

Dipole and quadrupole polarizabilities of spherical anions: F^- , Si^- , and Cl^-

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The static dipole and quadrupole polarizabilities of F^- , Si^- , and Cl^- are calculated using many-body perturbation theory and coupled-cluster methods. The results for the dipole polarizabilities, obtained using the double substitution coupled-cluster (CCD) plus single and triple CCD [CCD+ST(CCD)] scheme, the highest level of approximation, are 15.5, 145.4, and 36.4 a.u. for F^- , Si^- , and Cl^- , respectively. For the quadrupole polarizabilities, we obtained 1.98×10^2 , 2.48×10^3 , and 3.92×10^2 a.u., respectively. [S1050-2947(96)00709-3]

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Polarizabilities are very important for the understanding of a great variety of physical phenomena and therefore reliable values of these properties are highly desirable. Some problems where polarizabilities play an important role have been listed in previous articles [1]. In spite of the many applications, due to experimental difficulties, there is a great lack of measurements of dipole and quadrupole polarizabilities of the negative ions. The presence of an external electric field can disturb appreciably the electron density of these systems, making difficult both experimental measurements and theoretical calculations. In the absence of experimental results accurate theoretical estimates become even more important.

Recent calculations [1–5] have shown that in order to obtain reliable results, high-order electron correlation contributions have to be taken into account. This is not an easy task as the correlation contributions to electric properties are usually difficult to obtain and constitute the most time-consuming part of the calculation. Many-body perturbation theory (MBPT) and the coupled-cluster method (CC) are widely used with this purpose [1–5]. These methods add in different ways, high-order contributions to the electron correlation [6,7] allowing, when used simultaneously, interesting comparisons between them. The purpose of this work is to report on calculations for the dipole and quadrupole polarizabilities for these ions using MBPT and CC methods. All calculations were performed using the GAUSSIAN 92 program [8].

It has been already stressed [9] that even sophisticated electron correlation calculations, including high-order terms, are not capable of compensating for the basis sets deficiencies. Electrical properties are particularly sensitive [1–5] to the selection of the basis set and a bad choice can hopelessly jeopardize the results of a calculation. To guarantee the reliability of our results we initially focused our attention on the basis sets, carefully selecting the exponents until saturation was attained. As the self-consistent field (SCF) results are usually poor for electrical properties [1–5] we performed our test calculations at the second-order many-body perturbation theory [MBPT(2)] level. As the substrate basis sets we took ($9s5p/3s2p$) for F^- and ($11s7p/6s4p$) for Si^- and Cl^- contractions of Dunning and Hay [10]. In addition, these basis sets were augmented with some selected diffuse and polarization functions to ensure a proper description of the

system in the presence of an external electric field. These extra exponents are displayed in Table I.

When submitted to an external potential, the energy of a spherical atomic system is, according to McLean and Yoshimine [11], modified by

$$\Delta \varepsilon = -\frac{1}{2}\alpha[(\phi^x)^2 + (\phi^y)^2 + (\phi^z)^2] - \frac{1}{4}C[(\phi^{xx})^2 + (\phi^{yy})^2 + (\phi^{zz})^2 + 2\phi^{xy}\phi^{xy} + 2\phi^{xz}\phi^{xz} + 2\phi^{yz}\phi^{yz}] - \dots,$$

where ϕ is the external potential, ϕ^x is the x component of the electric field, and ϕ^{xy} is the second derivative of the potential with respect to x and y , with similar interpretations for the other components; α and C are the dipole and quadrupole polarizabilities, respectively. Since the systems treated here are spherical, it is convenient to use an electric field with axial symmetry, i.e., $\phi^x = \phi^y = 0$ and $\phi^z = E$. To satisfy Laplace's equation it is not possible to make $\phi^{xx} = \phi^{yy} = 0$ and, at the same time, $\phi^{zz} \neq 0$, so we took

TABLE I. Extra exponents for polarizability calculations of spherical anions.

