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Static dipole polarizabilities of open-shell negative ions

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Summary. Dipole polarizability estimates at $\lambda \Rightarrow \infty$ have been calculated for the $2p$ and $3p$ open-shell negative ions in their ground and valence excited states. To complete the sequence such estimates for F^- and Cl^- in their ground ^1S state have also been made. Single configuration based linear response theory has been adopted presently with a view to study the effect of RPA-type correlations on the polarizabilities of such systems. For the $3p$ open-shell systems the innermost $1s$ core has been kept frozen. Most of the results are reported for the first time. Agreement with existing data, wherever available, is reasonable. The convergence of the polarizability estimates towards basis sets has been studied.

Key words: Static polarizabilities – Negative ions – Open shell systems

1 Introduction

Dipole polarizability estimates of the negative ions of many electron systems are relatively few, although that of closed-shell alkali negative ions are found to be very useful in a diverse field of work [1–6]. The applications of dipole polarizability values to various physical phenomena have been described beautifully by Miller and Bederson [7]. The negative ion polarizability values have their possible applications in very low energy electron scattering or in studying the potential energy curves of weekly bound molecules containing such atoms, particularly at large internuclear distances. Despite their applications the experimental determination of static polarizability of free negative ions is rather difficult and their investigation is mostly confined to crystalline field environments [8–10]. Experimentally the dipole polarizability of F^- and Cl^- was determined by Fajans and Bauer [11] in aqueous solution, which was little underestimated. A number of empirical and semiempirical results exist for such ions [3, 12, 13]. But these results are not very reliable because of their underlying assumptions. The electronic charge cloud of free negative ions is very diffuse and as such correlation effects play a significant role in such systems. These are reflected in different types of calculations from uncoupled Hartree–Fock to higher order MBPT and coupled cluster calculations for F^- [14–21] predicting a range of about 1.2 Å^3 to 20 Å^3. For Cl^- the data are limited but quite diverse [7, 18, 21–23]. Explicit effect of correlation in F^- and alkali negative ions has been incorporated in the MBPT calculation of Diercksen and Sadlej [19], Kutzner et al. [23], CI calculation of Canuto et al. [24], Pouchan and Bishop [25], multiconfiguration linear response calculation of Agren et al. [26], coupled cluster-based MBPT calculation of Kucharski et al. [21]. These methods are very accurate but confined only to closed-shell negative ions so far. As far as the authors' knowledge goes no calculation at any level has been performed for $2p$ and $3p$ open-shell negative ions for which the effect of correlation has yet to be understood.

Coupled Hartree–Fock (CHF) method has been applied in the past for the calculation of polarizability of closed-shell negative ions [17, 22, 27]. Here a part of electron correlation (RPA type) is incorporated through effective summation of hole particle correlation diagrams up to infinite order [28, 29]. Time dependent coupled Hartree–Fock (TDCHF) (single configuration based linear response) theory yields the correct static limit of dipole polarizability values of coupled Hartree–Fock scheme. In recent years this theory has been applied successfully for open-shell systems [30–33]. In the present communication we applied the same theory to calculate the static limit of dipole polarizability for $2p$ and $3p$ open-shell negative ions in their ground and valence excited states and performed a detailed study of basis dependence of polarizability for such systems. To complete the sequence F^- and Cl^- are also included. For these systems data exist for comparison. The theory was detailed earlier [32, 33]. Results are discussed in the next section.

