated Taylor series, i.e. the $[2N+1/0]$ Padé approximant [66]. The full third-order calculations will give then the following approximate value of the correlation energy

$$E_{\text{corr}}\cong E_{\text{corr}}[3/0]=E_2+E_3. \tag{3}$$

Improved results can often be obtained [53, 67–69] by using the $[N+1/N]$ Padé approximants based on the first $2N+1$ terms of the expansion (2). Within the third-order MBPT approach this leads to

$$E_{\text{corr}}\cong E_{\text{corr}}[2/1]=\mu^{-1}E_2 \tag{4}$$

where

$$\mu=1-\frac{E_3}{E_2}. \tag{5}$$

This result follows also from the scaling of the zero-order Hamiltonian [52, 53] and has recently been given a firm variational justification [70]. To stress the importance of the approximation (4) let us mention that the $[N+1/N]$ Padé approximant is invariant to the changes of scale and of the origin of the zero-order spectrum [52, 53, 67, 71, 72]. The approximation (4) is frequently referred to as the geometric approximation based on E_2 and E_3, for it has the form of a geometric series. However, this analogy has only a formal character, since the expansion terms of (4) do not correspond to the higher-order terms in the perturbation series (2) [53].

In the present paper the diagrammatic MBPT calculations are carried out through the third-order in H_1. Both the diagrams and the corresponding algebraic formulae can be found elsewhere [5, 7, 65]. The third-order correlation energy E_3 can be conveniently expressed as a sum of the particle-particle, hole-particle, and hole-hole contributions which are denoted by $E_3(\text{pp})$, $E_3(\text{hp})$, and $E_3(\text{hh})$, respectively. Moreover, each term in the series (2) can be analysed according to the number of interacting bodies [7] and the k-body contribution to E_n will be denoted by E_n^k.

The knowledge of the first $2N+1$ terms in the expansion (2) is equivalent to the knowledge of the Nth order perturbed wave function which can be used to obtain a variational bound to the total energy. In the case of the third-order

MBPT calculations one has [65]:

$$E \leq E(\text{var}, \gamma) = E_0 + E_1 + [(2\gamma - \gamma^2)E_2 + \gamma^2 E_3]/(1 + \gamma^2 \Delta_{11}) \tag{6}$$

where Δ_{11} is the norm of the first-order perturbed function and γ is a variation parameter. Hence, we obtain the following approximate formulae for the correlation energy

$$E_{\text{corr}} \cong E_{\text{corr}}(\text{var}, \gamma = 1) = \frac{E_2 + E_3}{1 + \Delta_{11}} \tag{7}$$

and

$$E_{\text{corr}}(\text{var}, \gamma_{\text{opt}}) = \frac{(2\gamma_{\text{opt}} - \gamma_{\text{opt}}^2)E_2 + \gamma_{\text{opt}}^2 E_3}{1 + \gamma_{\text{opt}}^2 \Delta_{11}}, \tag{8}$$

where γ_{opt} is the value of γ calculated from the minimum of the variational energy (6) [65, 73, 74]. Both these formulae will be exploited in the present paper.

Finally, let us mention that instead of using the HF zero-order Hamiltonian H_0 which is hereafter referred to as the model Hamiltonian [5, 7, 65], $H_0 = H_{\text{model}}$, one can also employ a shifted zero-order operator, $H_0 = H_{\text{shifted}}$[5, 7], which commutes with H_{model}. This procedure is equivalent to the use of shifted denominators when computing the perturbed energies [1, 5]. The shifted Hamiltonian employed in the present paper is the same as that of Refs. [7] and [65], where details can be found. This completes the survey of basic formulae which will be referred to in subsequent sections.

2.2. Finite-Field MBPT Treatment of External Perturbations. Correlation Corrections to Polarizabilities

The perturbation treatment of the electron correlation effects in externally perturbed systems is somewhat ambiguous [22]. However, it has recently been demonstrated [22, 31, 34] that the diagrammatic MBPT approach based on what is known as the coupled Hartree–Fock (CHF) solutions for the perturbed system [38, 39] represents the most appropriate method. Since the CHF perturbation solutions follow from the expansion of the HF results for the perturbed system, the most convenient way of performing the appropriate computations is by using the so-called finite-field scheme [40–42].

In the finite-field perturbation method the total energy of a given system is considered as a numerical function $E = E(F)$ of the external field strength F. The kth order perturbed energies are obtained then via the numerical differentiation of $E(F)$ with respect to F. Since according to Eq. (2)

$$E(F) = E_0(F) + \Delta E(F) = E_{\text{HF}}(F) + E_2(F) + E_2(F) + \cdots, \tag{9}$$

where

$$E_{\text{HF}}(F) = E_0(F) + E_1(F), \tag{10}$$

one can define the nth order correlation correction to the kth order field-perturbed energy as

$$E_n^{(k)} = \frac{1}{k!}\left(\frac{\partial^k E_n(F)}{\partial F^k}\right)_{F=0}. \tag{11}$$

In terms of numerical calculations this means that one needs to compute first the field-dependent correlation energy diagrams [32, 34, 50] by using the field-dependent single-particle states. Thus, all correlation energy formulae presented in the previous section remain formally the same, except for being explicitly dependent on the external perturbation (field) strength F.

