Finite-Field Many-Body Perturbation Theory II. SD-MBPT Study of the Nuclear Charge Dependence of the Electron Correlation Contribution to the Dipole Polarizability of 10-Electron Atomic Systems

Geerd H. F. Diercksen

Max-Planck-Institut für Physik und Astrophysik, Institut für Astrophysik, Karl-Schwarzchild-Str. 1, D-8046 Garching bei München, Federal Republic of Germany

Andrzej J. Sadlej*

Chemical Center, Physical Chemistry 2, University of Lund, P.O.B. 740, S-22007 Lund 7, Sweden

The finite-field many-body perturbation theory limited to intermediate states involving single and double substitutions in the reference HF determinant is applied to the calculation of dipole polarizabilities of 10-electron atomic systems. The nuclear charge dependence of the convergence of the SD-MBPT series for correlation corrections to the dipole polarizability is investigated. It is concluded that the fourth-order SD-MBPT scheme is quite appropriate for neutral and positively charged species. For negatively charged systems the convergence of the SD-MBPT series becomes much poorer and including higher-order substitutions may be necessary. The role of the renormalization contributions to the SD-CI polarizability results is also considered. It follows that the corresponding data need to be corrected for the erratic treatment of unlinked clusters. The size inconsistency effects make quite important contributions to the SD-CI values of the correlation corrections to dipole polarizabilities.

Key words: Finite-field many-body perturbation theory – Dipole-polarizability – Nuclear charge dependence – 10-Electron atomic systems – F^- – Ne – Na^+.

* *Permanent address:* Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, PL-01-224 Warsaw 42, Poland

1. Introduction

The usefulness of the many-body perturbation theory (MBPT) methods [1] in calculations of atomic and molecular correlation energies is already well established [2, 3]. More recent studies [2, 4–9] show that MBPT techniques can also be made highly efficient in calculations of the electron correlation contribution to atomic and molecular properties. The analysis [10] of different formulations of the pertinent perturbation problem indicates several advantages of the MBPT scheme based on what is known as the coupled Hartree–Fock (CHF) [11, 12] solution for the externally perturbed system. The calculation of diagrammatic contributions [6, 10, 13] to the electron correlation corrections for atomic and molecular properties can be most easily accomplished by using the finite-field perturbation theory (FPT) [14]. Over the past few years the FPT MBPT method has been successfully employed to study the correlation contribution to electric properties of atoms and molecules [4–10, 15–23]. In most cases the correlation perturbation series converges relatively fast [6, 7, 10] and the fourth-order approach appears to provide sufficiently high accuracy of the calculated properties. It has also been found that limiting the intermediate states to those which arise from single (S) and double (D) substitutions in the reference HF determinant (SD-MBPT) [9] represents a convenient and fairly accurate approximation.

Some attention has recently been given to the accurate prediction of electric dipole polarizabilities of negative atomic ions [5, 21–24]. The main purpose of these studies is to estimate theoretically the so-called free negative ion polarizabilities whose direct experimental determination is hardly possible [25]. Their empirical estimates are affected by different assumptions concerning the effects of the surrounding [25, 26] in solutions and crystals. On the other hand, the corresponding theoretical data obtained so far are not conclusive as well. Obviously, they indicate the importance of the electron correlation contribution to the dipole polarizability of negative ions [5, 22–24]. However, in most cases the precise value of this contribution remains still uncertain [22, 24]. The only accurate data are available for two-electron isoelectronic systems [27] and the comparison of the correlation contribution to the dipole polarizability of Li^+, He, and H^- [5, 27] reveals that the CHF results for negative ions are rather doubtful. The same conclusion appears to apply also to halide ions [5, 21–24].

Accurate theoretical studies of electric properties of negative ions require a rather careful consideration of both the basis set choice and the convergence of the correlation perturbation series. The selected basis set must be appropriate for describing the diffuse character of the negative ion density distribution and its polarization due to the external electric field [5, 22, 24]. Simultaneously, within the algebraic approximation to the MBPT scheme [3] the same basis set must recover the most important correlation effects. The convergence of the correlation perturbation series for polarizabilities of negative ions appears to be much poorer [22, 24] than that for neutral species [6–9]. For this reason the study of the nuclear charge dependence of different correlation corrections within the isoelectronic series might be quite useful.

In the present paper we report the results of our SD-MBPT calculations of the electric dipole polarizability for the series of 10-electron atomic systems. This series includes Na^+, Ne, and F^- and some systems with non-integer nuclear charge and allows for a closer examination of the nuclear charge dependence of the CHF polarizabilities and the different correlation corrections. The main attention is given to the convergence of the correlation perturbation series and the usefulness of the low-order perturbation approaches. The theory underlying the present calculations is briefly surveyed in the next section and followed by some details of the numerical calculations reported in this paper. The results and their discussion are given in Section 4 and the main conclusions which follow from our study are presented.

2. Theory

The theory underlying the SD-MBPT approach for the calculation of correlation corrections to electric properties of many-electron systems has been given a detailed consideration in our previous paper [9] and only the basic definitions and formulae will be summarized here. Our notation closely follows that employed previously [9].

