

## Electrostatic Polarizability and Shielding Factors for Ions of Neon Configuration

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Dipole and quadrupole polarizabilities and shielding factors for 10-electron closed-shell ions from  $O^{--}$  to  $Si^{4+}$  have been calculated following the self-consistent perturbation procedure. Results are accurate in the coupled Hartree-Fock scheme. Interpolation relations have been obtained which may be used to relate these quantities to the radius of maximum electron density for ions in actual crystals.

### I. INTRODUCTION

THEORETICAL estimation of multipole polarizability and consequent nuclear shielding (or antishielding) of an atom or ion produced by an external electrostatic potential has received considerable attention. Recently, accurate methods have been adopted for such calculations.<sup>1,2</sup> A procedure for self-consistent perturbation calculation has been described earlier.<sup>2</sup> It yields results under coupled Hartree-Fock (HF) approximation. The perturbed wave function is accurate up to the first order. Advantage of such perturbation approach over a complete HF calculation including the perturbing Hamiltonian has also been discussed. Dipole and quadrupole polarizability and shielding parameters have been calculated for He, Li, and Be isoelectronic sequences and highly satisfactory results obtained.<sup>2,3</sup> This method has been extended to the case of 10-electron closed-shell ions from  $O^{--}$  to  $Si^{4+}$ , and the results are presented in this paper. A calculation of the dipole polarizability for some of the ions has recently been made by Cohen.<sup>4</sup>

For practical application of these results in the case of ions in actual crystals, an interpolation procedure correlating these parameters to the radius of maximum electron density ( $\rho_m$ ) has been postulated.<sup>5</sup> Relations of similar nature have also been obtained for the ions under study.

### II. THEORY

In essence, the self-consistent perturbation calculation lies in minimizing the energy difference

$$\Delta E = \langle \Psi | \mathcal{H} | \Psi \rangle - \langle \Psi_0 | \mathcal{H}_0 | \Psi_0 \rangle, \quad (1)$$

where  $\mathcal{H}_0$  is the unperturbed Hamiltonian and  $\mathcal{H}$  is the total Hamiltonian including perturbation.  $\Psi_0$  and  $\Psi$  are Slater determinants which are eigenfunctions of

$\mathcal{H}_0$  and  $\mathcal{H}$ , respectively, in the Hartree-Fock scheme. If  $\psi$  and  $\phi$  represent normalized single-particle orbitals constituting these determinants, then up to second order  $\Delta E$  can be expressed in terms of the deviations

$$\delta\psi = \phi - \psi. \quad (2)$$

$\psi$ 's are usually known and  $\delta\psi$ 's are obtained from the energy minimization procedure. For adequate flexibility, the radial part of  $\delta\psi$  is taken in the form

$$\delta\psi(r) = \sum_a C_a r^{n_a} \exp(-\zeta_a r). \quad (3)$$

The angular and spin parts are determined by the characteristics of the perturbing Hamiltonian and of the unperturbed orbital  $\psi$ . Through judicious choice, a fairly good set of values for the  $n$ 's and  $\zeta$ 's may be selected and the  $C$ 's remain as variable parameters.

The multipole polarizabilities and shielding factors are obtained in terms of the  $\delta\psi$ 's. The dipole shielding factor  $\beta_\infty$  is also obtained from physical considerations as the ratio  $N/Z$ , where  $N$  is the number of electrons and  $Z$  is the nuclear charge. A comparison of the computed  $\beta_\infty$  value with this ratio provides a test for the accuracy of the calculation.

### III. RESULTS

The computation time is proportional quadratically to the number of variation parameters. If one can start with better representative sets of orbital exponents, one can obtain satisfactory results with a smaller number of parameters. The final results are rather insensitive to variation of the exponents. The convergence of the magnitude of the computed quantities with increasing number of parameters for dipole calculation of Ne is demonstrated in Table I. It has been observed that the

TABLE I. Convergence of the computed dipole polarizability  $\alpha_d$  for Ne atom with increasing number of variation parameters.

Number of variation parameters				$\alpha_d$ ( $10^{-24}$ cm <sup>3</sup> )	$\beta_\infty$ ( $N/Z=1$ )
$1s \rightarrow p$	$2s \rightarrow p$	$2p \rightarrow s$	$2p \rightarrow d$		
5	5	4	4	0.3234	0.9848
6	6	6	4	0.3477	1.0280
6	6	8	6	0.3504	1.0188
8	8	8	6	0.3513	1.0080
8	8	8	8	0.3529	1.0010

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<sup>1</sup> See for example, A. Dalgarno, *Advan. Phys.* **11**, 281 (1962); H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34 (1965); L. C. Allen, *Phys. Rev.* **118**, 167 (1960).

<sup>2</sup> J. Lahiri and A. Mukherji, *J. Phys. Soc. Japan* **21**, 1178 (1966).

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TABLE II. Values of dipole and quadrupole polarizabilities  $\alpha_d$  and  $\alpha_q$ , dipole and quadrupole shielding factors  $\beta_\infty$  and  $\gamma_\infty$ , and the radii of maximum charge density  $\rho_m$ .