For the present paper the quantity of primary interest is the electric dipole polarizability [75] which is proportional to the second-order field-perturbed energy for the perturbation due to static homogeneous electric field. In the case of spherically sysmmetric systems the rotational average α of the polarizability tensor [75] is given by

$$\alpha = -\left(\frac{\partial^2 E(F)}{\partial F^2}\right)_{F=0}, \tag{12}$$

where F denotes the strength of the external electric field along some arbitrary direction. On substituting Eq. (9) into Eq. (12) we obtain the following perturbation expansion

$$\alpha = \alpha_{\mathrm{HF}} + \alpha_{\mathrm{corr}} = \alpha_{\mathrm{HF}} + \alpha_2 + \alpha_3 + \cdots, \tag{13}$$

where the first term corresponds to what is known as the CHF result and α_n, $n = 2, 3, \ldots$, denote the n-th order correlation corrections to the HF (CHF) value.

The total correlation correction α_{corr} can be approximated by using derivatives of different approximate formulae for the field-dependent correlation energy. From the second-order derivatives of the field-dependent counterparts of Eqs. (3), (4), (7), and (8) we obtain the estimates of the correlation contribution to the polarizability $\alpha_{\mathrm{corr}}[3/0]$, $\alpha_{\mathrm{corr}}[2/1]$, $\alpha_{\mathrm{corr}}(\mathrm{var},\ \gamma = 1)$, and $\alpha_{\mathrm{corr}}(\mathrm{var},\ \gamma_{\mathrm{opt}})$, respectively.

Though the diagrammatic analysis of correlation corrections α_n [21, 22, 31, 32, 34] reveals certain important features of the CHF-based MBPT approach, the appropriate calculations are most easily carried out by using a completely numerical scheme which consists in computing the field-dependent HF (SCF) orbitals and the field-dependent correlation energy diagrams. Then, the latter are differentiated numerically to give the contributions to α_n.

To complete the definitions employed in this paper let us also mention that the third-order term α_3 can be represented, similarly to E_3, as a sum of the particle-particle, hole-particle, and hole-hole components which are denoted by $\alpha_3(\mathrm{pp})$, $\alpha_3(\mathrm{hp})$, and $\alpha_3(\mathrm{hh})$, respectively. Moreover, each term in Eq. (13) can be analysed into k-body interaction contributions α_n^k in the same way as in the case of E_n [7]. Also using either H_{model} or H_{shifted} as the zero-order Hamiltonians for the

field-perturbed problem, $H_0(F)$, will lead to different correlation corrections in Eq. (13).

All calculations are obviously carried out by using the algebraic approximation [5], so that in final formulae all HF values should be replaced by their SCF counterparts. Accurate calculation of both SCF polarizabilities and correlation corrections to them imposes, however, rather specific requirements with regard to the flexibility of the finite basis set and this problem deserves a separate discussion.

2.3. The Basis Set Problem in Polarizability Calculations. The EFV GTO *Bases*

As already mentioned the calculation of polarizabilities including the correlation effects requires that a given finite basis set must simultaneously give a proper description of the electron density polarization due to external electric field and considerable portion of the correlation energy [22]. To satisfy both these conditions one has to employ basis sets which contain several polarization and diffuse functions [34, 35, 43–45, 54, 55]. An alternative solution of the basis set problem consists in using smaller bases of functions which can be inherently adapted to the electric field perturbation. This is the main idea behind the concept of the EFV bases [56, 57].

According to the EFV basis set approach a given initial set which has been employed in calculations for the unperturbed system is made explicitly dependent on the electric field strength. Each function $\chi_i(\boldsymbol{r};\alpha_i)$ of the inital set, where $\boldsymbol{r}$ is the electron coordinate vector and α_i denotes the orbital exponent, is transformed into a field-dependent function $\chi_i(\boldsymbol{r};\alpha_i, F)$. In the case of the GTO bases a natural form of the field dependence of GTO's can be guessed from the solutions for the field-perturbed harmonic oscillator [56]. The corresponding analysis has led to the following form of the EFV GTO basis functions [56]

$$\chi_i(\boldsymbol{r};\alpha_i, F) = \chi_i(\boldsymbol{r}(F, \alpha_i, \lambda);\alpha_i), \tag{14}$$

where

$$\boldsymbol{r}(F, \alpha_i, \lambda) = \boldsymbol{r} - \frac{\lambda F}{\alpha_i^2} \tag{15}$$

and λ is a parameter which is chosen the same for all GTO's. Its value can be determined variationally by the minimization of the second-order perturbed SCF energy [56–61].

