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Effect of crystal fields and self-consistency on dipole and quadrupole polarizabilities of closed-shell ions

P. C. Schmidt, Alarich Weiss, and T. P. Das*
Institut für Physikalische Chemie,
Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

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Dipole and quadrupole polarizabilities have been studied for 40 closed-shell ions in crystals including the influence of both the environment in the crystal and self-consistency. The effect of the crystal environment is incorporated by the Watson sphere model, while consistency effects are included by a procedure adapted from many-body perturbation theory. Both effects are found to be of importance and, when included, lead to satisfactory agreement with available experimental data on dipole polarizabilities. The influence of consistency effects is always found to reduce the polarizabilities with respect to the free ions while the influence of the crystal environment leads to a decrease for anions and an increase for cations. Comparison is also made for free ions with experimental results, and with theoretical results from other approaches to focus on the accuracy of calculated consistency contributions. Physical reasons are discussed for the observed trends in the various contributions to the polarizabilities for both free ions and ions in crystals.

I. INTRODUCTION

Over the past 25 years, there has been a considerable amount of effort directed at the understanding of the dipole (α_D) and quadrupole (α_Q) polarizabilities[1,2] of atoms and ions. Most of this effort has been applied to free atoms and ions. Since in the case of ions, the experimental polarizability data are obtained from solid-state systems, and it is known that crystal-field effects on the electronic structures of the ions in solid state are rather important, it is essential for a meaningful comparison of theoretical and experimental results that the former be obtained for ions in crystals rather than in the free state. In this connection, semiempirical estimates have been made in the literature[3,4] regarding the importance of crystal fields on the α_D of ions in crystals. These estimates indicate that α_D for a cation is increased by the influence of the crystal field, the opposite being the case for anions. This trend is to be expected physically, since the electrons of the cation experience the influence of the negative charges of the neighboring anions in ionic crystals, become more loosely bound, and therefore more polarizable compared to the free ions. The situation is reversed for electrons on anions which are surrounded by cation neighbors.

Among the earliest efforts at studying the influence of crystal-field effects on the polarizabilities is that of Hartmann and Kohlmaier.[5] These authors have attempted to include the effect of the crystal potential by cutting off the free-ion electronic wave functions at the ionic radius and renormalizing them appropriately. Such an approximation however leads to a reduction in α_D for both cations and anions. Paschalis and Weiss[6] have attempted to remedy this situation by using more realistic electronic wave functions in the crystal through the Watson sphere model.[7] In this model, the influence of the solid matrix on the electrons in an ion (charge q) is simulated by superimposing on the potential in the free ion the additional potential due to a hollow sphere with total charge $-q$ and an appropriately chosen radius [see Eq. (3) and Fig. 1]. One of the first applications of the Watson sphere model to perturbation problems was made by Sachs[8] who has studied the diamagnetic susceptibilities of Na^+ and F^- using wave functions obtained from the Watson model. Paschalis and Weiss[6] have obtained analytic electronic wave functions for a number of cations and anions in the Watson sphere model using the Hartree-Fock-Roothaan variational method to obtain the electronic wave functions. Using these wave functions they have obtained dipole polarizabilities α_D using an approximate procedure due to Buckingham.[9] They correctly reproduced the expected trend of increase in α_D over the free ion for the cations and decrease for anions. Sen and Narasimhan[10] have applied the Watson sphere model[7] to the calculation of α_Q. They used the Sternheimer differential-equation (DE) procedure[11,12] to obtain the perturbed wave functions in the presence of an electric-field gradient. However, their wave functions in the Watson sphere model were obtained using the Hartree-Fock-Slater (HFS) approximation to the exchange potential. Since the polarizabilities have been found[13,14] to be quite sensitive to the wave functions used, and HFS wave functions have been found to give substantial differences from Hartree-Fock (HF) results for other properties in atoms, it is desirable to use the HF approximation as far as possible for polarizability studies.

