

Electrostatic Polarizability and Shielding Factors for Ions of Argon Configuration

J. LAHIRI* AND A. MUKHERJI
Saha Institute of Nuclear Physics, Calcutta, India

(Received 6 September 1966)

Dipole and quadrupole polarizabilities and shielding factors for 18-electron closed-shell ions from Cl^- to Ca^{++} have been calculated following the self-consistent perturbation procedure. Interpolation relations correlating these quantities with the radii of maximum electron density of the ions have been obtained. These relationships may be used to assess the true polarizabilities and nuclear shielding (or antishielding) factors for such ions in actual crystals.

I. INTRODUCTION

THEORETICAL estimates of multipole polarizability and nuclear shielding for 18-electron closed-shell ions have been made by Sternheimer^{1,2} and by others.³⁻⁶ These calculations were made by procedures which may be classified under the uncoupled Hartree-Fock (HF) method.⁷ Here the perturbations of individual single-electron orbitals are determined independently and the influence of one perturbed orbital on the others is neglected. This omission is not justified and often leads to serious inaccuracy in the result. The effect of the interdependence of the perturbed single-electron orbitals is fully accounted for in the coupled HF scheme.⁷ Polarizabilities of ions with a lesser number of electrons have been calculated by accurate methods equivalent to the coupled HF procedure by Dalgarno and collaborators,⁷ by Cohen,^{8,9} and also by the present authors.^{10,11} The importance of the coupling has been demonstrated in I for the case of the Be atom. Watson and Freeman¹² treated the problem for Cl^- by the unrestricted HF method. No other calculation of comparable accuracy has yet been reported for ions with the argon configuration.

The self-consistent perturbation method has now been applied to estimate the dipole and quadrupole polarizabilities α_d and α_q and consequent nuclear-shielding factors β_∞ and γ_∞ for ions of the argon sequence. Correlation of these parameters with the radii of maxi-

mum electron density ρ_m has also been made¹³ and an interpolation relation has been obtained. This relation will be useful to estimate the polarizability values for these ions when present in crystal lattices, if their electron distribution is known from single-crystal x-ray analysis.

II. THEORY

The self-consistent perturbation method has been fully described in I and many of the interesting features have been discussed there and in II. The calculation lies in minimizing the second-order HF energy expression as derived in I, in which all the terms containing different perturbed orbitals together are retained. The energy minimization is performed through successive approximation to achieve full self-consistency while keeping the numerical computation within reasonable limits. The procedure is fully described in I.

III. RESULTS

The results of the present calculation are given in Tables I and II. The values obtained by others (mostly through uncoupled HF calculations or the equivalent) have also been quoted for comparison. It may be observed that for α_d and β_∞ these values are too far from

TABLE I. Dipole polarizability α_d and shielding factor β_∞ .

Ion	Present results	$\alpha_d (10^{-24} \text{ cm}^3)$		Present results	β_∞		N/Z
		Previous calculations ^{a-c}	Experimental values ^{d-i}		Present calculations ^e	Previous calculations ^e	
Cl^-	3.760	6.23-7.19	2.96-3.66	1.026	2.62	1.059	
Ar	1.493	2.32, 2.44	1.63	0.924	4.5-14.2	1.000	
K^+	0.789	1.08-1.24	0.80-1.33	0.898	2.69	0.947	
Ca^{++}	0.475	0.62, 0.65	0.47-1.1	0.869	2.35	0.900	

* Present address: Department of Chemistry, New York University, New York.

¹ H. M. Foley, R. M. Sternheimer, and D. Tycko, *Phys. Rev.* **93**, 734 (1954).

² R. M. Sternheimer, *Phys. Rev.* **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959).

³ E. G. Wikner and T. P. Das, *Phys. Rev.* **109**, 360 (1958).

⁴ G. Burns, *J. Chem. Phys.* **31**, 1253 (1959).

⁵ M. Yoshimine and R. P. Hurst, *Phys. Rev.* **135**, A612 (1964).

⁶ P. W. Langhoff and R. P. Hurst, *Phys. Rev.* **139**, A1415 (1965).

⁷ For an excellent review, see A. Dalgarno, *Advan. Phys.* **11**, 281 (1962).

⁸ H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34, (1965).

⁹ H. D. Cohen, *J. Chem. Phys.* **43**, 3558 (1965).

¹⁰ J. Lahiri and A. Mukherji, *J. Phys. Soc. Japan* **21**, 1178 (1966); *Phys. Rev.* **141**, 428 (1966); hereafter referred to as I and II, respectively.

¹¹ J. Lahiri and A. Mukherji, *Phys. Rev.* **153**, 386 (1967).

¹² R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250 (1963).

^a R. M. Sternheimer, *Phys. Rev.* **115**, 1198 (1959).

^b M. Yoshimine and R. P. Hurst, *Phys. Rev.* **135**, A612 (1964).

^c P. W. Langhoff and R. P. Hurst, *Phys. Rev.* **139**, A1415 (1965).

^d K. Fajans and G. Joos, *Z. Physik* **23**, 1 (1924).

^e M. Born and W. Heisenberg, *Z. Physik* **23**, 388 (1924).

^f L. Pauling, *Proc. Roy. Soc. (London)* **A114**, 191 (1927).

^g J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).

^h L. Bornstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, Atome und Ionen* (Springer-Verlag, Berlin, 1950), Vol. I, Part I.

ⁱ J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

¹³ J. Lahiri and A. Mukherji, *Proc. Phys. Soc. (London)* **87**, 913 (1966).