The efficiency of the EFV GTO bases has already been illustrated in a number of atomic and molecular polarizability calculations at the CHF level [56–61]. The corresponding results which have been obtained by using rather standard and relatively small bases [58, 60, 61] compare favourably with the most accurate CHF polarizabilities computed within the fixed, i.e. field-independent, basis set approximation [45]. More recently the EFV GTO bases have also been successfully employed for the calculation of correlation corrections to polarizabilities [21, 22, 32, 33, 62]. It is of particular importance that when using the EFV GTO's

for the study of correlation effects one can select the initial GTO/CGTO basis set primarily according to the correlation energy criteria [22]. The effects of the electric field perturbation are automatically accounted for by the analytic dependence of the basis set functions on the field strength [22, 32, 33, 62] without any increase in the basis set size. It is also convenient that the dependence of the basis set functions on F amounts to a shift of the orbital origin for each primitive Gaussian. This feature of the EFV GTO bases enables all calculations to be easily performed by using standard computational schemes and programs. The variation parameter λ can also be efficiently evaluated by a completely numerical method [61, 76]. Its numerical value which follows from the optimization of the CHF polarizability has been found [22, 32, 33, 62] quite suitable for calculating the field-dependent correlation energies.

The usefulness of the EFV GTO bases should also be stressed in the context of recent studies of correlation energies using universal even-tempered basis sets and systematic sequences of even-tempered basis sets [16, 69, 77–81]. Employing EFV GTO bases in such an approach certainly requires some additional computational effort because of the optimization of the parameter λ. However, this method provides a tractable scheme for accurate studies of electric properties of many-electron systems within the restricted basis set approximation.

3. Computational Details

3.1. Basis Sets

The initial GTO/CGTO basis sets employed in the present diagrammatic MBPT studies of the fluoride ion polarizability are the same as those used previously [33]. They form a sequence of three bases of increasing size and complexity. The smallest basis A has been taken from the paper by Kistenmacher et al. [82] and consists of 13s, 8p, and 1d primitive GTO's contracted to 7s, 4p, and 1d CGTO.

The SCF energy for this basis set appears to be fairly close to the HF limit for the fluoride ion [82]. However, because of the lacks of GTO's with relatively small orbital exponents the representation of the outer region of the electron density distribution should be rather inaccurate. The second set, basis B, has been generated in order to improve the quality of SCF orbitals in the outer atomic region and this has been effected by the addition of s and p GTO's with orbital exponents equal to 0.035 and 0.032, respectively [33]. These values have been selected by assuming that the orbital exponents of a given subset form approximately a geometric series. The CGTO set B used in the present calculations corresponds to the contraction scheme (14.9.1/8.5.1). The valence shell orbitals are left virtually uncontracted.

In order to recover a considerable portion of the correlation energy one needs a number of higher angular momentum functions be included in the basis set. For this reason the largest set C has been generated from the set B by the addition of a single set of d-type GTO's with the orbital exponent equal to 0.6 [33]. This set corresponds to the following contraction scheme (14.9.2/8.5.2).

In the presence of the external electric field the initial GTO/CGTO basis sets are transformed into the corresponding EFV GTO bases according to Eq. (14). The variation parameter λ has been optimized in the CHF calculations of the electric dipole polarizability of the fluoride ion [33] and is equal to 0.1158, 0.1080, and 0.1129 for basis sets *A*, *B*, and *C*, respectively. The λ-optimization of the EFV GTO bases has been carried out by using the numerical scheme described previously [61, 76].

3.2. Calculations of Correlation Energies and Polarizabilities

The diagrammatic MBPT calculations of the second- and third-order correlation energy for bases *A*, *B*, and *C* have been performed by using the methods described in previous papers [5–8]. The results of the corresponding field-independent basis set calculations are reported in the next section.

More detailed information appears to be appropriate in the case of the polarizability calculations. They have been carried out for both the field-independent and the EFV GTO bases *A*, *B*, and *C*. In the first step the corresponding SCF orbitals have been determined by using the SCF HF scheme with the external electric field included in the Hamiltonian. When using the finite-field perturbation methods a particular care has to be taken of the appropriate choice of the numerical values of the electric field strength [40–42, 60, 61, 76]. They must be large enough to produce meaningful changes of the total energy of a given system and simultaneously they must be small enough to allow for a simple numerical determination of the field-dependent energy derivatives [60, 61, 76]. According to the previous CHF studies of the fluoride ion polarizability [33] and a series of numerical experiments which have been carried out within the present paper, the electric field strength of 0.005 a.u. appears to satisfy the above-mentioned requirements.

The SCF orbitals calculated with $F = 0.005$ a.u. have been then employed for the evaluation of the field-dependent diagrammatic contributions to the second- and third-order correlation energy. Both the SCF (CHF) polarizability and the corresponding correlation corrections have been computed numerically from the energy values for $F = 0$ a.u. and $F = 0.005$ a.u. It follows from our calculations for other values of the external field strength that the results reported in this paper are accurate to 10^{-2} a.u. of polarizability. This accuracy is completely sufficient for a meaningful discussion of different components of correlation contributions to the fluoride ion polarizability and different approximations for the total correlation correction α_{corr}.

