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Static polarizabilities and shielding factors of the magnesium isoelectronic sequence

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The static dipole quadrupole polarizabilities and shielding factors of Mg, Al^+, Si^{2+}, P^{3+}, S^{4+}, Cl^{5+}, and Ar^{6+} have been calculated using the variation perturbation technique in a coupled Hartree-Fock scheme. For the dipolar calculation the two innermost cores have been kept frozen, whereas for the quadrupolar calculation all the cores have been relaxed. The results compare favorably with the existing values. For the quadrupolar shielding factor in all cases an antishielding effect is noted. Systematic behavior is observed for the isoelectronic polarizability values.

I. INTRODUCTION

In recent years much interest has been given to evaluating the linear response properties of atoms towards external fields.[1-7] In this communication we present the results of our calculation on static dipole and quadrupole polarizabilities (α_d, α_q) and shielding factors (β_∞, γ_∞) of a few ions of magnesium isoelectronic sequence in their ground states. A variational formulation in coupled Hartree-Fock (CHF) scheme has been adopted here.

Much work in this line has been done using uncoupled and coupled HF schemes for both closed- and open-shell atoms.[5,7-11] Thomas-Fermi statistical model has been applied by Witschel and Haars[12] to evaluate the dipole and quadrupole polarizabilities of a large number of atoms; however, their results seem to deviate often appreciably from those of CHF calculations.

In this paper we have adopted our previous method[7,13] for evaluating the static dipole and quadrupole polarizabilities. A closed-shell reduction for the formulas[7,13] has been done for the present case. This is just to ensure the validity of the open-shell deduction which should reduce to those of closed-shell systems under special cases.

In the present case, polarizabilities have been evaluated from induced moment rather than from the second-order change in energy of the system to obtain better numerical accuracy. For the dipole polarizability calculation, the innermost 1s, 2s cores have been kept frozen. The reason for this is explained in Sec. III. For the quadrupole polarizability calculation, all the orbitals have been relaxed and full coupling has been taken care of. The present theory ignores the relativistic and other finer interactions. Core rearrangement effects have also been neglected. However, it includes an appreciable amount of correlation. This is apparent from a detailed diagrammatic analysis performed by Caves and Karplus.[14] Here it was shown that the CHF theory includes an infinite term summation over all the bubble-type correlation diagrams together with their exchanges in the residual interactions to all orders. Actually these are the same correlations which occur in the perturbation expansion of the particle-hole propagator in the random-phase approximation (RPA).[15,16] In Sec. II the theory is discussed briefly and Sec. III deals with the numerical results and discussions.

II. THEORY

We consider a functional of the form

$$J=\langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle-\langle\Psi|H_0|\Psi\rangle , \tag{1}$$

where Φ represents the total wave function of the system described by the Hamiltonian $H=H_0+H'$, H_0 and H' being, respectively, the unperturbed and perturbing Hamiltonian. Ψ represents the normalized unperturbed wave function; i.e.,

$$\langle\Psi|\Psi\rangle=1 , \tag{2}$$

In (a.u.) the usual form of H_0 for atoms is

$$H_0=\sum_i\left(-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}=\sum_i t_i+\sum_{i<j}g_{ij} . \tag{3}$$

Here we have for dipolar perturbation

$$H'=-F\sum_i r_i P_1(\cos\theta_i)=\sum_i h_i' , \tag{4}$$

and for quadrupolar perturbation

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$$H' = \frac{F'}{2} \sum_i r_i^2 P_2(\cos\theta_i) = \sum_i h_i' ,$$
$$P_2(\cos\theta_i) = (3\cos^2\theta_i - 1) . \tag{5}$$

F and F' represent the applied field and field gradient, respectively.

Here Ψ is a single determinant formed out of orbitals $\{\psi\}$ and Φ has a similar structure involving perturbed orbitals $\{\phi\}$.