We consider a many-electron-system embedded in the external electric field whose strength is denoted by μ. We assume that an acceptable zero-order approximation is given by the HF model. The exact μ-dependent energy of the system, $E(\mu)$, can be expanded into the following correlation perturbation series [9, 10]:

$$E(\mu) = E_{HF}(\mu) + E_2(\mu) + E_3(\mu) + E_4(\mu) + \cdots, \tag{1}$$

where $E_{HF}(\mu)$ is the μ-dependent HF energy and $E_n(\mu)$, $n = 2, 3, 4, \ldots$, denote the n-th order μ-dependent correlation energies. What is called the k-th order property of the system related to the given external perturbation is represented by the quantity Q which is proportional to the k-th order perturbed energy [28]:

$$Q \sim E^{(k)} = \frac{1}{k!} \left(\frac{\partial^k E(\mu)}{\partial \mu^k} \right)_{\mu=0}. \tag{2}$$

According to this definition different approximations to $E(\mu)$ lead to the corresponding approximate values for the property Q. In what follows we shall use the same set of subscripts and superscripts for both E and Q, though as a matter of fact their explicit meaning may only be applicable to the energy expansion.

The diagrammatic MBPT approach to the evaluation of the correlation energy:

$$E_{corr}(\mu) = E_2(\mu) + E_3(\mu) + E_4(\mu) + \cdots, \tag{3}$$

is primarily based on the so-called linked cluster theorem [29]. According to this theorem the correlation perturbation series (3) is expressible solely in terms of linked [1] (conjoint [30]) diagrams. Disjoint diagrammatic contributions which may appear in intermediate energy expressions must be exactly cancelled out by other terms. This is so, provided the set of intermediate states is complete.

On restricting the intermediate states to some selected classes of substitutions in the reference HF determinant one can satisfy the linked cluster theorem only by neglecting all non-cancelled disjoint diagrams.

In the SD-MBPT scheme [2, 31–33] the intermediate states comprise all determinants that can be obtained by single and double substitutions in the reference HF function. Hence,

$$E_2(\mu) = E_2^{\text{SD-MBPT}}(\mu) = E_2^{D}(\mu), \tag{4a}$$

$$E_3(\mu) = E_3^{\text{SD-MBPT}}(\mu) = E_3^{D}(\mu), \tag{4b}$$

and

$$E_n(\mu) \simeq E_n^{\text{SD-MBPT}}(\mu) = E_{nd}^{\text{SD}}(\mu), \qquad n = 4, 5, 6, \ldots, \tag{4c}$$

where the superscripts S and D refer to the type of excitations involved in intermediate states and the subscript "d" distinguishes what is called the direct part of the nth order term [1, 9, 34]. In comparison with the ordinary Rayleigh–Schrödinger perturbation theory (RSPT) based on the same class of intermediate states (SD–RSPT) the SD-MBPT approach neglects all renormalization terms [31–34]. Nonetheless, the SD-MBPT scheme can be given a firm variational background [23, 35]. By including the renormalization terms $E_{nr}^{\text{SD}}(\mu)$ one obtains the subsequent approximations to the result of the configuration interaction scheme based on single and double excitations (SD–CI), i.e.,

$$E_n^{\text{SD-CI}}(\mu) = E_n^{\text{SD-RSPT}}(\mu) = E_n^{\text{SD-MBPT}}(\mu) + E_{nr}^{\text{SD}}(\mu), \qquad n = 4, 5, 6, \ldots. \tag{5}$$

However, the renormalization terms involve disjoint diagrams and result in the size-inconsistency of the SD-CI approach [2]. The size-inconsistent contribution to the property values can be quite important [36] and can be partly removed from the SD–CI results by using approximate corrections due to Davidson [37] and Siegbahn [38].

It is worth while to define several partial sum approximations to the total correlation energy. The nth order approximation to Eq. (3) obtained according to the method X will be

$$E_{corr}^{X}(\mu, n) = \sum_{i=2}^{n} E_i^{X}(\mu), \tag{6}$$

and similarly

$$Q_{\text{corr}}^{X}(n) = \sum_{i=2}^{n} Q_i^{X}, \tag{7}$$

where the separate terms in Eq. (7) are defined with the aid of Eq. (2). The SD-CI correlation energy and the corresponding property values are denoted by $E_{\text{corr}}^{\text{SD-CI}}(\mu)$ and $Q_{\text{corr}}^{\text{SD-CI}}$, respectively. On adding Davidson's energy correction, $E_D(\mu)$, one obtains [36, 37]:

$$E_{\text{corr}}^{\text{SD-CI/D}}(\mu) = E_{\text{corr}}^{\text{SD-CI}}(\mu) + E_D(\mu), \tag{8}$$

while the next term due to Siegbahn, $E_S(\mu)$, gives [36, 38]:

$$E_{corr}^{SD\text{-}CI/DS}(\mu) = E_{corr}^{SD\text{-}CI/D}(\mu) + E_S(\mu).\tag{9}$$

Analogous expressions are employed for the corresponding approximations to Q_{corr}.

The total energy and property values following from the partial summation of the correlation perturbation series will be denoted by similar symbols without the subscript "corr". The leading term in these expressions is the HF value. In the case of properties it corresponds to the result of what is known as the CHF approximation [6, 9, 10]. Hence, the correlation effects involved in Q_{corr} represent solely the "true" correlation contribution to a given property [10]. All self-consistency terms are accounted for in $Q_{HF} = Q_{CHF}$ [10, 12], and

$$Q = Q_{CHF} + Q_2 + Q_3 + \cdots.\tag{10}$$

Some advantages of this formulation of the correlation perturbation series for properties have already been discussed [10]. In comparison with the ordinary double perturbation treatment of correlation contributions to properties [39–41] the first non-vanishing correlation correction in the CHF-based perturbation schemes is of the second-order in the correlation perturbation [4–10, 13, 17, 18]. Hence, in the CHF-based approach the calculation of correlation contributions corresponds to the same level of accuracy as in the case of correlation corrections to the HF energy.