The present work was aimed at an *ab initio* study of α_d and α_Q for a series of closed-shell ions up to Ba^{2+}, including both crystal-field and self-consistency effects in the course of perturbation of the ions by the applied electric field. Such effects have been found to be rather important in the study of polarizabilities of free atoms.[15] In our work we have used the Hartree-Fock approximation in conjunction with the Watson sphere model to obtain the electronic wave functions for the ions in the crystal. The perturbations by the electric field and field gradient are carried out by the variational equivalent[16,17] of the Sternheimer DE procedure.[11,12] Self-consistency effects are included here by a method[12] adapted from diagrammatic many-electron perturbation theory.[18] As we shall see, consistency effects which have not been included in earlier polarizability calculations for ions in crystals are rather important, and have to be included in order to obtain satisfactory agreement with experiment.

II. THEORY AND PROCEDURE

The procedure that we shall adopt for evaluation of the polarizabilities for ions in a crystal, in the framework of the Watson sphere model[7] including self-consistency, involves essentially three steps. The first is the determination of the unperturbed Hartree-Fock electronic wave functions in the potential corresponding to the Watson sphere model. The second step is the evaluation of the perturbed wave functions in the presence of the electric field or field gradient. This will be done in the framework of the uncoupled Hartree-Fock model[1,11,17] using a variational approach.[16] With these perturbed wave functions, one obtains the polarizabilities (α_D^0 and α_Q^0) in the uncoupled Hartree-Fock approximation, which do not include self-consistency effects arising from the influence of electron-electron interaction during the process of perturbation by the electric field[15] or field gradient.[12,18,19] The third step involves the incorporation of self-consistency effects which will be carried out in the spirit of the many-body diagrammatic procedure,[18] as has been done already[12] for nuclear quadrupole antishielding effects in a number of cases, and shall be shown later in this section to be equivalent to a determinantal procedure involving the perturbed wave functions in the presence of the electric field or field gradient.

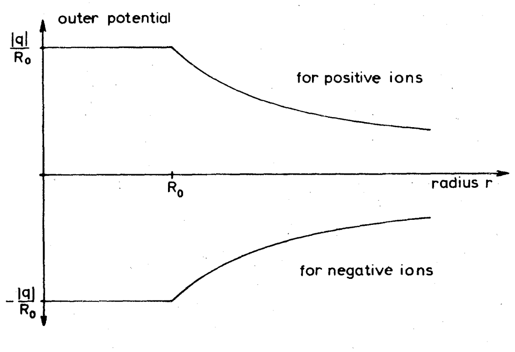

FIG. 1. Watson-sphere-model potential for the positive and negative ions; R_0 is the radius of the Watson sphere.

Each of these steps is described individually in detail in the literature. However, for the sake of completeness, we shall briefly present the essential parts of the formalism involved. Thus, considering first the calculation of the unperturbed electronic wave functions, the Hamiltonian $\mathcal{H}_f^0$ for a free ion with nuclear charge Ze and N electrons is given by

$$\mathcal{H}_f^0 = -\sum_{i=1}^{N}\left[\frac{\hbar^2}{2m_e}\Delta_i + \frac{Ze^2}{r_i}\right] + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} , \tag{1}$$

m_e being the mass of the electron and $\vec{r}_i$ is the radius vector for electron i with respect to the nucleus. For an ion in a crystal, one has to augment $\mathcal{H}_f^0$ by the influence of interaction of the electrons and nucleus in the ion under question with the electrons and nuclear charges on the surrounding ions. In the Watson sphere model, the interaction between the central ion and neighboring ions is simulated by the influence of the potential described in the Introduction. Thus, the unperturbed Hamiltonian in the crystal in this model is given by

$$\mathcal{H}_c^0 = \mathcal{H}_f^0 + \sum_{i=1}^{N} V(r_i) , \tag{2}$$

where

$$V(r_i) = \begin{cases} \dfrac{qe}{R_o} & \text{for } r_i \le R_o , \\[2ex] \dfrac{qe}{r_i} & \text{for } r_i > R_o , \end{cases} \tag{3}$$

where

$$q = -(Z-N)e \tag{4}$$

and R_0 is the radius of the Watson sphere. The form of the potential $V(r_i)$, due to the Watson sphere, is shown in Fig. 1. For R_0, in keeping with earlier practice in the literature,[6-8,10] we have chosen the Pauling ionic radii of the ions under study. There can, of course, be small variations in the ionic radius for an ion in going from one crystal to another.[20,21]

We have examined the influence of changes in R_0 on α_D and α_Q, as will be discussed in Sec. III dealing with the results.