The orbitals satisfy the usual orthonormality constraints

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} ,$$
$$\langle \phi_i | \phi_j \rangle = \delta_{ij} . \tag{6}$$

We choose the perturbed orbital ϕ as

$$\phi_i = (\psi_i + \delta\psi_i)/(1 + \langle \delta\psi_i | \delta\psi_i \rangle)^{1/2} , \tag{7}$$

where $\delta\psi_i$ is a first-order correction to ψ_i due to the external perturbation. It satisfies the constraints

$$\langle \psi_i | \delta\psi_i \rangle = 0 , \quad \forall i \tag{8}$$

$$\langle \psi_i | \delta\psi_j \rangle + \langle \delta\psi_i | \psi_j \rangle = 0 , \quad \forall \text{ pairs } i, j . \tag{9}$$

Using (7)–(9), we expand Eq. (1) and retain terms up to second order in $\delta\psi$. This will give us a series of terms linear and quadratic in $\delta\psi$'s the general form of which is shown below:

$$J = \sum_k [W(k,k) + W(k,\delta k) + W(\delta k, k) + I(\delta k, \delta k) - \epsilon_k S(\delta k, \delta k)] + \sum_{k,l} [A(\delta k, k | \delta l, l) + A(\delta k, k | l, \delta l) + A(\delta k, \delta k | l, l)] . \tag{10}$$

The notation used here is as follows:

$$W(k, \delta k) = \langle \psi_k | h' | \delta\psi_k \rangle ,$$
$$T(\delta k, \delta k) = \langle \delta\psi_k | t | \delta\psi_k \rangle ,$$
$$S'(\delta k, \delta k) = \langle \delta\psi_k | \delta\psi_k \rangle , \tag{11}$$
$$A(\delta k, k | \delta l, l) = \langle \delta\psi_k^{(1)} \delta\psi_l^{(2)} | g_{12}(1 - P_{12}) | \psi_k^{(1)} \psi_l^{(2)} \rangle .$$

The summation in (10) has been performed over all the spin orbitals k. ϵ_k is the kth orbital energy and P_{12} is the usual permutation operator. The radial part of the perturbed orbital $\delta\psi_k$ is chosen as

$$\delta\psi_k = \sum_q C_{kq} r^{n_{kq}} \exp(-\rho_{kq} r) ; \tag{12}$$

the angular parts have been fixed by the nature of perturbation and the orbital on which it acts. The spin will remain unchanged since we are considering a spin-independent perturbation. In Eq. (12), C_{kq}'s are the variation parameters. Suitable values of n_{kq} and ρ_{kq} are preassigned. The functional J now reduces to terms quadratic and linear in C_{kq}'s. We now impose the variational condition

$$\frac{\partial J}{\partial \mathfrak{C}} = 0 . \tag{13}$$

This will reduce the problem to solving a set of simultaneous linear equations of the form

$$\mathfrak{X}\mathfrak{C} = \Lambda , \tag{14}$$

which readily yield C_{kq}'s, hence the $\delta\psi_k$'s.

The polarizability and shielding factor values are evaluated following standard definitions:

$$\alpha_d = \frac{2}{F} \sum_k \langle \delta\psi_k | r P_1(\cos\theta) | \psi_k \rangle , \tag{15}$$

$$\beta_\infty = \frac{2}{F} \sum_k \langle \delta\psi_k | \frac{P_1(\cos\theta)}{r^2} | \psi_k \rangle , \tag{16}$$

$$\alpha_q = \frac{4}{F'} \sum_k \langle \delta\psi_k | r^2 P_2(\cos\theta) | \psi_k \rangle , \tag{17}$$

$$\gamma_\infty = \frac{4}{F'} \sum_k \langle \delta\psi_k | \frac{P_2(\cos\theta)}{r^3} | \psi_k \rangle , \tag{18}$$

where (α_d, α_q) and $(\beta_\infty, \gamma_\infty)$ are, respectively, the dipole and quadrupole polarizabilities and the corresponding shielding factors.