4. Results

4.1. Correlation Energy Studies

The SCF energies and the diagrammatic MBPT contributions to the correlation energy of the unperturbed fluoride ion obtained with bases *A*, *B*, and *C* are reported in Tables 1 and 2. Both the model expansion ($H_0 = H_{\text{model}}$) and the

Table 1. Calculated energy data for the unperturbed fluoride ion in three different GTO/CGTO bases (in a.u.)

	Basis A	Basis B	Basis C
E_{SCF}	−99.45824	−99.45844	−99.45861
Correlation energy: model expansion			
E_2	−0.26394	−0.26481	−0.29112
E_3(pp)	+0.03942	+0.03956	+0.04508
E_3(hp)	−0.07141	−0.07155	−0.08399
E_3(hh)	+0.04463	+0.04519	+0.05090
E_3	+0.01264	+0.01322	+0.01199
$E_{corr}[3/0]$	−0.25130	−0.25158	−0.27913
$E_{corr}[2/1]$	−0.25188	−0.25222	−0.27961
$E_{corr}(\text{var}, \gamma=1)$	−0.23840	−0.23849	−0.26284
$E_{corr}(\text{var}, \gamma_{opt})$	−0.24056	−0.24077	−0.26522
γ_{opt}	0.91139	0.90922	0.91103
Correlation energy: shifted expansion			
E_2	−0.31684	−0.31420	−0.34655
E_3(pp)	+0.02294	+0.0445	+0.02925
E_3(hp)	+0.05937	+0.05231	+0.05266
E_3(hh)	+0.00391	+0.00379	+0.00431
E_3	+0.08622	+0.08056	+0.08622
$E_{corr}[3/0]$	−0.23063	−0.23364	−0.26033
$E_{corr}[2/1]$	−0.24907	−0.25008	−0.27751
$E_{corr}(\text{var}, \gamma=1)$	−0.21280	−0.21618	−0.23850
$E_{corr}(\text{var}, \gamma_{opt})$	−0.23736	−0.23845	−0.26289
γ_{opt}	0.74913	0.75890	0.75859

shifted expansion ($H_0 = H_{shifted}$) [5, 7, 8] are examined as a function of the order of the correlation perturbation (Table 1) and as a function of the number of interacting bodies (Table 2). Table 1 also gives various estimates of the total correlation energy which follow from the third-order MBPT treatment.

For all three bases utilized in the present paper the SCF energies are nearly the same and fairly close to the estimated HF limit (−99.4594 a.u. [82]). Passing from the set A to the set B has practically no effect on the calculated correlation energy components. However, a considerable decrease of the E_2 value is observed for the basis C. This value can be compared with the recent highly accurate second-order correlation energy computed by Jankowski et al. [83]. Their calculated result for E_2 for the fluoride ion amounts to −0.3995 a.u. while the extrapolated value is −0.4004 a.u.. Obviously, one can hardly compete with the accuracy of the second-order perturbation calculations of Jankowski et al. when using finite and rather small GTO/CGTO bases. However, the accurate value of E_2 is very close to the empirical estimate of the total correlation energy of the fluoride ion (−0.393 a.u. [84]). Within the model expansion the present calculations with the largest basis C give more than 70% of the accurate second-order energy. This is a rather typical result for basis sets of that size.

Table 2. N-body interaction components of the calculated correlation energy for the unperturbed fluoride ion in three different GTO/CGTO basis sets. The superscripts at the energy symbols denote the number of interacting bodies; the subscripts refer to the order of perturbation expansion. All entries in a.u.

Basis	A		B		C	
H_0	H_{model}	H_{shifted}	H_{model}	H_{shifted}	H_{model}	H_{shifted}
Two-body contributions						
E_2^2	−0.26394	−0.31684	−0.26481	−0.31420	−0.29112	−0.34655
E_3^2(pp)	+0.03942	+0.02294	+0.03956	+0.02445	+0.04508	+0.02925
E_3^2(hp)	−0.12875	−0.03106	−0.12958	−0.03547	−0.14554	−0.04048
E_3^2(hh)	+0.04193	0 0	+0.04248	0.0	+0.04782	0.0
Total	−0.31134	−0.32496	−0.31232	−0.32522	−0.34376	−0.35778
Three-body contributions						
E_3^3(hp)	+0.05734	+0.09043	+0.05803	+0.08778	+0.06154	+0.09314
E_3^3(hh)	+0.00006	+0.00007	+0.00006	+0.00007	+0.00006	+0.00007
Total	+0.05741	+0.09050	+0.05809	+0.08785	+0.06161	+0.09321
Four-body contribution						
E_3^4(hh)	+0.00263	+0.00384	+0.00264	+0.00372	+0.00302	+0.00424

Both the model and the shifted expansion display a fairly regular behavior for all basis sets used in the present calculations. Similar regularities have been observed in other cases [5, 7, 8, 16]. For both choices of the zero-order Hamiltonian the third-order correlation energy is positive and considerably smaller than the absolute value of E_2. However, the use of H_{model} appears to give a better convergence.