Ion	$\alpha_d$ ( $10^{-24}$ cm <sup>3</sup> )	Computed $\beta_\infty$	$N/Z$	$\alpha_q$ ( $10^{-40}$ cm <sup>5</sup> )	$\gamma_\infty$	$\rho_m$ (a.u.)
O <sup>2-</sup>	(10.56)	(1.102)	1.250	(412.5)	(-1045.8)	0.881
F <sup>-</sup>	1.40	1.120	1.111	2.937	-29.88	0.756
Ne	0.350	1.019	1.000	0.268	-9.213	0.651
Na <sup>+</sup>	0.140	0.923	0.909	0.0632	-5.178	0.569
Mg <sup>2+</sup>	0.0697	0.841	0.833	0.0215	-3.485	0.504
Al <sup>3+</sup>	0.0393	0.774	0.769	0.00895	-2.570	0.452
Si <sup>4+</sup>	0.0241	0.717	0.714	0.00424	-2.003	0.409

value of  $\beta_\infty$  approaches the ideal value of unity very closely. For most practical purposes, values of  $\alpha_d$  accurate up to the second significant figure are adequate, hence dipole calculation for all the ions of the series are made with 6, 6, 8, 6 combination of parameters. Out of them, four parameters are determined by the radial orthogonality conditions, and the rest can be independently varied. For the quadrupole calculation, orthogonality conditions are satisfied by the angular factors themselves, except for the  $2p \rightarrow p$  excitation. A combination 4, 4, 6, 4 of the number of parameters for  $1s \rightarrow d$ ,  $2s \rightarrow d$ ,  $2p \rightarrow p$ , and  $2p \rightarrow f$  excitations, respectively, has been found to be adequate. For the unperturbed wave function, use has been made of

TABLE III. Values of interpolation parameters  $a_i$  in Eq. (4).

	$i$	Range of $\rho_m$ in atomic units		$i$	$a_i$
		0.4-0.57	0.57-0.9		
Dipole polarizability	0	-2.8111	0	-23.9065	
$\alpha_d$ in Å <sup>3</sup>	1	8.1813	1	93.6831	
$y = \log_{10} (10^3 \times \alpha_d)$	2	-8.8895	2	-124.4529	
$x = \log_{10} (10 \times \rho_m)$	3	6.6178	3	58.7024	
Quadrupole polarizability	0	-4.9159	0	-210.3633	
$\alpha_q$ in Å <sup>5</sup>	1	15.6886	1	794.1117	
$y = \log_{10} (10^3 \times \alpha_q)$	2	-18.6629	2	-1001.9740	
$x = \log_{10} (10 \times \rho_m)$	3	12.8010	3	426.9797	
Quadrupole shielding	0	-2.4790	0	-234.3967	
Factor $\gamma_\infty$	1	10.1614	1	880.6484	
$y = \log_{10} (-\gamma_\infty)$	2	-14.8262	2	-1103.3310	
$x = \log_{10} (10 \times \rho_m)$	3	9.2300	3	462.7353	

Clementi's computed Hartree-Fock functions.<sup>6,7</sup> The results of these calculations are listed in Table II.

Our computed  $\beta_\infty$  values are in general slightly larger than  $N/Z$ , while for O<sup>2-</sup> it is smaller. In fact, it is even smaller in magnitude than the  $\beta_\infty$  value for F<sup>-</sup>. This throws doubt on the reliability of the starting  $\Psi_0$  for O<sup>2-</sup>. Hence the computed quantities for O<sup>2-</sup> in Table II are quoted in parentheses, signifying uncertainty.

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

#### IV. INTERPOLATION

A correlation of  $\rho_m$ , the radius of maximum charge density, to polarizability and shielding has been demonstrated earlier.<sup>5</sup> For the ions of Ne sequence, two peaks are observed in the radial-electron-density-distribution curves.  $\rho_m$  is the distance of the farthest peak from the nucleus. A plot of  $\log \alpha$ , or  $\log \gamma$  against  $\log \rho_m$  in this case shows appreciable deviation from a straight line. It was found that a polynomial relationship among these quantities can be easily established. If  $y$  and  $x$  represent  $\log \alpha$  or  $\log \gamma$  and  $\log \rho_m$ , respectively, then

$$y = \sum_i a_i x^i. \quad (4)$$

For better representation, the whole range of  $\rho_m$  is split up into two regions and a four-parameter fit is obtained for each. The values of  $\rho_m$  for the ions are also listed in Table II, and the parameters for interpolation in Table III. For convenience of calculation, the  $\alpha$ 's and  $\rho_m$ 's are multiplied by suitable factors before fitting to Eq. (4).

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<sup>6</sup> E. Clementi, J. Chem. Phys. **38**, 996 (1963).

<sup>7</sup> E. Clementi and A. D. McLean, Phys. Rev. **133**, A419 (1964).