Function type	F^-	Si^-	Cl^-
s	0.1211, 0.0404	0.0331, 0.0110, 0.0037	0.0628, 0.0209,
p	0.0911, 0.0304	0.0322, 0.0107, 0.0036, 0.0012	0.0613, 0.0204,
d	54.15, 10.05, 3.350, 1.117, 0.3722, 0.1241, 0.0137	148.9, 39.63, 13.21, 4.475, 1.744, 0.4668, 0.1556, 0.0519, 0.0173	23.05, 7.600, 2.566, 0.8166, 0.2722, 0.0907, 0.0302
f	3.667, 1.222, 0.4073, 0.1378, 0.0453, 0.0050	34.98, 11.66, 3.888, 1.296, 0.4620, 0.1440	43.44, 14.48, 4.827, 1.222, 0.4073, 0.0136, 0.0045

$\phi^{zz} = -2\phi^{xx} = -2\phi^{yy} = G$ and all other components to be zero. With this simplification the above expression is reduced to

$$\Delta\varepsilon = -\frac{1}{2}\alpha E^2 - \frac{3}{8}CG^2 - \dots$$

According to the finite field method [2,12], the computation of the energy in the presence of an electric field E and an electric field gradient G provides the necessary information to calculate the dipole and quadrupole polarizabilities. This approach is a very convenient one because it allows the evaluation of different properties using standard programs for energy calculations, without violating the Hellmann-Feynman theorem [13]. In this work we used an electric field of 0.001 a.u. for all systems, while the values for the electric field gradient were, respectively, 0.0004, 0.0002, and 0.0008 a.u. for F^- , Si^- , and Cl^- . These values were chosen as a compromise between not disturbing appreciably the electron density and, at the same time, ensuring the expected numerical accuracy.

For the systems treated here, F^- is the only one for which we have found other results including electron correlation. Table II displays our results for the dipole and quadrupole polarizabilities of F^- together with the results of previous papers. In our calculations we adopted the frozen-core approximation since MBPT calculations performed until fourth order have shown that core contributions to the electron correlation do not affect the properties calculated here. It is worthwhile noticing that these previous results, obtained by different authors, although close to each other, show discrepancies among them at all levels of calculations, leaving opened the question of the correct values of these properties. This is probably due to deficiencies of the basis sets used, which were not saturated for calculations of polarizabilities. Our results show that the improvement of the basis set by the inclusion of additional polarization functions, especially f type, changes appreciably the correlated results for the dipole polarizability. For the quadrupole polarizability the differences become dramatically more relevant, as shown by the SCF results of Table II and other values quoted by Das *et al.* [22]. This disagreement makes evident the care to be taken in

TABLE II. Calculated dipole and quadrupole polarizabilities of the F^- anion in a.u.

Method	α		C	
	This paper	Other work	This paper	Others work ^a
SCF	10.86	10.63 ^b , 10.67 ^c , 10.67 ^d , 10.62 ^e , 10.49 ^f , 10.40 ⁱ	109.3	93.8 ^e , 66.5 ^g , 67.7 ^h , 67.3 ⁱ
MBPT(2)	15.74	16.89 ^c , 16.81 ^d , 15.32 ^f	208.3	
MBPT(3)	12.26	12.79 ^c , 12.74 ^d , 12.59 ^f	135.3	
DQ-MBPT(4)	13.44	14.22 ^d	161.2	
SDQ-MBPT(4)	16.28	17.47 ^d	224.8	
MBPT(4)	19.14	20.83 ^d , 17.82 ^f	281.2	
CCD	13.18		154.8	
CCD+S(CCD)	14.32		177.8	
CCD+ST(CCD)	15.48		198.3	
CCSD		15.63 ^d		
CCSD+T		16.91 ^f , 18.84 ⁱ , 18.99 ^d		144.2 ⁱ
MCPF		17.58 ^b		

^aIn this work we followed McLean and Yoshimine's convention for quadrupole polarizability and so our values for C are four times the values quoted in Refs. [21,17].

^bReference [14].

^cReference [15].

^dReference [16].

^eReference [17].

^fReference [18].

^gReference [19].

^hReference [20].

ⁱReference [21].

choosing the basis sets, since a poor representation of diffuse and polarization functions may lead to nonrealistic predictions of electrical properties.

Our results for F^- , Si^- , and Cl^- are in Table III, together with previous results for C^- [5,23]. In these calculations we used extensive basis sets, augmenting well-established basis sets by judicious inclusion of diffuse and

TABLE III. Calculated dipole and quadrupole polarizabilities of the C^- , F^- , Si^- , and Cl^- anions in a.u.