According to the third-order MBPT data of Table 2 the contribution of the two-body interaction terms to the correlation energy is certainly dominant. Also the convergence with the number of interacting bodies appears to be quite rapid, though this result must be considered with some caution, since it refers to the MBPT results through the third order only. Nonetheless, a more rapid convergence is once again observed for the model expansion.

Among the estimates of the total correlation energy which are presented in Table 1 the [2/1] Padé approximant leads to the most negative value for both choices of the zero-order Hamiltonian. For the model expansion the usual Taylor series result and the [2/1] Padé approximant to the correlation energy are within less than 10^{-3} a.u.. The corresponding difference is much larger for the shifted expansion. This result implies also that the [2/1] Padé approximant should represent a better functional form for the correlation energy than the [3/0] approximant [65].

It should be pointed out that the [2/1] Padé approximant is equivalent to the result of the scaling procedure based on the vanishing of the third-order

correlation energy for the scaled expansion [52, 53, 67, 71, 72]. Since the same result is also obtained from the second-order energy variation principle [70] in a modified perturbation scheme [85, 86], the study of the [2/1] Padé approximants deserves a particular attention. Use of the [2/1] Padé approximants can be justified using variational arguments [70]. This variational origin of the [2/1] Padé approximant is accompanied by its invariance with respect to the scaling of the zero-order Hamiltonian and the shift of the reference eigenvalue spectrum [52].

It should be also pointed out that for the two perturbation expansions illustrated by the data of Table 1, the $E_{\mathrm{corr}}[2/1]$ values are almost the same, while the usual Taylor series gives significantly different results. Above all this indicates some preference of the model expansion in the perturbation treatment of correlation effects. Because of its invariance properties and its variational justification, the [2/1] Padé approximant is expected to form a useful third-order approximation when H_{model} is chosen as the zero-order Hamiltonian. The denominator shifts which are involved in the shifted perturbation expansion, though they result in a significant lowering of E_2, may not be properly balanced.

Considerable attention has recently been given to the possibility of transferring the scaling factor μ of Eq. (4) between the correlation energy calculations in different bases [67, 53, 87, 88]. According to the present data for the model expansion the scaling factor μ appears to be fairly independent of the basis set. From the numerical values of E_2 and E_3 reported in Table 1 we obtain $\mu =$ 1.04789, 1.04987, and 1.04119 for the basis sets A, B, and C, respectively. Much larger and less stable values of μ follow from the results for the shifted expansion.

Finally, let us comment on the variation estimates of the correlation energy based on the third-order MBPT results. In comparison with $E_{\mathrm{corr}}[3/0]$ and E_{corr} [2/1] they are systematically less negative owing to the positive contribution of the renormalization term [12, 18, 89]. Since the renormalization contributions are cancelled by the higher-order diagrams the variational estimates should be in fact corrected for this effect [12]. This would lead again to the lowering of their numerical values. Moreover, it should be pointed out that for the model expansion the optimized value of the variational parameter γ is closer to unity than for the shifted expansion.

According to the present discussion it appears that the [2/1] Padé approximant based on the E_2 and E_3 values which follow from the model perturbation expansion provides the most reliable estimate of the total correlation energy. For the basis set C our value of $E_{\mathrm{corr}}[2/1]$ gives about 70% of the empirical estimate of the correlation energy for the flouride ion [84]. A comparison with similar data for other systems [5, 7, 8, 18, 34, 64–68] leads to the conclusion that a major part of this discrepancy should be rather due to the restricted basis set approximation than the higher-order effects. Moreover, let us also mention that recent fourth-order MBPT calculations indicate a possibility of some cancellation

of the third- and fourth-order correlation energy contributions to polarizabilities [34]. However, it should be noted that these calculations neglected the fourth-order triple-excitation component of the energy which has been shown to be quite large [90–95]. In some cases the second-order value E_2 may provide a very good approximation to the total correlation energy [96–98].

4.2. Dipole Polarizability of the Fluoride Ion

The field-dependent energy values follow in general the results discussed for the field-independent case and several subtle differences are revealed only when considering the appropriate energy derivatives. The results of the polarizability calculations with initial field-independent GTO/CGTO basis sets are shown in Table 3. Even for the largest basis set C the standard fixed basis set approach gives only a little more than 50% of the accurate CHF value reported by Cohen (1.56 $Å^3$ = 10.53 a.u. [99]). For this reason the field-independent basis set results of Table 3 will not be given a detailed discussion. However, certain features of these data need to be commented upon.

The first observation is that the shifted expansion leads to completely absurd values of correlation corrections to polarizability. The third-order correction

Table 3. Results of the fluoride ion polarizability calculations in three different field-independent GTO/CGTO bases (in a.u.)