The determinantal eigenfunctions Φ_c^0 of $\mathcal{H}_c^0$ satisfying the equation

$$\mathcal{H}_c^0\Phi_c^0 = E_c^0\Phi_c^0 \tag{5}$$

and built out of the corresponding one-electron Hartree-Fock wave functions, were determined variationally by the Hartree-Fock-Roothaan procedure.[22]

The next step involves the calculation of the polarizabilities α_D^0 and α_Q^0 in the uncoupled perturbation approach (see method d, Ref. 17). The electric field and field gradient acting on the electrons are assumed[11,23,24] to arise from an external charge Qe at distance R, large enough to assume $r_i << R$. In this case,

$$\lambda\mathcal{H}' = -\lambda e^2 \sum_i r_i^L P_L(\cos\vartheta) \quad \text{with } \lambda = Q/R^{L+1} \tag{6}$$

is a satisfactory form for the perturbation Hamiltonians acting on the electrons due to the electric field ($L=1$) and field gradient ($L=2$), the angle ϑ being measured from the line joining the external charge and the nucleus of the ion (Fig. 2). The perturbation $\lambda\delta_1\Phi$ in the many-electron determinantal wavefunction Φ_c^0 is obtained by minimizing the energy functional

$$J(\delta\Phi) = \langle\delta\Phi|\mathcal{H}_c^0 - E_c^0|\delta\Phi\rangle + 2\langle\Phi_c^0|\mathcal{H}'|\delta\Phi\rangle \ , \tag{7}$$

with respect to variations in the perturbations $\lambda\delta_1\phi_i$ of the one-particle functions ϕ_i^0. In the uncoupled approximation, this corresponds to the minimization of a one-electron functional similar to that in Eq. (7) for each one-electron state ϕ_i^0. For the variational forms of $\delta_1\phi_i$ we have employed the power series form used in the literature[16,17], namely,

$$\delta_1\phi_i = \phi_i^0 r^L \sum_{s=0}^{M} a_s r^s P_L(\cos\vartheta_i) \ . \tag{8}$$

Once the $\delta_1\phi_i$ have been determined by the minimization procedure, the polarizabilities are given by

$$\alpha_{D,Q}^0 = -2E_2 = -2J(\delta_1\Phi) = -2\langle\Phi_c^0|\mathcal{H}'|\delta_1\Phi\rangle \ . \tag{9}$$

The third step of incorporating self-consistency effects can of course be carried out as in the fully coupled variation perturbation procedure (method a, Ref. 17) by minimizing the second-order energy involving the electric field or field gradient, using the perturbed determinantal function $\Phi_c^0 + \lambda\delta_1\Phi$ built out of the one-electron perturbed functions $\phi_i^0 + \lambda\delta_1\phi_i$. In carrying out the energy minimization, one must retain the coupling between different perturbed states i and j. This is however, rather time consuming when a substantial number of one-electron states are involved, especially in the medium heavy and heavy ions. We shall use an alternate procedure[12,25] adapted from many-body perturbation approach, which involves only a knowledge of the $\delta_1\phi_i$ from the uncoupled variation-perturbation procedure.[18] With this approach, the first-order self-consistency contributions to the polarization energies corresponding to α_D and α_Q are given by

$$\begin{aligned}E_3 = 2\sum_{i>j}\Bigg[&\langle\delta_1\phi_i(1)\delta_1\phi_j(2)|\frac{e^2}{r_{12}}|\phi_i^0(1)\phi_j^0(2)\rangle + \langle\phi_i^0(1)\delta_1\phi_j(2)|\frac{e^2}{r_{12}}|\delta_1\phi_i(1)\phi_j^0(2)\rangle \\ &- \langle\delta_1\phi_i(1)\delta_1\phi_j(2)|\frac{e^2}{r_{12}}|\phi_i^0(2)\phi_j^0(1)\rangle - \langle\delta_1\phi_i(1)\phi_j^0(2)|\frac{e^2}{r_{12}}|\phi_i^0(2)\delta_1\phi_j(1)\rangle\Bigg] \ .\end{aligned} \tag{10}$$