The polarizability values here have been evaluated from induced moments. This can also be obtained from the second-order change in energy of the system in the presence of applied fields. However, we observe that the functional J [Eq. (10)] apart from the term involving $\sum_k W(k,k)$ which gives the permanent moment of the system, gives the second-order change in energy of the system in the presence of applied fields. In expanded form it involves a number of terms which may be of a similar order of magnitude. Hence, a direct calculation of the change in energy might involve the loss of numerical accuracy. A better result is expected if the simultaneous linear equations involving the variation parameters are solved [Eq. (14)] properly to yield the perturbed orbitals which may be used in Eqs. (15)–(18) to get the relevant quantities.

III. RESULTS AND DISCUSSIONS

The static dipole and quadrupole polarizabilities (α_d, α_q) and the corresponding shielding factors $(\beta_\infty, \gamma_\infty)$ have been calculated for Mg, Al^+, Si^{2+}, P^{3+}, S^{4+}, Cl^{5+}, and Ar^{6+} ions in their ground ^1S states. In Table I we display the results of the dipole polarizability and shielding factor calculation whereas Table II contains the results for the quadrupole calculation.

The unperturbed orbital basis set is that of

TABLE I. Dipole polarizability (α_d) and shielding factor (β_∞) for magnesium isoelectronic sequence.

		α_d (Å^3)			β_∞	
Ion	State	Present calculation	Other values	Present calculation	Other values	Theoretical values
Mg	^1S	11.97	12.04,[a] 7.8,[b] 10.5,[c] 19.4,[d] 7.0 ± 1.8,[e] 7.4 ± 1.8,[f] 11.1 ± 0.5[g] 6.97 to 9.32[h]	1.69	1.002,[a] 5.6[d]	1
Al^+	^1S	3.96	5.89[d] 4.02[i]	1.48	4.44[d]	$\frac{12}{13}$
Si^{2+}	^1S	1.88	2.57[d] 1.67[i]	1.31	3.76[d]	$\frac{12}{14}$
P^{3+}	^1S	1.07	1.35[d] 0.85[i]	1.18	3.28[d]	$\frac{12}{15}$
S^{4+}	^1S	0.67	0.79[d] 0.49[i]	1.08	2.93[d]	$\frac{12}{16}$
Cl^{5+}	^1S	0.45	0.50[d]	1.00	2.65[d]	$\frac{12}{17}$
Ar^{6+}	^1S	0.32		0.93		$\frac{12}{18}$

[a] Reference 10.
[b] Reference 12.
[c] Reference 20.
[d] Reference 2.
[e] Reference 18.
[f] Reference 19.
[g] Reference 21.
[h] Reference 23.
[i] Reference 24.

Clementi[17] whereas for the perturbed orbitals we took an eight-parameter representation of Slater-type orbitals. The exponents shown in Tables III and IV are chosen in such a way that they may represent the perturbed polarization orbitals in an adequate manner. In the case of dipole polarizability calculation the innermost cores 1*s* and 2*s* have been kept frozen. The motivation for this is to reduce the computer time without affecting the α_d values to an appreciable extent. An analysis shown earlier[13] indicates that our approximation is quite justified for α_d calculation. However, this affects the β_∞ values which should be N/Z theoretically[1] where N is the number of electrons and Z is the nuclear charge of the system. Since β_∞ depends upon the matrix element of $1/r^2$, it depends on the relaxation of the core orbitals. This discrepancy has also been observed earlier[13] but there it is less affected because of the presence of one more shell in the system. A plot of α_d against Z in Fig. 1 shows a very systematic behavior. For Mg we obtain $\alpha_d = 11.97$ Å^3 as compared with 19.4 Å^3 obtained by Langhoff and Hurst[2] using the uncoupled Hartree-Fock (UHF) approxi-

TABLE II. Quadrupolar polarizability (α_q) and quadrupolar shielding factor (γ_∞) for magnesium isoelectronic sequence.

		α_q (Å^5)		γ_∞	
Ion	Configuration	Present calculation	Other values	Present calculation	Other values
Mg	^1S	36.64	34.0,[a] 23.1,[b] 40.36[c]	−1.69	−1.78[c]
Al^+	^1S	5.69	6.21[c]	−1.09	−1.27[c]
Si^{2+}	^1S	1.56	1.66[c]	−0.92	−0.90[c]
P^{3+}	^1S	0.58	0.60[c]	−0.84	−0.65[c]
S^{4+}	^1S	0.26	0.26[c]	−0.74	−0.48[c]
Cl^{5+}	^1S	0.13	0.13[c]	−0.66	−0.36[c]
Ar^{6+}	^1S	0.07		−0.59	

[a] Reference 12.
[b] Reference 20.
[c] Reference 2.