Usually the final result computed for E_{corr} (Q_{corr}) amounts to the knowledge of a few lowest-order terms in the perturbation expansion. The truncated correlation series can be approximately summed up by using different methods. In most cases improved results are obtained by applying the method of Padé approximants [42, 43]. Particular attention has been given to the [2/1] Padé approximant to the series (3):

$$E_{corr}(\mu, [2/1]) = [1 - E_3(\mu)/E_2(\mu)]^{-1}E_2(\mu).\tag{11}$$

This result is usually referred to as the geometric approximation to the correlation energy [44, 45] and has certain interesting invariance features [43, 46]. Moreover, Eq. (11) can be given a firm variational justification [23]. Its differentiation with respect to μ leads to $Q_{corr}([2/1])$. The latter result should be distinguished from that following from the direct application of the [2/1] Padé approximant to the property correlation series [15, 22, 23].

Interesting results can also be obtained [9, 21, 24] by using the invariant fourth-order quantity introduced recently by Wilson [46]:

$$E_{corr}(\mu, \tilde{4}) = E_{corr}(\mu, [2/1]) + [E_{corr}(\mu, [2/1])/E_2(\mu)]^3[E_4(\mu) - E_3^2(\mu)/E_2(\mu)],\tag{12}$$

where all terms are replaced by their SD-MBPT counterparts. The corresponding approximate value of Q_{corr} calculated according to Eq. (2) will be denoted by $Q_{corr}(\tilde{4})$. This completes the survey of basic formulae and definitions which are

referred to in subsequent sections of this paper. More details can be found in our previous papers [9, 10, 21, 24, 47, 48].

3. Computational Details

In order to study the nuclear charge dependence of correlation corrections to the CHF polarizability of 10-electron systems the calculations have been carried out for several different values of the nuclear charge Z. In addition to the study of F^- ($Z = 9$), Ne ($Z = 10$), and Na^+($Z = 11$) we have also performed the corresponding calculations for $Z = 9.2$, 9.4, 9.6, and 9.8. A rather dense grid of points in the range between $Z = 9.0$ and $Z = 10.0$ allows for a careful examination of the pertinent Z-dependence in this region. However, all calculations must be performed in such a way that the accuracy of the polarizability data obtained in the FPT SD-MBPT approach is practically independent of the value of Z. This brings about the problem of the appropriate choice of both the basis set functions and the field strength μ which is employed to obtain the field-dependent energies.

3.1. Basis Sets

Since all calculations reported in this paper are carried out within what is known as the algebraic approximation scheme [3, 49], the appropriate choice of the basis set functions is of particular importance. The basic quantity which is computed within the FPT method is the field-dependent correlation energy. Hence, the selected basis set must recover a considerable portion of the total atomic correlation energy. Additional requirements concerning the basis set functions follow from the fact that the main object of this paper is the calculation of correlation corrections to polarizabilities. Hence, the basis sets employed for this purpose must be flexible enough to represent properly the electron density polarization due to the external electric field.

Several different strategies have been proposed over the past few years as regards the basis set choice for the calculation of atomic and molecular polarizabilities including the correlation effects [50–56]. According to these proposals one can either use a large basis set with several diffuse and polarisation functions [50, 51, 53, 54] or one can employ more standard bases of moderate size which explicitly depend on the external field strength [52, 55, 56]. The latter choice has already been shown to be very efficient in calculations of correlation corrections to the dipole polarizability of the fluoride ion [5, 22, 23]. However, the corresponding computations require a little more effort concerned with the optimization of what is called to orbital origin shift parameter [52, 57]. Hence, in some cases it is more convenient to use large field-independent bases.

All calculations reported in this paper have been carried out by using uncontracted GTO basis sets comprising 13 s-type functions, 9 p-type functions and 5 d-type functions. For all values of Z the corresponding GTO exponents have been derived from the GTO exponents of the (11.7) GTO basis sets of Huzinaga

[58]. The latter are available only for neutral atoms. The first step in attempting to produce the basis sets which may provide a fairly uniform accuracy for all values of Z considered in this paper was to obtain the initial (11.7) sets for non-integer nuclear charges. This has been done by using a parabolic approximation formula based on the energy optimized exponents for O, F, and Ne. The corresponding parameters derived from Huzinaga's Tables [58] are given in Table 1.

The final (13.9.5) GTO basis sets have been derived from the (11.7) GTO bases by using method similar to that employed by Werner and Meyer [50, 51]. Two diffuse s-type GTO's have been added to the s subset; the corresponding orbital exponents, $\zeta(s_{12})$ and $\zeta(s_{13})$, being equal to $1/2.5$ and $1/2.5^2$ of the lowest s-type GTO exponent ($\zeta(s_{11})$) of the initial basis set, respectively. The p subset has also been augmented with two additional p-type GTO's, whose exponents $\zeta(p_8)$ and $\zeta(p_9)$ are derived in the same way from the lowest orbital exponent $\zeta(p_7)$ of the initial subset of p-type GTO's, i.e. $\zeta(p_8) = \zeta(p_7)/2.5$, $\zeta(p_9) = \zeta(p_8)/2.5$. The (13.9) GTO bases devised according to the above scheme have been supplemented with 5 d-type GTO's, whose orbital exponents $\zeta(d_1), \ldots, \zeta(d_5)$ are obtained from the second lowest orbital exponent ($\zeta(p_8)$) in the corresponding