2 Results

The static limit of the dipole polarizability value $(\alpha_d(\omega)_{\omega \to 0})$ of $2p$ open-shell ions B^-, C^-, N^-, O^- and of the $3p$ open-shell ions Al^-, Si^-, P^-, S^- in their ground and valence excited states and the closed-shell ions F^- and Cl^- in ^1S state have been calculated. The ground-state wavefunction is the single configuration *HF* function of Clementi and Roetti [34]. Calculations have been omitted for the valence excited ^1S state of B^- and Al^- for which the single configuration *HF* orbital energy for the outermost orbital ($2p$ in the case of B^- and $3p$ in the case of Al^-) is reported positive [34]. A multiconfiguration approach is necessary to have any reasonable estimate of polarizability for such systems. The radial part of the first-order perturbed admixtures, which are of s and d symmetry are chosen as linear combinations of Slater type orbitals (STO's):

$$\delta\psi_i^{\pm} = \sum_q C_{iq}^{\pm} r^{n_{iq}} e^{-\varrho_{iq} \cdot r} \tag{1}$$

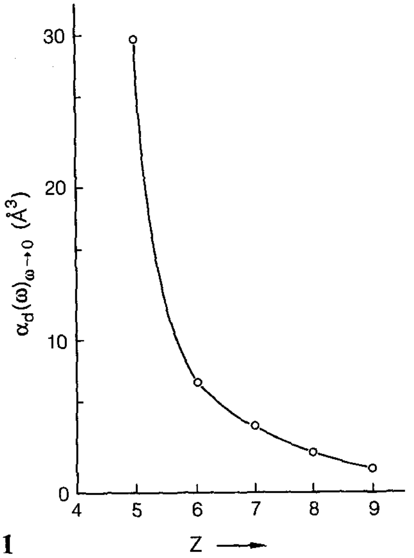
where C_{iq}'s are linear variation parameters and n_{iq}'s and ϱ_{iq}'s are preassigned. The terms have been clearly explained earlier [30]. The choice of n_{iq} depends upon the symmetry and principal quantum number of the orbital $\delta\psi_i$. The starting value depends on the angular symmetry and the range depends on the number of nodes. In most cases an allowance for the effect of higher-order configurations is given. The choice of the exponents ϱ_{iq} is, however, more difficult and its maximum and minimum value depends on the short- and long-range behaviour of the orbital. To this end the unperturbed optimized exponents of Clementi and Roetti [34] along with experience set a guideline. Once the maximum and minimum values of the exponent are set, the intermediate ones

Table 1. Static polarizabilities of negative ions in Å^3

Ion		Static polarizability Present calculation* A	 B	 C	Other values
B^-	^3P	28.16	29.85	29.85	
	^1D	57.66	76.28	76.49	
C^-	^4S	7.12	7.15	7.15	
	^2D	10.66	10.93	10.93	
	^2P	14.69	15.64	15.66	
N^-	^3P	4.36	4.41	4.41	
	^1D	5.12	5.23	5.23	
	^1S	6.66	7.04	7.04	
O^-	^2P	2.58	2.60	2.60	
F^-	^1S	1.41	1.55	1.56	1.89[a], 0.759[b], 0.76[c], 0.95[d], 1.90[e], 1.21[f], 1.56[g], 1.58[h,i,j,k] 1.05[l], 2.66–2.96[m] 2.24[i], *1.56*[n], *1.83*[n], 1.48[o]
Al^-	^3P	79.54	80.33	80.39	
	^1D	151.88	169.40	169.60	
Si^-	^4S	19.18	19.23	19.24	
	^2D	27.32	27.81	27.81	
	^2P	35.39	36.91	36.92	
P^-	^3P	11.67	11.73	11.73	
	^1D	13.24	13.36	13.36	
	^1S	15.96	16.28	16.29	
S^-	^2P	7.06	7.11	7.11	
Cl^-	^1S	4.55	4.59	4.59	4.11[o], 4.37[p], 4.68[k], 4.41[n], 4.03[q], 3.69[l], 2.974[b]