	Basis A	Basis B	Basis C
α_{SCF}	3.25	4.65	6.05
Correlation corrections: model expansion			
α_2	+0.79	+2.91	+2.74
α_3(pp)	−0.29	−0.82	−0.78
α_3(hp)	+0.45	+1.04	+0.97
α_3(hh)	−0.47	−2.00	−1.94
α_3	−0.31	−1.78	−1.76
$\alpha_{corr}[3/0]$	0.48	1.13	0.98
$\alpha_{corr}[2/1]$	0.51	1.29	1.12
α_{corr}(var, $\gamma=1$)	0.31	0.43	0.24
α_{corr}(var, γ_{opt})	0.38	0.81	0.62
Correlation corrections: shifted expansion			
α_2	+47.24	+8.75	+12.19
α_3(pp)	+0.92	+1.34	+2.03
α_3(hp)	−115.83	−15.69	−23.98
α_3(hh)	+1.94	+0.14	+0.27
α_3	−103.97	−14.21	−21.68
$\alpha_{corr}[3/0]$	−56.73	−5.46	−9.49
$\alpha_{corr}[2/1]$	−19.73	−0.62	−2.19
α_{corr}(var, $\gamma=1$)	−65.37	−7.27	−12.03
α_{corr}(var, γ_{opt})	−21.75	−1.40	−3.14

turns out to be much larger than α_2 and this makes the use of the perturbation approach based on H_{shifted} rather questionable. Moreover, the sum of contributions through the third order, i.e. $\alpha_{\text{SCF}} + \alpha_{\text{corr}}$ [3/0], which should give an estimate of the total polarizability, is negative for all basis sets. This result rules out the use of the CHF-based MBPT scheme which employs the shifted zero-order Hamiltonian. This also indicates that a partial summation of certain diagrams via the denominator shifts may be a dangerous procedure, for it may not be properly balanced. Even worse performance of the shifted expansion is observed in the case of the EVF GTO calculations and for this reason the corresponding data will not be presented and discussed.

In contrast to the shifted expansion results, the data obtained for $H_{\text{model}}(F)$, though they suffer from the basis set incompleteness, appear to be reasonable. On comparing the correlation corrections calculated for bases B and C one can expect that their values will mostly depend on the quality of the wave function with regard to its ability to give a proper description of the electric field perturbation effects. Moreover, independently of the basis set choice, the correlation corrections and their components display a fairly regular behaviour. The second-order correction is dominant and positive, though the contribution of α_3 is not negligible as well. The estimates of the total correlation correction to the SCF polarizability are systematically positive. However, the corrections which are obtained from variational approximations for the field-dependent energy are much smaller than α_{corr} [3/0] and α_{corr} [2/1].

The calculations with EFV GTO bases which are reported in Table 4 are qualitatively similar to the data obtained for field-independent bases and the model expansion. For the SCF polarizability values calculated by using the λ-optimized EFV GTO basis sets [33], the results obtained for bases B and C are certainly close to the expected HF limit and seem to be even slightly better than Cohen's CHF value (10.53 a.u. [99]). It is appropriate to mention that recent calculations using a very large and properly selected GTO/CGTO set [100] have led to the CHF polarizability of 10.67 a.u..

On comparing the SCF data of Table 4 for different bases one can also observe the role played by the basis functions with relatively small values of orbital exponents. The importance of a proper description of the outer region of the electron density distribution in the context of the EFV GTO approach has already been indicated in previous calculations [56, 57, 101]. In the present case extending the set A by diffuse s and p functions is sufficient for the appropriate description of the electric field polarization effects within the EFV GTO approach at the SCF level. The correlation-oriented extension of the set B has only a little effect on α_{SCF}.

The correlation corrections given in Table 4 are much larger than those computed with field-independent bases. However, the contribution due to α_2 is again dominant. Different components of the third-order correction α_3 seem to be equally important for all three EFV GTO bases. Their sum results in a rather large negative value of the third-order correction, indicating that the correlation

Table 4. Results of the fluoride ion polarizability calculations in three different EFV GTO bases (in a.u.) [a]

	Basis A	Basis B	Basis C
α_{SCF}	9.23	10.57	10.62
Correlation contributions: model expansion			
α_2	+3.35	+6.27 [b]	+5.92
α_3(pp)	−1.10	−1.85	−1.78
α_3(hp)	+1.46	+2.31	+2.15
α_3(hh)	−1.94	−4.37	−4.35
α_3	−1.58	−3.91	−3.98
$\alpha_{corr}[3/0]$	1.77	2.36	1.94
$\alpha_{corr}[2/1]$	1.191	2.71	2.24
α_{corr}(var, $\gamma=1$)	1.07	0.86	0.30
α_{corr}(var, γ_{opt})	1.41	1.70	1.16

[a] All data correspond to the EFV GTO bases optimized with respect to the SCF polarizability value. The optimized scale factors $\hat{\lambda}$ taken from previous calculations [33].
[b] On repeating the calculations of the field-dependent EFV GTO second-order energy an error has been found for previously reported [33] value of α_2.

perturbation series for polarizabilities does not converge as rapidly as the corresponding series for the total energy. This implies that the higher-order correlation contributions to polarizabilities can be quite important [34].