TABLE III. Exponents of Slater basis for the perturbed orbitals (dipolar case).

		$s \to p$		$p \to s$		$p \to d$	
Ion	State	n	ρ	n	ρ	n	ρ
Mg	^1S	1	6.0	0	14.0	2	5.5
		1	4.0	0	8.0	2	3.0
		2	4.0	1	8.0	3	3.0
		2	2.5	1	4.5	2	2.0
		3	2.5	2	4.5	3	2.0
		2	1.4	2	2.6	2	1.2
		3	1.4	3	2.6	3	1.2
		4	0.8	3	1.3	4	0.7
Al^+	^1S	1	6.6	0	14.6	2	6.0
		1	4.6	0	8.4	2	3.4
		2	4.6	1	8.4	3	3.4
		2	3.0	1	5.0	2	2.3
		3	3.0	2	5.0	3	2.3
		2	1.8	2	3.0	2	1.5
		3	1.8	3	3.0	3	1.5
		4	1.0	3	1.6	4	0.9
Si^{2+}	^1S	1	7.3	0	15.4	2	6.6
		1	5.0	0	9.0	2	3.9
		2	5.0	1	9.0	3	3.9
		2	3.5	1	5.5	2	2.8
		3	3.5	2	5.5	3	2.8
		2	2.0	2	3.4	2	1.9
		3	2.0	3	3.4	3	1.9
		4	1.3	3	1.9	4	1.1
P^{3+}	^1S	1	8.0	0	16.0	2	7.0
		1	5.5	0	9.5	2	4.4
		2	5.5	1	9.5	3	4.4
		2	3.9	1	5.9	2	3.2
		3	3.9	2	5.9	3	3.2
		2	2.5	2	3.8	2	2.2
		3	2.5	3	3.8	3	2.2
		4	1.6	3	2.1	4	1.3
S^{4+}	^1S	1	8.9	0	16.8	2	7.5
		1	6.1	0	10.1	2	4.9
		2	6.1	1	10.1	3	4.9
		2	4.4	1	6.5	2	3.6
		3	4.4	2	6.5	3	3.6
		2	2.9	2	4.3	2	2.6
		3	2.9	3	4.3	3	2.6
		4	1.9	3	2.4	4	1.6
Cl^{5+}	^1S	1	9.8	0	17.6	2	8.0
		1	6.9	0	10.7	2	5.5
		2	6.9	1	10.7	3	5.5
		2	5.0	1	7.0	2	4.0
		3	5.0	2	7.0	3	4.0
		2	3.4	2	4.8	2	3.0
		3	3.4	3	4.8	3	3.0
		4	2.2	3	2.7	4	1.9
Ar^{6+}	^1S	1	10.8	0	18.5	2	8.2
		1	7.5	0	11.3	2	6.0
		2	7.5	1	11.3	3	6.0
		2	5.5	1	7.5	2	4.5
		3	5.5	2	7.5	3	4.5
		2	3.9	2	5.2	2	3.4
		3	3.9	3	5.2	3	3.4
		4	2.5	3	3.0	4	2.2

TABLE IV. Exponents of Slater basis for the perturbed orbitals (quadrupolar case).