This expression can also be derived[26] by an alternate procedure involving the evaluation of the expectation value of the difference in the Hamiltonian $\mathcal{H}_c^0$ and its Hartree-Fock counterpart, namely,

$$\mathcal{H}'' = \sum_{i>j}\frac{e^2}{r_{ij}} - V_{\text{HF}} \tag{11}$$

over the perturbed determinantal function for the many-electron state, built out of the perturbed one-electron functions $\phi_i^0 + \lambda\delta_1\phi_i$. For some perturbation problems, such as the nuclear quadrupole antishielding effect, the first-order consistency contribution analogous to Eq. (10), has been found to be quite satisfactory.[19,25] However, for polarizabilities, the first-order consistency effect is rather substantial and one needs to incorporate higher-order consistency effects. This will be done by the geometric series approximation,[27] often used in many-body perturbation calculations[28] and found to be satisfactory for a number of atomic properties. Thus, the net polarizabilities α_D and α_Q including self-consistency can be obtained from the expression

$$\alpha_{D,Q} = \alpha_{D,Q}^0\left(1 - \frac{\alpha_{D,Q}^1}{\alpha_{D,Q}^0}\right)^{-1} \ , \tag{12}$$

where $\alpha_{D,Q}^1 = -2E_3$, E_3 being given in Eq. (10).

For all the ions we have studied here in ionic crystals by the Watson sphere model, we have also carried out corresponding calculations for the free ions. The purposes for this were to allow comparisons between the free ions and ions in crystals, for both the uncou-

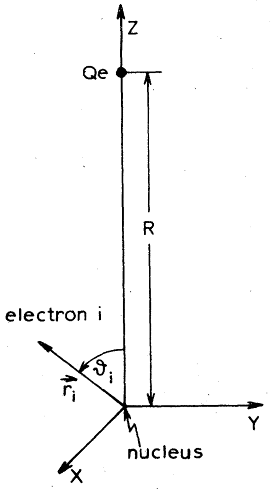

FIG. 2. Choice of the coordinate system for an ion perturbed by a point charge Qe.

pled $\alpha^0_{D,Q}$ and $\alpha_{D,Q}$ including consistency, and also to make comparisons with the results of some other calculations[13,14,29] on free ions including consistency effects by different procedures.

III. RESULTS AND DISCUSSION

We have presented in Table I the results of our calculation for dipole and quadrupole polarizabilities for a number of ions isoelectronic with the rare gases, from helium to xenon. Also included are the results for a few systems with $3d^{10}$ and $4d^{10}$ outermost shells. For both the dipole and quadrupole cases, the uncoupled values α^0_D and α^0_Q, and the values including consistency, namely, α_D and α_Q, and tabulated for the ions in a crystal as well as free ions. Also for ready reference, we have listed the values of R_0 that we have used for the ions in the crystal.

In Table II we have made a comparison of the experimental values of α_D that are available for both ions in a crystal as well as free ions and rare-gas atoms with the results of our calculation. For the ions in the crystal, the experimental values presented from Ref. 30 are obtained from analysis of refractive index data using additivity approximation. The experimental values listed from Ref. 4 were obtained from a more detailed analysis of refractive index data and allowed for variation in α_D for a particular ion with different ligands. The ranges listed for each ion represented the variation in α_D over a series of alkali halides of the same structure. These variations were fitted to empirical relations

$$(\alpha_D)_{\text{crystal}}=(\alpha_D)_{\text{free}}\exp(-b/r_e^2)\quad\text{for anions}\ , \tag{13}$$

$$(\alpha_D)_{\text{crystal}}=(\alpha_D)_{\text{free}}\,(1-c/r_e)^{-2}\quad\text{for cations}\ ,$$

where r_e is nearest-neighbor distance and the parameters b and c are adjusted for best fit with the observed variation of $(\alpha_D)_{\text{crystal}}$. The empirical values of $(\alpha_D)_{\text{free}}$ obtained in this way are listed as the experimental values for free ions in the second column. For the rare gases, the values listed are[2] from either refractive index data or from beam experiments. No experimental results are available for α_Q for either free ions or ions in a crystal.