Table 1. Parameters of the parabolic fit $\zeta(Z) = \zeta_0 + \zeta_1(Z-9) + \zeta_2(Z-9)^2$ used to determine the GTO exponents ζ for different values of the nuclear charge Z[a]

GTO	ζ_0	ζ_1	ζ_2
s-type GTOs			
1	37736.00	9174.852	2103.355
2	5867.0791	1399.9229	106.0452
3	1332.4679	311.81665	8.90115
4	369.44060	87.53996	4.00410
5	116.84300	27.677051	1.203629
6	40.348770	9.574576	0.445384
7	14.966270	3.598339	0.239835
8	5.8759295	1.43368915	0.15051915
9	1.6533352	0.41362395	0.03146035
10	0.61083583	0.156342185	0.017646525
11	0.23328922	0.057854195	0.003530315
p-type GTOs			
1	102.26192	25.6735985	2.1146215
2	23.938381	6.0832385	0.5541185
3	7.5205914	1.9492871	0.1817792
4	2.7724566	0.72478335	0.06303815
5	1.1000514	0.288275615	0.025345085
6	0.44677512	0.116764075	0.009065255
7	0.17187009	0.041701040	0.002094050

[a] The parameters correspond to the GTO exponents of the (11.7) basis set. For the determination of additional s- and p-type GTO exponents as well as for the d-type GTO exponents of the (13.9.5) basis set see text

subset of p-type GTO's: $\zeta(d_1) = 32\zeta(p_8)$, $\zeta(d_2) = 9\zeta(p_8)$, $\zeta(d_3) = 3\zeta(p_8)$, $\zeta(d_4) = \zeta(p_8)$, and $\zeta(d_5) = \zeta(p_8)/3$. The scheme used to derive the GTO exponents for the d subset follows that of Werner and Meyer [50, 51].

Adding several diffuse s and p functions to the initial (sp) set allows for a reliable description of the outer region of the electron density distribution. This is of particular importance in the case of the fluoride ion. The use of diffuse functions for the Na^+ ion is definitely less important. The d-type orbital exponents are selected according to both the correlation energy and polarizability criteria [50, 51] and the corresponding functions are presumably of similar importance for all 10-electron systems considered in this paper. A useful check on the quality of basis sets derived for the present study can be obtained by computing the CHF polarizabilities for F^-, Ne, and Na^+. For all these systems accurate near-HF data are available. According to the results presented in the next section our (13.9.5) GTO basis sets give the electric dipole polarizability values very close to the corresponding most accurate CHF results. At the same time they recover a considerable portion of the total correlation energy.

Let us also mention that different studies for similar systems [59, 60] indicate that including the f-type GTO's in the basis set has only little effect on the calculated polarizability values. Thus, the present (spd) bases are expected to provide a high accuracy for correlation corrections to the CHF polarizabilities.

3.2. FPT *Calculations of Dipole Polarizabilities*

The method of computing the dipole polarizabilities according to the FPT scheme has already been described in our previous papers [9, 21, 24, 36, 47] and follows the methods employed by the other authors [14, 61]. In principle all polarizability data are obtained as the second-order numerical derivatives of the field-dependent energy. In the case of the SCF HF results the corresponding numerical CHF polarizability values can be checked against those obtained as the first-order derivatives of the induced dipole moment. However, this procedure is not applicable in the case of the SD-CI data [20] since limited CI wave functions do not satisfy the Hellmann–Feynman theorem [62]. Moreover, computing the polarizability as the field-dependent energy derivative appears to be the only feasible way for the CHF-based MBPT scheme and similar perturbation approaches [8, 10, 17, 18].

The numerical differentiation of field-dependent energies brings about the problem of contamination of the calculated polarizability values by the hyperpolarizability terms. However, according to the present experience in most cases this contamination does not seriously affect the calculated polarizabilities provided the values of the external field strength are carefully selected. All results reported in this paper have been obtained by using the parabolic fit to the field-dependent energies $E(\mu)$ with the value of μ adapted to the nuclear charge of the given system.

It follows from our previous calculations for the fluoride ion [5, 22–24] that the contamination by the hyperpolarizability contribution is relatively small if the parabolic fit for $E(\mu)$ is obtained with $\mu = 0.005$ a.u. The dipole polarizability of the fluoride ion calculated in this way has an accuracy better than 2×10^{-2} a.u. For systems with higher values of Z the dipole polarizability is obviously much smaller than that for F^-. Hence, to achieve the same absolute accuracy of the numerical differentiation one has to use higher values of the external electric field strength. By comparing the known CHF polarizabilities of F^-, Ne, and Na^+ one can guess the appropriate value of μ for each system studied in this paper. According to this comparison the following form of the Z-dependence of μ has been assumed:

$$\mu(Z) = 0.005 + 0.005(Z-9) \text{ a.u.} \tag{13}$$

in the range $9.0 \le Z \le 10.0$, while for Na^+ $\mu = 0.020$ a.u. has been used.

In order to determine the appropriateness of the above field strength values the CHF dipole polarizabilities have been calculated as the energy derivatives and as the dipole moment derivatives. The corresponding results are shown in Table 2. In the same table our CHF results are compared with other accurate CHF data for F^-, Ne and Na^+. A very good agreement of our CHF values with the most accurate CHF polarizabilities obtained by using different methods shows also the appropriateness of the present basis sets.