* A 8 parameter calculation
B 12 parameter calculation
C 15 parameter calculation
[a] Langhoff and Hurst (1965)
[b] Winslow (1975)
[c] Tessman et al. (1953)
[d] Bauer and Fajans (1942)
[e] Sadlej (1983)
[f] Donath WE (1979) J Chem Phys 83:1653
[g] Cohen (1966)
[h] Schmidt et al. (1980)
[i] Diercksen and Sadlej (1982)
[j] Maroulis and Bishop (1986a)
[k] McEachran et al. (1979)
[l] Brumer and Karplus (1973)
[m] Kucharski et al. (1984)
[n] Wilson and Curtis (1970)
[o] Coker (1976)
[p] Kutzner et al. (1988)
[q] Stewart (1975)

can be assigned. However, given a sufficiently flexible basis set, the choice of largest and smallest exponents are relatively flexible. The linear variation coefficients change in such a way as to maintain identical results within our accuracy limit. Since the negative ions are highly polarizable we have tested the convergence of the static limit by varying the basis sets. For each ion the number of coefficients is chosen as eight, twelve and fifteen successively and the results for each ion in their ground and valence excited states have been displayed in Table 1. For comparison results of previous calculations have also been listed in Table 1. The convergence of the polarizability values with increase in the number of Slater parameters is clearly observed. It is clear that a fifteen parameter calculation yields consistent results for all the ions for the states under study. To observe the regularity we plot in Figs. 1 and 2 the polarizability values against



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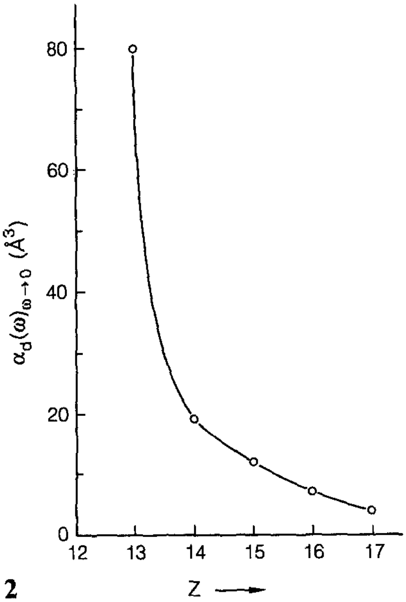

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Fig. 1. Plot of the polarizability value, $\alpha_d(\omega)_{\omega \to 0}$, versus nuclear charge Z for the $2p$ open-shell ions in their ground state

Fig. 2. Plot of the polarizability value, $\alpha_d(\omega)_{\omega \to 0}$, versus nuclear charge Z for the $3p$ open-shell ions in their ground state

atomic number for the $2p$ and $3p$ open-shell ions respectively, in their ground state. As is observed the behaviour is extremely regular showing the consistency of the values obtained in our calculation.

For F^- our result 1.56 Å^3 compares well with the CHF result 1.58 Å^3 of McEachran et al. [17] and 1.56 Å^3 of Cohen [15]. The experimental results 0.76 Å^3 of Tessman et al. [12] and 0.95 Å^3 of Bauer and Fajans [11] and the empirical evaluation 1.48 Å^3 by Coker [13], however, underestimated the polarizability values. The finite field MBPT result of Wilson and Sadlej [36] and also of Sadlej [20] gives 1.91 Å^3, whereas the SD-MBPT result of Diercksen and Sadlej [19] is 2.24 Å^3. Kucharski et al. [21] estimated the value to be within 2.66 Å^3 to 2.96 Å^3 using MBPT with coupled cluster expansion. It appears that the correlation effect increases substantially the polarizability value for F^-. The MBPT results have the feature that sometimes higher order contributions give larger correction than the lower ones. A large CI calculation in this regard is needed for correlation convergence. For Cl^- our result 4.59 Å^3 is in good agreement with the CHF result 4.68 Å^3 of McEachran et al. [17] and empirical result of 4.41 Å^3 of Wilson and Curtis [3]. The MBPT result 4.37 Å^3 of Kutzner et al. [23] shows that for Cl^- there is a decrease of polarizability value due to the effect of correlation. Our main aim is to calculate the polarizability for the open-shell negative ions for which as far as we know no other results exist and as such the values could not be compared but the consistency is clearly observed from Figs. 1 and 2. Our partially correlated results may serve as future reference for these systems, in which a complete CI calculation can establish the true nature of correlations.

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