As regards the quality of the calculated correlation corrections, the results obtained for the basis set C are supposedly the most accurate ones. This basis set gives presumably the best EFV GTO CHF value of the fluoride ion polarizability and at the same time leads to the best estimates of the total correlation energy. However, the set B does not seem to be much inferior in this respect.

On passing to the estimates of the total correlation correction to α_{SCF} one should take into account the previously mentioned slow convergence of the correlation perturbation series. The previous estimate [33] of the total polarizability obtained from the second-order correlation correction and the SCF (CHF) value,

$$\alpha \cong \alpha_{SCF} + \alpha_2, \tag{16}$$

may represent a fairly accurate approximation. The corresponding result for the basis set C amounts to 16.52 a.u. and is much larger than the uncorrelated value. The Taylor series and the [2/1] Padé approximant give the following estimates (basis C) of the total polarizability:

$$\alpha \cong \alpha[3/0] = \alpha_{SCF} + \alpha_{corr}[3/0] = 12.56 \text{ a.u.}, \tag{17}$$

and

$$\alpha \cong \alpha[2/1] = \alpha_{SCF} + \alpha_{corr}[2/1] = 12.86 \text{ a.u.}. \tag{18}$$

Rather low values of the total polarizability which follow from the variational estimates of the correlation correction indicate that there is a considerable contribution due to renormalization effects. Thus, the variation results calculated by using the limited configuration-interaction (CI) methods must be certainly corrected for the erroneous treatment of unlinked clusters [12, 102, 103, 104]. This is most probably the reason for substantially lower polarizability values obtained by Werner and Meyer [45] within the PNO-CI scheme in comparison with their CEPA results. The latter method is known to have a proper dependence on the number of particles [18, 105, 106]. In this context it is interesting to mention that the second-order correlation corrected polarizability values are very close to the CEPA values calculated for the same basis set [36]. Hence, one can expect that the final polarizability value should be closer to the estimate given by Eq. (16) than to the results of Eqs. (17) and (18). Nonetheless, the third-order diagrammatic MBPT calculations predict consistently a much higher value of α than that which follows from the CHF calculations.

In Table 5 the correlation corrections obtained by using the model expansion and both the field-independent and the EFV GTO bases are analysed in terms of the N-body interaction contributions. In all cases the qualitative structure of these data is very similar. Of note is a very large contribution of the three-body interaction component. Hence, the convergence of the polarizability expansion in terms of the number of interacting bodies is also expected to be rather slow.

Table 5. Components of correlation corrections to the polarizability of the fluoride ion arising from the N-body interaction terms in the correlation energy. Results of calculations with field-independent GTO/CGTO and EFV GTO bases. All data refer to the HF model Hamiltonian. All entries in a.u. [a]

	Basis A		Basis B		Basis C	
	GTO/CGTO	EFV GTO	GTO/CGTO	EFV GTO	GTO/CGTO	EFV GTO
Contribution from two-body terms in correlation energy						
α_2^2	+0.79	+3.35	+2.91	+6.27	+2.74	+5.92
α_2^2(pp)	−0.29	−1.10	−0.82	−1.85	−0.78	−1.78
α_3^2(hp)	+1.11	+4.08	+3.60	+7.73	+3.49	+7.63
α_3^2(hh)	−0.48	−1.90	−1.98	−4.28	−1.92	−4.27
Total	+1.13	+4.43	+3.71	+7.87	+3.53	+7.50
Contribution from three-body terms in correlation energy						
α_3^3(hp)	−0.66	−2.62	−2.56	−5.42	−2.52	−5.48
α_3^3(hh)	+0.03	+0.03	+0.04	+0.03	+0.03	+0.03
Total	−0.63	−2.60	−2.52	−5.39	−2.49	−5.45
Contribution from the four-body term in the correlation energy						
α_3^4(hh)	−0.03	−0.07	−0.06	−0.11	−0.06	−0.11

[a] Superscripts refer to the number of interacting bodies in the corresponding energy term; subscripts denote the order with respect to the correlation perturbation.

A number of different CHF calculations of the dipole polarizability of the fluoride ion has already been reported [33, 99, 100, 107, 108] and all these data have recently been reviewed by Coker [101, 110] in order to solve the disagreement between the empirical estimates and the available theoretical values. Calculations including the correlation effects are scarce. In 1963, Donath [111] has performed a sum-over-states calculation using the CI functions for excited states of appropriate symmetry. His final result amounts to 1.206 $Å^3 = 8.14$ a.u. and is lower than the expected HF limit. However, the quality of Donath's value is quite uncertain, for his correlation correction involves both the self-consistency and the true correlation contribution [21, 22]. Also the sum-over-states method may not be appropriate for computing the correlation corrections to polarizabilities as indicated by our MBPT data for the shifted expansion. It can be seen from the data of Table 3 that the correlation corrections which result from the shifted expansion are also negative.