Finally, let us mention that all calculations reported in this paper have been carried out by using a combination of the MUNICH Molecular Program System [63] and the direct CI program of Roos [64, 65]. Some additional details concerning the numerical calculations can be found in Refs. [8, 9] and [22–24].

4. Results and Discussion

4.1. Correlation Energies

Since the present report is mainly concerned with the nuclear charge dependence of dipole polarizabilities we avoid a more extensive presentation and discussion of the correlation energy data. Our correlation energy results are summarized in Table 3. Additionally, to give some idea concerning the quality of basis sets employed in this study also the corresponding SCF energies are reported. They are fairly close to the appropriate HF limits [71].

As regards the correlation energy values calculated in this paper our E_2^D results for F^-, Ne, and Na^+ can be directly compared with recent accurate data by Jankowski et al. [69, 70]. For all these systems more than 75 per cent of the accurate value of E_2^D is recovered by the present truncated GTO basis set calculations. Since the second-order correlation energies for 10-electron atomic systems seem to be rather close to the corresponding total correlation energies similar conclusion holds also for E_{corr}[69, 70]. The latter can be considered as approximately given by $E_{corr}^{SD-MBPT}(4)$. Of note is the closeness of $E_{corr}^{SD-MBPT}(4)$ to the invariant fourth-order result $E_{corr}^{SD-MBPT}(\tilde{4})$ obtained according to Wilson's

Table 2. Accuracy of FPT SCF (CHF) calculations of the dipole polarizability of 10-electron systems. All entries in atomic units

$Z =$	9.0	9.2	9.4	9.6	9.8	10.0	11.0
This work							
External field strength μ	0.005	0.006	0.007	0.008	0.009	0.010	0.020
Polarizability[a] I	10.68	7.16	5.14	3.86	2.99	2.375	0.945
II	10.70	7.17	5.14	3.86	2.99	2.374	0.945
Reference CHF results	9.45[b] [66]	—	—	—	—	2.366 [67]	0.942 [66]
	10.53 [67]					2.368 [51]	0.942 [67]
	10.62 [5, 22]					2.377 [68]	
	10.67 [24]						

[a] The first entry (I) in each column corresponds to the numerical second-order derivative of the field dependent energy obtained from the parabolic fit for $E_{SCF}(\mu)$ with the value of μ as given above. The second entry (II) is the induced dipole moment derivative obtained with the linear dependence on the field strength

[b] As discussed elsewhere this value is most probably too low [5, 24, 66]

Table 3. Nuclear charge dependence of correlation energies for 10-electron atomic systems. All energies in atomic units[a]

$Z =$	9.0	9.2	9.4	9.6	9.8	10.0	11.0
$E_{SCF(HF)}$	-99.457889	-104.950243	-110.605568	-116.423364	-122.403261	-128.544977	-161.674285
Correlation energy contributions							
E_2^D [b]	-0.320639	-0.313620	-0.308171	-0.303784	-0.300157	-0.297097	-0.304800
E_3^D	0.012542	0.008268	0.005335	0.003224	0.001653	0.000458	0.001955
E_{4d}^{SD}	-0.012240	-0.008964	-0.006952	-0.005606	-0.004652	-0.003945	-0.002196
E_{4r}^D	0.020436	0.017089	0.014668	0.012823	0.011364	0.010180	0.007056
Estimates of the total correlation energy							
$E_{corr}^{SD-MBPT(2)}$	-0.320639	-0.313620	-0.308171	-0.303784	-0.300157	-0.297097	-0.304800
$E_{corr}^{SD-MBPT(3)}$	-0.308097	-0.305353	-0.302836	-0.300560	-0.298504	-0.296639	-0.306755
$E_{corr}^{SD-MBPT(4)}$	-0.320337	-0.314316	-0.309788	-0.306166	-0.303156	-0.300584	-0.308952
$E_{corr}([2/1])$	-0.308569	-0.305565	-0.302927	-0.300594	-0.298513	-0.296639	-0.306768
$E_{corr}^{SD-MBPT(\tilde{4})}$	-0.319041	-0.313654	-0.309442	-0.305992	-0.303080	-0.300566	-0.308994
$E_{corr}^{SD-CI(4)}$	-0.299901	-0.297227	-0.295120	-0.292344	-0.291792	-0.290404	-0.301896
E_{corr}^{SD-CI}	-0.301533	-0.298704	-0.296356	-0.294353	-0.292608	-0.291061	-0.302176
$E_{corr}^{SD-CI/D}$	-0.317753	-0.312932	-0.309001	-0.305710	-0.302895	-0.300444	-0.308959
$E_{corr}^{SD-CI/DS}$	-0.319586	-0.314251	-0.309994	-0.306484	-0.303513	-0.300948	-0.309201

[a] For the explanation of symbols see text. All energies correspond to the external field strength $\mu = 0.0$ a.u.

[b] Accurate second-order correlation energies [69, 70] for F^- ($Z=9$), Ne($Z=10$), and Na$^+$($Z=11$) are -0.4004 a.u., -0.3879 a.u., and -0.3843 a.u., respectively

formula [46]. On the other hand the geometric approximation does not seem to be highly efficient.

Both fourth-order estimates of the total correlation energy given in Table 3 are also fairly close to the cluster-corrected SD-CI correlation energies $E_{corr}^{SD\text{-}CI/DS}$ [36–38, 72]. This indicates that the higher-order many-body effects make relatively small contributions to the total correlation energy.