We would like to discuss the features of our results in three different categories. The first is the nature of trends of variation in the crystal potential and consistency contributions for different ions. The second is the question of the nature of agreement between our theoretical results and experiment. Finally we shall make comparison with other theoretical[13,17,24,31–34] results available in the literature for α_D and α_Q for free ions. To our knowledge, no theoretical results besides the present ones are available for ions in crystals including consistency effects.

A. Nature and trends of crystal potential and consistency contributions to α_Q and α_D

The first important feature of our results in Table I is that both consistency and crystal potential contributions in the case of both α_D and α_Q are of comparable order of magnitude, the consistency contribution being the larger one for all the ions studied except the helium like ones.

The consistency effect as represented by the ratio α^0_D/α_D-1 increases as one goes to the heavier isoelectronic series, ranging from 8% for the helium-like ions to about 80% for the xenon-like ions. Interestingly, within a particular isoelectronic series, the consistency effect appears to be nearly constant and is also nearly the same for free ions and ions in crystals. The rapid increase in going to heavier ions is readily explained. The consistency effect represents essentially the influence of the polarization of one orbital by the action of another orbital that has been perturbed by the electric field or field gradient. Since the outer orbitals, the ones which make the major contribution to α_D, are more polarizable for heavier ions, it is easy to understand the rapid increase in importance of the consistency effect in going to heavier ions.

Another important feature of the results in Table I associated with the consistency effect is that this effect leads to a decrease from the uncoupled perturbation values α_D^0 and α_Q^0 for both cations and anions. This is understandable, because the electron-electron interaction imposes a constraint on the perturbation of the outermost orbitals by the electric field, making them less polarizable. In contrast, the crystal potential effects are of opposite signs for the cations and anions as had been found in earlier semiempirical treatments[3,4] and from quantum-mechanical calculations[6] within the Watson sphere model. The qualitative reason for the difference in sign for the crystal potential effect, an increase from the free ion values of α_D and α_Q for the cations and decrease for the an-

TABLE I. Electronic dipole and quadrupole polarizabilities for free ions and ions in crystals.