TABLE II. Quadrupole polarizability α_q , antishielding factor γ_∞ , and the radius of maximum charge density ρ_m .

Ion	$\alpha_q (10^{-40} \text{ cm}^5)$		γ_∞		ρ_m (in atomic units)
	Present results	Previous calculations ^{a-d}	Present results	Previous calculations ^{e-h}	
Cl ⁻	11.92	11.79 -13.77	-63.21	-49.3-87.5	1.392
Ar	1.957	0.84- 2.94	-28.62	-5.1-30.2	1.239
K ⁺	0.674	0.717- 0.733	-18.27	-12.2-16.3	1.118
Ca ⁺⁺	0.290	0.309	-13.32	-12.1	1.017

^a R. M. Sternheimer, Phys. Rev. 107, 1565 (1957).

^b G. Burns, Phys. Rev. 115, 357 (1959).

^c P. W. Langhoff and R. P. Hurst, Phys. Rev. 139, A1415 (1965).

^d P. C. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. 126, 594 (1962).

^e R. M. Sternheimer and H. M. Foley, Phys. Rev. 102, 731 (1956).

^f G. Burns and E. G. Wikner, Phys. Rev. 121, 155 (1961).

^g E. G. Wikner and T. P. Das, Phys. Rev. 109, 360 (1958).

^h R. E. Watson and A. J. Freeman, Phys. Rev. 131, 250 (1963).

the present results. This illustrates the inadequacy of the uncoupled method.¹⁴ For α_q and γ_∞ , this discrepancy is much less spectacular. The apparent agreement should be considered as accidental because there is no *a priori* reason why the effect of coupling should be less important in the quadrupole calculation than in the dipole one.

The dipole shielding factor β_∞ for an ion can be evaluated from purely electrostatic considerations to be N/Z , where Z is the nuclear charge and N is the number of electrons present.¹⁵ Comparison of the computed value of β_∞ with this ratio gives an idea of the accuracy of the calculation. The deviation between the two is about 7.6% for Ar and much less for the other ions listed in Table I. It has been demonstrated earlier¹¹ that with a sufficiently large number of variation parameters this discrepancy can be considerably reduced. However, such accuracy of the calculated results would cost much computer time and would be of hardly any physical significance. For the dipole calculation, 6 parameters were used to represent each $ns \rightarrow p$ and $np \rightarrow s$ excitation, and 4 parameters to describe each $np \rightarrow d$ orbital perturbation, while for the quadrupole calculation 4, 4, 6, 6, 4, 6, and 6 combination of parameters were taken for $1s \rightarrow d$, $2s \rightarrow d$, $3s \rightarrow d$, $2p \rightarrow p$, $2p \rightarrow f$, $3p \rightarrow p$, and $3p \rightarrow f$ excitations, respectively. The unperturbed wave functions were taken to be those determined by Clementi and his collaborators.^{16,17}

Referring to Table I, it may be observed that our calculated values of α_d are in excellent agreement with

¹⁴ More detailed discussion of this point had been incorporated in I and II. It is particularly illustrated in Table IV of I.

¹⁵ R. P. Feynman, Phys. Rev. 56, 340 (1939).

¹⁶ E. Clementi, J. Chem. Phys. 38, 996 (1963).

¹⁷ E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. 133, A1274 (1964).

the experimental values. But there is a large disparity between the experimental values obtained by different workers. This is because α_d is not directly obtained through experiments, but derived indirectly from the refractive index and other data. Further, when comparing theoretical values with experimental ones, it should be remembered that the former are calculated for free ions while the latter are measured for ions in crystalline lattices. The effect of a crystalline environment is to distort the electron distribution from the free-ion state.¹³ This naturally would alter the effective α_d value. Such a change can be obtained through the interpolation relation discussed in Sec. IV, while the actual electron distribution in the ion can be studied through single-crystal x-ray analysis.

IV. INTERPOLATION

The values of ρ_m , the radii of maximum charge density, are also listed in Table II. They represent the distance from the nucleus of the farthest peak in the radial electron-density distribution curves. A polynomial relationship of the form

$$y = \sum_i a_i x^i \quad (1)$$

makes a satisfactory representation, where y stands for $\log_{10}(10\alpha_d)$ or $\log_{10}(-\gamma_\infty)$ and x for $\log_{10}\rho_m$, with α_d in \AA^3 , α_q in \AA^5 , and ρ_m in atomic units. Table III lists

TABLE III. Values of interpolation parameters a_i in Eq. (1).

Range of ρ_m : 1.0-1.4 atomic units	a_i	
	i	a_i
Dipole polarizability	0	0.63945
α_d in \AA^3	1	5.13684
$y = \log_{10}(10\alpha_d)$	2	0.82074
$x = \log_{10} \rho_m$	3	61.05845
Quadrupole polarizability	0	0.39364
α_q in \AA^5	1	9.51328
$y = \log_{10}(10\alpha_q)$	2	-24.21245
$x = \log_{10} \rho_m$	3	275.24443
Quadrupole shielding factor γ_∞	0	1.10108
	1	3.23167
$y = \log_{10}(-\gamma_\infty)$	2	-3.08926
$x = \log_{10} \rho_m$	3	100.99908

the values of a_i to be used with Eq. (1). If the value of ρ_m for any 18-electron ion in a crystalline lattice is known from experiment, this relation may be used to obtain its polarizabilities and nuclear antishielding *in situ*.

All the computations were performed on the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay, India.