Recently a series of similar perturbation calculations for the fluoride ion polarizability has been carried out by using large field-independent GTO/CGTO bases involving a number of *d* functions [100]. The corresponding results are very similar to the present ones and confirm our conclusions with regard to the accuracy of the correlation corrections reported in this paper. They also indicate a very high efficiency of the EFV GTO bases in both the SCF (CHF) and the finite-field MBPT calculations of polarizabilities.

5. Empirical and Theoretical Estimates of the Free Fluoride Ion Polarizability. Discussion and Conclusions

Most of the theoretical and computational aspects of the present polarizability calculations have already been discussed in previous sections. To summarize our conclusions we point out that the second-order correlation, Eq. (16), may be quite accurate [36]. On the other hand the estimate obtained by using the [2/1] Padé approximant to the field-dependent energy also deserves some attention, for it can be given a variational justification [70] in addition to its invariance properties.

However, according to recent perturbation calculations of molecular polarizabilities [36] one can expect that the true value of the fluoride ion polarizability should be higher than that given by Eq. (18). Hence, the theoretical estimates of α can be rather safely placed in the range between ca. 13 and 16 a.u..

The accurate value of the free fluoride ion polarizability, though it represents a measurable quantity, has not been yet determined. Some empirical estimates can be obtained indirectly from the polarizability data for ionic crystals [112–115] or from the solution polarizabilities of salts [114]. The corresponding methods and results have recently been reviewed and discussed by Coker [109, 110]. One of the best known and commonly accepted values of the empirical polarizability of the free fluoride ion is due to Fajans and his coworkers [116] and amounts to 0.95 $Å^3 = 6.4$ a.u.. This value follows from the study of molar refractions of

salts at infinite dilution and is quite unexpectedly lower than the accurate CHF result. In principle this discrepancy could have been attributed to the neglect of correlation effects in the CHF scheme [21, 38, 39]. However, the analysis of the pertinent data for the isoelectronic Ne atom shows that the correlation effects should rather increase the polarizability value [33].

Recently a new set of empirical free ion polarizabilities has been proposed by Coker [109, 110]. It follows from Coker's analysis of the solution data that the free fluoride ion polarizability should be at least as large as 1.4 Å = 9.45 a.u.. However, the polarizability value finally recommended by this author is 1.48 ± 0.08 $Å^3$ (ca. 10 a.u.) [109, 110], being still lower than the best CHF values (ca. 10.6 a.u.). Moreover, the present calculations clearly show that the correlation contribution to the fluoride ion polarizability must be large and positive, leading to a much larger final value of α. The third-order MBPT results confirm our previous conclusions [33] with regard to the estimate of the free fluoride ion polarizability.

The discrepancy between the best available empirical estimates [109, 110], and the correlation-corrected theoretical values has been discussed previously and interpreted in terms of the medium effects. It appears that the extrapolation procedures employed to obtain the free ion polarizabilities from the solution data can only lead to what has been termed the apparent free ion polarizability [33]. In other words, the empirical values which follow from the crystal or solution data must always account for some portion of the medium effect. This effect can be rationalized theoretically either in terms of the orbital contraction effects [117, 118] or by allowing for some transfer of the electronic charge between the negative ion and its environment [33]. Both these effects are known to reduce the effective values of polarizabilities of negative ions [113, 115, 117, 119].

It follows that in the case of negative ions the theoretical calculations including correlation effects represent currently the only reliable source of the free ion polarizabilities. It is worth while mentioning that a similar discrepancy between the empirical estimates and the theoretical data exists also for the chloride ion [33, 109, 110, 120]. Recent perturbation calculations [121] performed by using the third-order finite-field MBPT method and extended GTO/CGTO bases indicate that the correlation contribution to the CHF polarizability of the chloride ion is also large and positive. Hence, the empirical values of the free ion polarizabilities for negative ions need a careful reconsideration.

The present MBPT calculations are not conclusive with regard to the final accurate value of the fluoride ion polarizability. However, they are certainly accurate enough for the present discussion. They evidently indicate that the empirical values of the free ion polarizability commonly accepted for F^- are much too low [33, 109, 110, 114–116]. Obviously, to obtain accurate theoretical value of the fluoride ion polarizability it is necessary to include the higher-order correlation effects. They are, as shown by the data of Tables 3–5, by no means

negligible. The finite-field diagrammatic MBPT approach is certainly very useful and promising in this respect especially when used in conjunction with scaling and Padé approximant techniques and the use of the EFV GTO bases helps to overcome the problems arising from the restricted basis set approximation.

Acknowledgement. This work was supported in part by S.R.C. Research Grant GR/B/4738.6.

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Received April 1, 1981