		$s \to d$		$p \to p$		$p \to f$	
Ion	State	n	ρ	n	ρ	n	ρ
Mg	^1S	2	6.0	1	7.0	3	5.0
		2	4.0	1	5.0	3	3.6
		3	4.0	2	5.0	4	3.6
		2	2.8	1	3.0	3	2.2
		3	2.8	2	3.0	4	2.2
		2	1.6	2	2.0	3	1.5
		3	1.6	3	2.0	4	1.5
		3	0.9	3	1.0	4	0.8
Al^+	^1S	2	6.8	1	7.9	3	5.7
		2	4.7	1	5.2	3	4.2
		3	4.7	2	5.2	4	4.2
		2	2.9	1	3.1	3	2.6
		3	2.9	2	3.1	4	2.6
		2	1.7	2	1.9	3	1.6
		3	1.7	3	1.9	4	1.6
		3	1.1	3	1.3	4	1.0
Si^{2+}	^1S	2	7.3	1	8.5	3	6.2
		2	5.0	1	5.6	3	4.3
		3	5.0	2	5.6	4	4.3
		2	3.2	1	3.5	3	2.8
		3	3.2	2	3.5	4	2.8
		2	1.9	2	2.2	3	1.8
		3	1.9	3	2.2	4	1.8
		3	1.2	3	1.3	4	1.1
P^{3+}	^1S	2	8.0	1	9.2	3	6.9
		2	5.6	1	6.2	3	4.8
		3	5.6	2	6.2	4	4.8
		2	3.7	1	4.0	3	3.2
		3	3.7	2	4.0	4	3.2
		2	2.2	2	2.4	3	2.0
		3	2.2	3	2.4	4	2.0
		3	1.4	3	1.5	4	1.3
S^{4+}	^1S	2	8.8	1	10.0	3	7.7
		2	6.2	1	6.9	3	5.3
		3	6.2	2	6.9	4	5.3
		2	4.2	1	4.5	3	3.6
		3	4.2	2	4.5	4	3.6
		2	2.6	2	2.8	3	2.3
		3	2.6	3	2.8	4	2.3
		3	1.6	3	1.7	4	1.4
Cl^{5+}	^1S	2	9.6	1	10.9	3	8.5
		2	6.8	1	7.6	3	5.8
		3	6.8	2	7.6	4	5.8
		2	4.7	1	5.0	3	4.0
		3	4.7	2	5.0	4	4.0
		2	3.0	2	3.2	3	2.7
		3	3.0	3	3.2	4	2.7
		3	1.8	3	1.9	4	1.6
Ar^{6+}	^1S	2	10.5	1	12.0	3	9.4
		2	7.5	1	8.2	3	6.6
		3	7.5	2	8.2	4	6.6
		2	5.3	1	5.6	3	4.6
		3	5.3	2	5.6	4	4.6
		2	3.4	2	3.7	3	3.2
		3	3.4	3	3.7	4	3.2
		3	2.0	3	2.2	4	1.8

mation. The CHF value of Kaneko and Arai[10] is 12.04 Å^3, whereas the experimental values range from 7.0 ±1.8 Å^3 (Ref. 18) to 7.4 ±1.8 Å^3 (Ref. 19). The value obtained by Adelman and Szabo[20] is 10.5 Å^3 using the Coulomb approximation, whereas 11.1 ±0.5 Å^3 has been obtained in the accurate semiempirical method of Stwallay.[21] For other isoelectronic sequence we compared with the values obtained in the UHF (Refs. 2 and 24) approximation. The shielding factor values β_∞ are far away from the accurate value N/Z in the UHF[2] approximation. Our results should improve if the innermost cores have not been kept frozen. This has been shown explicitly in earlier calculations.[5,22]

For quadrupole polarizabilities not many calculations are available. For Mg we obtained a value 36.64 Å^5 in the fully coupled HF scheme. The UHF (Ref. 2) result is 40.36 Å^5 whereas 34.0 Å^5 has been obtained by using the statistical procedure[12] and 23.1 Å^5 in the Coulomb approximation.[20] Plots of quadrupolar polarizabilities α_q and the quadrupolar shielding factors γ_∞ are shown in Figs. 2 and 3. Systematic behavior is observed. Accurate calculation of γ_∞ is necessary to estimate