Method	α				C			
	C^- ^a	F^-	Si^-	Cl^-	C^- ^b	F^-	Si^-	Cl^-
					(units of 10^3)	(units of 10^2)	(units of 10^3)	(units of 10^2)
SCF	14.5	10.9	136.3	31.5	1.04	1.09	2.28	3.12
MBPT(2)	21.3	15.7	141.8	36.7	1.62	2.08	2.48	4.12
MBPT(3)	17.3	12.3	142.3	35.0	1.57	1.35	2.43	3.67
DQ-MBPT(4)	17.7	13.4	141.5	34.5	1.52	1.61	2.40	3.58
SDQ-MBPT(4)	20.8	16.3	142.3	35.1	1.64	2.25	2.42	3.71
MBPT(4)	24.6	19.1	144.9	37.1	1.86	2.81	2.48	4.08
CCD	17.9	13.2	141.0	34.7	1.52	1.55	2.38	3.62
CCD+S(CCD)	19.2	14.3	142.0	35.1	1.63	1.78	2.40	3.71
CCD+ST(CCD)	21.0	15.5	145.4	36.4	1.76	1.98	2.48	3.92

^aReference [5].

^bReference [23].

polarization functions, until the calculated values of the polarizabilities remained stable. This procedure gives us enough confidence in the quality of the results reported here. For the dipole polarizability of Cl^- , our SCF result (31.5 a.u.) is in excellent agreement with the coupled Hartree-Fock result (31.6 a.u.) of McEachran *et al.* [24] and the time-dependent coupled Hartree-Fock result (31.0 a.u.) of Das *et al.* [25]. For Si^- the dipole polarizability calculated by Das *et al.* [25] (129.9 a.u.) is also in good agreement with our result (136.3 a.u.). Concerning the quadrupole polarizability, for Si^- we have not found other results in the literature, while for Cl^- the results of 281 and 265 a.u. obtained, respectively, by Schmidt *et al.* [26] and by Sen and Annapoorna [27], approaches our result of 312 a.u. reasonably well. An overall view of Table III, however, shows how important are the correlation contributions to the calculated polarizabilities, especially in the case of F^- and C^- , for which the values are dramatically modified. Another interesting conclusion may also be drawn from the fact that systems with similar shell structure present correlation contributions of approximately the same magnitude, although the absolute values of the calculated polarizabilities are much larger for the second row system. Comparing the SCF results with those at the highest level of approximation, double substitution coupled-cluster (CCD) plus single and triple CCD [CCD+ST(CCD)], we can see, for instance, that correlation contribution for dipole polarizability of F^- and Cl^- are, respectively, 4.6 and 4.9 a.u., while the correlated absolute values are 15.5 and 36.4 a.u. For the quadrupole polarizability the correlation contributions for these systems are 89 and 80 a.u. while the correlated absolute values are 198 and 392 a.u. The same pattern is observed for the dipole polarizability of C^- and Si^- . The correlation contributions are 6.5 and 9.1 a.u., while the correlated absolute values are 21.0 and 145.4 a.u., respectively, for C^- and Si^- . The quadrupole polarizability of Si^- is approximately 40% greater than that of C^- , even though the correlation contribution is larger for C^- . This trend suggests that the correlation contribution to the calculation of electrical properties is less important for

systems with larger number of electrons, giving some hope that accurate estimates of these properties may be obtained at the SCF level for more complex systems.

The double and quadruple substitutions fourth-order many-body perturbation theory [DQ-MBPT(4)] and double substitution coupled-cluster (CCD) results for both polarizabilities of all systems are very close, indicating a small contribution of terms arising from double substitutions beyond fourth order. Another comparison shows that the full MBPT(4) and CCD+ST(CCD) results are also very similar for Si^- and Cl^- . For the F^- the relative differences amount to 23% and 42%, respectively, for the dipole and quadrupole polarizabilities. Regarding C^- , these differences are 15% and 5%. For these systems we believe that the coupled-cluster results constitute a better approximation since this scheme includes important contributions of higher-order double substitutions. Also there is evidence [7] that CCD+ST(CCD) treats the single and triple substitution contributions more appropriately than MBPT(4), leading to results in closer agreement with experiment. For F^- in particular, Raghavachari [28] has suggested that the electron affinity is overestimated by MBPT(4).

For the electrical properties treated here we have only found experimental results for the dipole polarizability of F^- and Cl^- , obtained by Bauer and Fanjas [29]. However, these measurements do not have the desired accuracy to allow a fair comparison with our results. Also, as it has been mentioned before, these systems are very sensitive to the presence of an electric field, making them very difficult to be studied experimentally. In this context, theoretical results play an even more important role as they become practically the only source of information concerning the polarizabilities of the negative ions studied here. Despite the lack of experimental results for comparison, we may invoke the quality of our results supported by the use of extensive basis sets carefully selected, the utilization of sophisticated methods to get the electron correlation, and the systematic convergence of the values displayed in Table III.

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