The correlation energy results can be conveniently analysed in terms of the pair contributions. Similarly to the analysis carried out for F^- [24] comparing the present data for F^-, Ne, and Na^+ with those of Jankowski et al. [69, 70] shows that the missing portion of the second-order correlation energy is mostly due to the inadequate description of the inner shells. For the p-shell our second-order correlation results are fairly close to the corresponding spd limits [69, 70]. Improving the total correlation energy by some improvement in the description of inner shells should not produce any significant changes in the calculated polarizability values. The major factor which determines the accuracy of the final polarizability results is the basis set flexibility rather than its high efficiency in reproducing accurate correlation energy values [22, 23, 50, 51, 73, 74].

4.2. Dipole Polarizabilities of 10-Electron Atomic Systems

Correlation corrections to the CHF polarizability of 10-electron atomic systems calculated according to the method described in Section 3.2 are collected in Table 4. In the same table different approximations for the total correlation

Table 4. Nuclear charge dependence of different correlation contributions to the dipole polarizability[a] of 10-electron atomic systems. All polarizability data in a.u.

$Z =$	9.0	9.2	9.4	9.6	9.8	10.0	11.0
Q_2^D	6.32	2.80	1.50	0.88	0.52	0.33	0.056
Q_3^D	−4.19	−1.54	−0.70	−0.36	−0.19	−0.11	−0.013
Q_{4d}^{SD}	5.08	1.56	0.61	0.28	0.14	0.07	0.006
Q_{4r}^D	−2.43	−0.88	−0.41	−0.21	−0.11	−0.06	−0.007

Estimates of the total correlation contribution

$Q_{corr}^{SD\text{-}MBPT}(2)$	6.32	2.80	1.50	0.88	0.52	0.33	0.056
$Q_{corr}^{SD\text{-}MBPT}(3)$	2.14	1.26	0.80	0.52	0.33	0.22	0.044
$Q_{corr}^{SD\text{-}MBPT}(4)$	7.21	2.82	1.41	0.80	0.47	0.29	0.049
$Q_{corr}[2/1])$	2.44	1.34	0.82	0.53	0.33	0.22	0.043
$Q_{corr}^{SD\text{-}MBPT}(\tilde{4})$	6.31	2.59	1.34	0.78	0.45	0.29	0.049
$Q_{corr}^{SD\text{-}CI}(4)$	4.80	1.93	1.00	0.59	0.36	0.23	0.042
$Q_{corr}^{SD\text{-}CI}$	3.38	1.63	0.93	0.57	0.35	0.23	0.043
$Q_{corr}^{SD\text{-}CI/D}$	4.94	2.32	1.34	0.83	0.44	0.28	0.049
$Q_{corr}^{SD\text{-}CI/DS}$	5.78	2.59	1.45	0.87	0.46	0.29	0.050

[a] All contributions to the dipole polarizability (Q) are calculated according to Eq. (2), i.e. as the second-order numerical derivatives of the field-dependent energy. For the explanation of symbols see Section 2

Table 5. Estimates of the total dipole polarizability of 10-electron atomic systems.[a] Comparison with other theoretical and experimental data. All polarizability values in a.u.

Z =	9.0	9.2	9.4	9.6	9.8	10.0	11.0
This work							
$Q^{SD\text{-}MBPT}(2)$	17.00	9.96	6.64	4.74	3.51	2.71	1.001
$Q^{SD\text{-}MBPT}(3)$	12.82	8.42	5.94	4.38	3.32	2.60	0.989
$Q^{SD\text{-}MBPT}(4)$	17.89	9.98	6.55	4.66	3.46	2.67	0.994
$Q([2/1])$	13.12	8.50	5.96	4.39	3.32	2.60	0.988
$Q^{SD\text{-}MBPT}(\tilde{4})$	16.99	9.75	6.48	4.64	3.44	2.67	0.994
$Q^{SD\text{-}CI}$	14.06	8.79	6.07	4.43	3.34	2.61	0.988
$Q^{SD\text{-}CI/DS}$	16.46	9.75	6.59	4.73	3.45	2.67	0.995
Reference theoretical values[b]							
Q	$12.5 \div 16.5$ [5, 22]	—	—	—	—	2.603 [75]	—
	$14.5 \div 16.9$ [24]					2.672 [76]	
	12.99 [7]					2.676 [51]	
Experimental values and empirical estimates							
Q	$5.1 \div 12.3^{c}$	—	—	—	—	2.663 [78]	1.1 [79]
						2.669 [80]	0.995 [81]
						2.6724 [82]	$1.1 \div 1.3^{d}$

[a] All polarizability values calculated in the present paper correspond to the numerical second-order derivatives of the field-dependent energy. For the explanation of symbols see Section 2

[b] Only those theoretical results which include the correlation effects are considered.

[c] A compilation of different empirical estimates of the free fluoride ion polarizability can be found in Ref. [24]. See also Refs. [25] and [26].

[d] Empirical estimates taken from Ref. [26]

correction to the dipole polarizability are also presented. Various estimates of the total polarizability obtained by combining the CHF data of Table 2 and the correlation corrections of Table 4 are presented in Table 5. In order to facilitate the analysis of the nuclear charge dependence of these results some of them have been plotted against Z in Fig. 1.