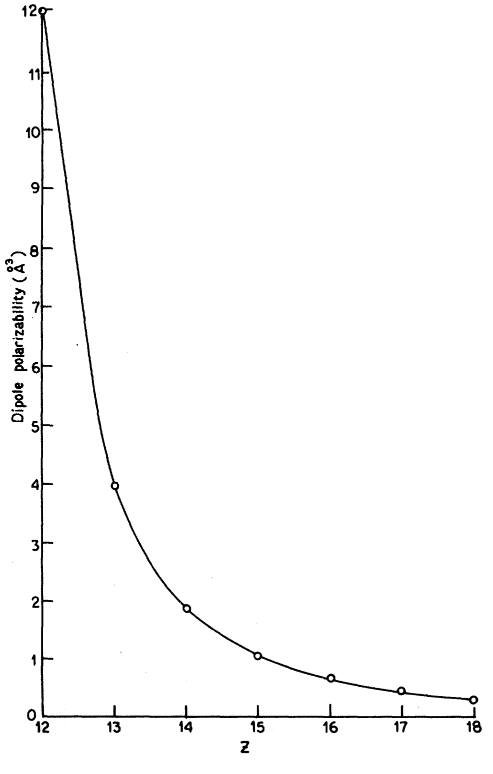

FIG. 1. Plot of dipolar polarizability values (α_d) against atomic number Z for magnesium isoelectronic sequence.

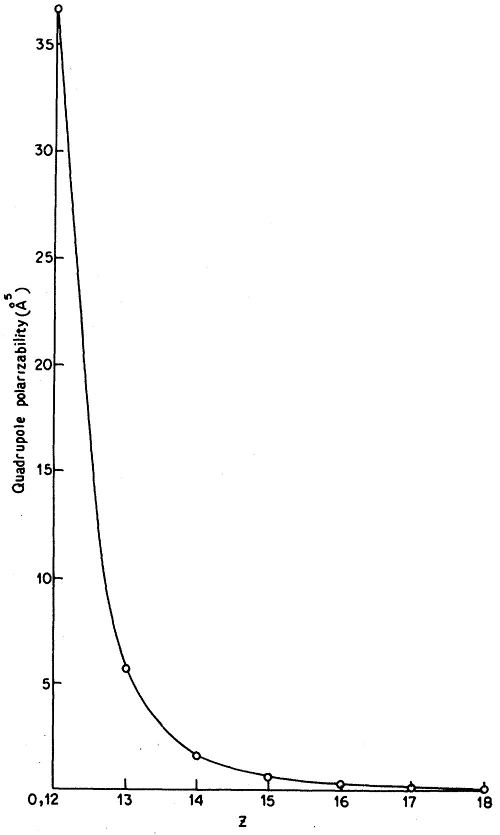

FIG. 2. Plot of quadrupolar polarizability values (α_q) against atomic number Z for magnesium isoelectronic sequence.

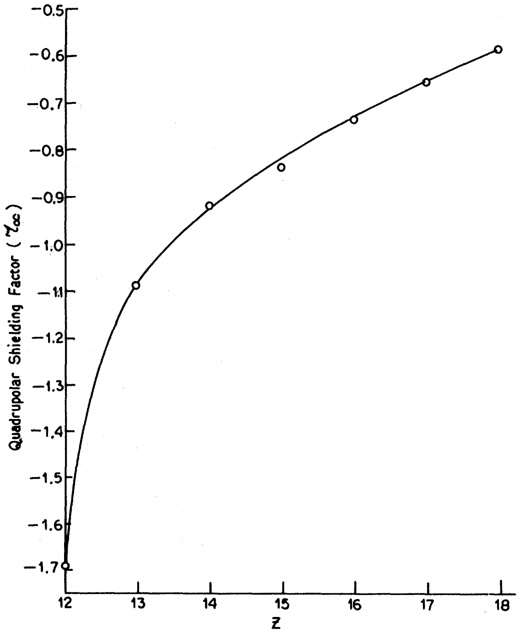

FIG. 3. Plot of quadrupolar shielding factors (γ_∞) against atomic number Z for magnesium isoelectronic sequence.

the correct nuclear quadrupole moments from experimental measurements.

In a CHF calculation the first-order correlation effect is accounted for fully; in addition, parts of higher-order correlation are taken care of.[14] This yields reliable results in the CHF scheme. The computation has been performed in the Burroughs 6700 system at the Regional Computer Centre at Jadavpur, Calcutta.

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