Ion	Radius R_0 of the Watson sphere (Å)	Dipole polarizability[a]				Quadrupole polarizability[b]			
		ions in a crystal		free ions		ions in a crystal		free ions	
		α_D^0	α_D	α_D^0	α_D	α_Q^0	α_Q	α_Q^0	α_Q
Li^+	0.60	0.0347	0.0321	0.0304	0.0280	0.00673	0.00667	0.00470	0.00466
Be^{2+}	0.34	0.0133	0.0125	0.0081	0.0077	0.00183	0.00182	0.00063	0.00063
B^{3+}	0.20	0.0117	0.0112	0.0030	0.0029	0.00166	0.00165	0.00014	0.00014
C^{4+}	0.15	0.0094	0.0090	0.0014	0.0013	0.00113	0.00112	0.00004	0.00004
N^{5+}	0.11	0.0082	0.0078	0.0007	0.0007	0.00066	0.00066	0.00002	0.00002
N^{3-}	1.59	3.846	2.684	576.2	227.7	12.99	12.12	8878.5	1698.0
O^{2-}	1.32	1.717	1.349	137.9	79.9	3.943	3.694	1045.7	425.6
F^-	1.33	0.908	0.731	1.884	1.541	0.724	0.631	2.757	2.359
Na^+	0.95	0.171	0.147	0.166	0.143	0.0674	0.0628	0.0645	0.0601
Mg^{2+}	0.65	0.0927	0.0809	0.0809	0.0706	0.0266	0.0250	0.0218	0.0207
Al^{3+}	0.50	0.0600	0.0530	0.0452	0.0400	0.01367	0.01295	0.00917	0.00878
P^{5+}	0.37	0.0303	0.0273	0.0178	0.0160	0.00471	0.00451	0.00227	0.00220
S^{6+}	0.35	0.0232	0.0211	0.0119	0.0108	0.00330	0.00316	0.00123	0.00120
S^{2-}	1.84	7.709	4.893	38.09	21.92	21.54	19.68	138.66	82.05
Cl^-	1.81	4.270	2.694	6.527	4.198	6.22	5.53	11.65	9.73
K^+	1.33	1.216	0.827	1.144	0.773	0.816	0.751	0.724	0.669
Ca^{2+}	0.99	0.807	0.564	0.660	0.453	0.450	0.418	0.311	0.291
Sc^{3+}	0.73	0.753	0.540	0.418	0.292	0.396	0.362	0.153	0.145
Ti^{4+}	0.68	0.663	0.506	0.279	0.199	0.449	0.418	0.0844	0.0804
V^{5+}	0.65	0.179	0.107	0.197	0.142	0.404	0.112	0.0489	0.0468
Mn^{7+}	0.51	0.164	0.122	0.107	0.079	0.0388	0.0372	0.0194	0.0187
Ni^0				0.4072	2.385				
Cu^+	0.96	1.350	0.942	1.058	0.763	1.921	1.308	1.183	0.830
Zn^{2+}	0.74	0.919	0.676	0.427	0.332	1.072	0.774	0.276	0.196
Ga^{3+}	0.62	0.612	0.458	0.225	0.182	0.512	0.370	0.1000	0.0713
Se^{2-}	1.98	8.165	4.572	54.82	31.01	16.24	14.68	248.78	138.98
Br^-	1.95	5.645	3.263	9.431	5.731	7.19	6.25	18.96	15.69
Rb^+	1.48	2.223	1.383	2.081	1.284	1.855	1.688	1.641	1.499
Sr^{2+}	1.13	1.631	1.039	1.310	0.817	1.176	1.081	0.805	0.746
Y^{3+}	0.93	1.360	0.870	0.946	0.635	0.936	0.866	0.450	0.421
Pd^0				4.375	2.462			6.980	4.465
Ag^+	1.26	2.044	1.299	1.935	1.226	2.190	1.440	1.943	1.150
Cd^{2+}	0.97	1.359	0.890	1.046	0.696	1.162	0.788	0.772	0.517
I^-	2.16	9.335	5.013	14.64	8.251	17.33	15.54	38.50	33.11
Cs^+	1.69	4.373	2.492	3.996	2.237	5.676	5.181	4.520	4.096
Ba^{2+}	1.35	3.711	2.273	2.667	1.507	7.198	6.891	2.374	2.166

[a] In units of $Å^3$, α_D^0 referring to uncoupled results and α_D including consistency.

[b] In units of $Å^5$, α_Q^0 and α_Q having similar meaning as α_D^0 and α_D.

TABLE II. Comparison between theoretical and experimental dipole polarizabilities.[a]

Ion (atom)	Crystal ions				Free ions (atoms)		
	Experimental[c]		Theoretical[b]		Experimental[d]	Theoretical[b]	
	TKS	WC	α_D^0	α_D	α_D	α_D^0	α_D
Li^+	0.029	0.033 − 0.032	0.0347	0.0321	0.0283	0.0304	0.0278
Na^+	0.255	0.164 − 0.159	0.171	0.146	0.148	0.166	0.143
K^+	1.201	0.863 − 0.855	1.216	0.827	0.811	1.144	0.773
Rb^+	1.797	1.417 − 1.406	2.223	1.383	1.37	2.08	1.30
Cs^+	3.137	2.483	4.373	2.273	2.45	4.00	2.24
F^-	0.759	0.882 − 1.206	0.909	0.719	1.56	1.88	1.54
Cl^-	2.974	2.891 − 3.408	4.270	2.750	4.41	6.53	4.20
Br^-	4.130	4.023 − 4.606	5.638	3.261	5.84	9.43	5.95
I^-	6.199	5.857 − 6.726	9.335	5.013	8.91	14.64	8.25
He					0.2068	0.220	0.195
Ne					0.41	0.423	0.357
Ar					1.65	2.591	1.94
Kr					2.480	3.773	2.303

[a] Units of Å^3.