In Table 5 our estimates of the total dipole polarizability of F^-, Ne and Na^+ are compared with available theoretical data and with experimental values. Among the theoretical reference results only those which have been obtained at the correlated level are considered [5, 22, 24, 51, 75–77]. As a matter of fact the theoretical data for the F^- polarizability represent the ranges for its expected value. The corresponding data for Ne seem to be far more accurate and certain. Similar comments can be made as regards the experimental polarizability values. The dipole polarizability of Ne is known with a rather high accuracy [78, 80, 82]. For F^- and Na^+ the commonly accepted values are the empirical estimates obtained either from the solution data or from the study of ionic crystals [25, 26]. As discussed previously [5, 22–24] they seem to be much too low in the case of the fluoride ion and presumably too high in the case of Na^+. Hence, on discussing both the convergence and the accuracy of our MBPT calculations one should primarily refer to the data for Ne.
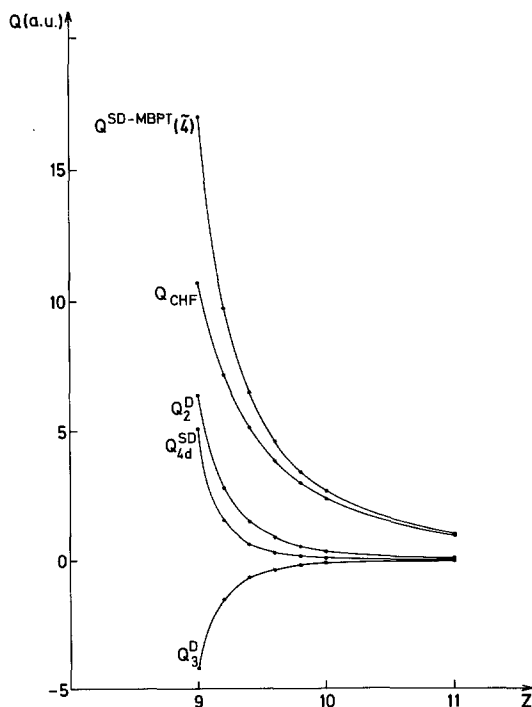

Fig. 1. Nuclear charge (Z) dependence of different estimates of the dipole polarizability of 10-electron atomic systems and the Z-dependence of SD-MBPT correlation corrections to the CHF polarizability.

It follows from the final polarizability results presented in Table 5 that the fourth-order SD-MBPT scheme is capable of predicting the right polarizability value of Ne. The results obtained from the ordinary Taylor series and the formula of Wilson [46] are practically the same and almost coincide with the corresponding experimental data. On the other hand the SD-CI scheme gives a too low value of the Ne atom polarizability. On inspecting the data of Table 4 one finds that this is mostly caused by the size-inconsistency of the SD-CI approach. The contribution of the fourth-order renormalization term is quite significant. Correcting the SD-CI result according to Davidson and Siegbahn [36–38] brings about nearly complete agreement with the experimental result. Let us also note that for Ne the convergence of the SD-MBPT series is quite good. The direct fifth-order contribution Q_{5d}^{SD} would lower the present fourth-order results by about 0.01 a.u.

The fourth-order SD-MBPT approach appears to be also very accurate in the case of Na^+. The convergence of the SD-MBPT series is in this case even better than that for the Ne atom. Moreover, the direct fifth-order SD-MBPT correction to the dipole polarizability tensor becomes negligibly small. Hence, the fourth-order results $Q^{SD-MBPT}(4)$ and $\tilde{Q}^{SD-MBPT}(4)$ possess sufficient accuracy. Obviously, these results do not account for the contribution of triple and quadruple excitations. However, at least the latter do not seem to be highly important for dipole polarizabilities of neutral species and positively charged ions [6, 7]. According to our previous results [8, 9, 18] it can be expected that a considerable portion of the contribution due to quadrupole excitations is cancelled out by the conjoint part of the renormalization term [30, 34].

On passing to smaller values of the nuclear charge all SD-MBPT contributions to the correlation correction to the dipole polarizability significantly increase and the convergence of the SD-MBPT series becomes much poorer than for Ne and Na^+. Also the absolute value of the fourth-order renormalization contribution becomes more important than for neutral and positively charged systems. Therefore, the SD-CI corrections to dipole polarizabilities of negatively charged species need to be corrected for the erratic treatment of unliked clusters [36–38]. For the fluoride ion the corresponding corrections due to Davidson [35] and Siegbahn [36] result in a considerable modification of the SD-CI result. Finally, the truncated Taylor series $Q_{corr}^{SD-MBPT}(4)$, the formula of Wilson and the cluster corrected SD-CI approach give fairly similar values for the total correlation contribution to the dipole polarizability of F^-.

Using the invariant formula of Wilson [46] can be interpreted as performing some approximate summation of the higher-order SD-MBPT contributions. On the other hand the cluster corrected quantity $Q_{corr}^{SD-CI/DS}$ should not be significantly affected by the contribution of the higher-order renormalization terms. Since both these estimates of Q_{corr} are relatively close, one can expect that the total SD-MBPT correction should be in the range between $Q_{corr}^{SD-MBPT}(4)$ and $Q_{corr}^{SD-CI/DS}$. This is obviously the correct result in the case of Ne and Na^+ but the accuracy of this estimate may become poorer for lower values of Z.

One of the characteristic features of the SD-MBPT corrections to the dipole polarizability is that there is a near-cancellation of the third- and fourth-order contributions. This observation gives some support to the validity of the second-order corrected results [8, 9, 19] though the SD-MBPT correlation perturbation series for polarizabilities may not have an alternating character in some other cases [47]. Nonetheless, the second-order correlation correction can provide a reasonable and useful information about Q_{corr}. On the other hand, the near-cancellation of Q_3^D and Q_{4d}^{SD} requires the consideration of other terms involved in Q_4 as well as a more careful study of the higher-order contributions. In the case of the fluoride ion the contribution due to strongly coupled quadruple excitations amounts to -2.15 a.u. and its addition results in lowering the estimate of Q_{corr} to about 3.6 a.u. and about 4.2 a.u. for the cluster corrected DS-CI approach and the fourth-order SD-MBPT results following from Wilson's formula, respectively. Also the fifth-order direct SD-MBPT correction to the dipole polarizability of F^- is quite significant and amounts to -2.97 a.u. However, because of the alternating character of the SD-MBPT series for Q_{corr}, the effects due to Q_{5d}^{SD} will be considerably cancelled in higher orders. Hence, the estimates based on either $Q_{\mathrm{corr}}^{SD\text{-}CI/DS}$ or $Q_{\mathrm{corr}}^{SD\text{-}MBPT}(\tilde{4})$ and the approximate value of the contribution due to quadruple excitations appear to be quite appropriate. When added to the CHF value of Table 2 they lead finally to the dipole polarizability of the fluoride ion in the range between 14.3 a.u. and 14.9 a.u. The correctness of the latter estimates of the free fluoride ion polarizability is confirmed by the results of recent FPT complete active space (CAS) SCF [83–85] calculations for the same system [65].

On using the same approximations for Ne one obtains a polarizability value of about 2.6 a.u. The addition of the contribution due to quadruple excitations spoils the spectacular agreement with the experimental value observed for our fourth-order SD-MBPT data. However, some worsening of the final result in a more appropriate approach appears to be quite understandable. One should remember that all calculations are carried out within the truncated basis set approximation. Also the higher-order many-body effects, though presumably rather small for neutral systems of the size of the Ne atom, can be of some importance. Hence, it is rather surprising to shoot right at the experimental polarizability value [51, 76] in spite of a number of different approximations. On the other hand, estimating the dipole polarizability of Ne at 2.6 a.u. results in less than 3 per cent error in comparison with the experimental value. It appears that a better accuracy of theoretical calculations of the dipole polarizability is hardly possible at the moment.

The study of the Z-dependence of the electron correlation contribution to the dipole polarizability of simple atomic systems reveals several important features of the SD-MBPT series and indicates the differences and similarities among the correlation corrections for neutral and charged species. Our recent studies on the applicability of the SD-MBPT method to the calculation of correlated dipole polarizabilities show the usefulness of the fourth-order scheme in the case of neutral atoms and molecules [9, 18]. However, treating the negatively charged

systems is far more difficult; particular care has to be taken of both the appropriate choice of the basis set functions and the convergence of the MBPT series. Accurate calculations for negative ions may also require the explicit consideration of the effect of higher then double substitutions.

It also follows from the present data that the renormalization terms which are included in the SD-Cl approach need to be taken into account when calculating the correlation corrections to electric properties of many-electron systems. The unwanted contribution due to unlinked clusters is automatically accounted for within the SD-MBPT scheme, while the SD-CI results can be corrected a posteriori [36] by using the correction schemes due to Davidson [37] and Siegbahn [38]. It is important to stress that for all isoelectronic systems studied in this paper the contribution of Q_{4r}^D is negative and artificially lowers the final Q_{corr}^{SD-CI} values for the dipole polarizability. This is also the reason that the SD-CI polarizability of F^- calculated recently by Botschwina [77] is much lower than the present estimates.

The nuclear charge dependence of correlation corrections to the dipole polarizability of isoelectronic species reveals the importance of the appropriate treatment of the pertinent correlation effects for negatively charged systems. The total correlation correction to the CHF polarizability of the fluoride ion is certainly dominated by the lower-order terms in the SD-MBPT series. However, to obtain the accurate result one has to consider all different contributions, including those due to higher than double excitations. The final result follows to some extent from near-cancellations of different contributions. This is far less important in the case of neutral and positively charged species. For these systems the ordinary SD-MBPT scheme gives quite acceptable results and can be safely used for predicting the unknown polarizability data.

The implications of the present study for the estimation of the true value of the fluoride ion dipole polarizability follow from the plots presented in Fig. 1. It can be seen that a small amount of the charge transfer between the ion and its surrounding may considerably reduce the apparent polarizability value. The corresponding increase in the dipole polarizability of positive ions is much smaller. Hence, on analysing the solution data [25, 26] in terms of polarizabilities of separate ions one can rather safely assume that the positive ion polarizability in solution is fairly close to that of the corresponding isolated system. Moreover, the present study confirms our previous [5, 22–24] conclusions concerning the correct value of the dipole polarizability of F^-. Taking into account the SD-MBPT results and the effect of higher excitations as well as some, presumably positive, contribution due to the conjoint part of the renormalization corrections one can estimate the dipole polarizability of the free fluoride ion at about $14.0 \div 16.0$ a.u.

Finally, let us mention some implications of the present study for the calculation of intermolecular interaction potentials. It seems that fairly reasonable data can be achieved from the SD-CI calculations in the case of neutral or positively charged subsystems. On the contrary, the corresponding calculations for systems

involving negatively charged species can be seriously affected by the size-incon-sistency of the SD-CI scheme. This is particularly important for theoretical predictions for weakly interacting subsystems.

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