[b] α_D^0 refers to uncoupled results, and α_D including consistency.

[c] TKS: Tessmann, Kahn, and Shockley, Ref. 30; WC: Wilson and Curtis, Ref. 4, the ranges quoted indicating variations in α_D for individual ions in different crystals.

[d] The values listed here for the free ions were obtained (Ref. 4) from semiempirical fits of the type represented in Eq. (13), while the values listed for the rare gases are from atomic beam data and from index of refraction measurements, see Ref. 2.

ions, has been remarked upon in Sec. I. One can obtain further insight into this trend by examining the results in Fig. 3, where the charges densities for outermost shell $4p$ in the krypton-like ions Br^- and Sr^{2+} in the Watson sphere model, are compared with those for the free ions. This comparison demonstrates quantitatively the compression and expansion effects due to the crystal potential for the anion and cation respectively.

Additionally, there is an interesting trend in the percentage strengths of the crystal potential contributions to α_D and α_Q in going from the monovalent positive ion to the monovalent negative ion or the divalent positive ion. In both cases, the strengths of the crystal-field contributions are seen to increase for α_D as well as α_Q, the extents of increase being of course different for the two types of polarizabilities. The increase for the anion can be understood by realizing that the outermost electrons in this case are more polarizable, and therefore more severely affected by the crystal potential. The increase of the percentage strength of the crystal potential effect on α_D, in going to the divalent positive ion from the monovalent, is most likely a consequence of the stronger crystal potential for the former, since we have $q = -2$ in Eq. (3) as compared to $q = -1$ for the monovalent positive ion.

B. Comparison with experiment

Considering first the free ion (and rare-gas atom) results, the important role of consistency effects can be clearly seen from Table II from the remarkable improvement in all the systems of the agreement between theory and experiment,[2,4,30] when the decrease in α_D due to the consistency effect is incorporated. Overall, the agreement between the theoretical values of α_D and experiment is quite good, within 5% for almost all the systems, except for Cs^+ and I^-, where the difference between theory and experiment is close to 10%.

The importance of the consistency effect is also seen for the ions in the crystals from Table II, where the agreement with experiment is considerably better for α_D than for α_D^0. Also the crystal-field effect is seen to be of comparable importance in obtaining agreement with experiment by noticing the substantial increase in α_D in the direction of experiment in going from the free ion results to those for the ions in crystals. The overall good agreement between the theoretical α_D and experiment for all the ions in crystals indicates that the two important corrections to the free ion uncoupled α_D^0, namely, consistency and crystal potential effects, have been satisfactorily incorporated by the methods adopted here.

It is interesting however, that the agreement between our theoretical values of α_D and experiment are somewhat better for the positive ions, where $(\alpha_D)_{\text{theor}}$ are all seen to lie within the range of variation in $(\alpha_D)_{\text{expt}}$ over various crystals containing the same ions. For the negative ions, however, from Table II it is seen that the $(\alpha_D)_{\text{theor}}$ lie slightly outside (smaller than) the experimental range. We have examined a possible source for this difference in the extent of agreement with experiment for the cations and anions, namely possible uncertainty in the choice of R_0 in the Watson sphere model. Thus, on increasing the value of R_0 by as much as 10%, the changes in α_D for cations were found to be less than 4%, while for the anions the changes were closer to 10%, as seen for example from Fig. 4 for Cl^-. Thus, minor adjustments in R_0 could remove the small differences between experimental and theoretical α_D for the anions, although one cannot rule out similar small errors from the approximations in the procedures used for calculating[1,11,16,17,24] α_D^0 and the consistency contribution.[12,25]

C. Comparison with results from other procedures for free ions:

No comparable theoretical results including self-consistency are available for α_D and α_Q for ions in crystals to make comparisons with the present work. However, theoretical results are available for a number of free ions through application of the fully coupled Hartree-Fock (FCHF) method[13,17,31–34] and the effective-field (EF) method.[29] We have compared the results by these methods with ours in Table III for those cases where results are available by both, or at least one of these two methods. The results by the uncoupled procedure[1,11,16,17] are also

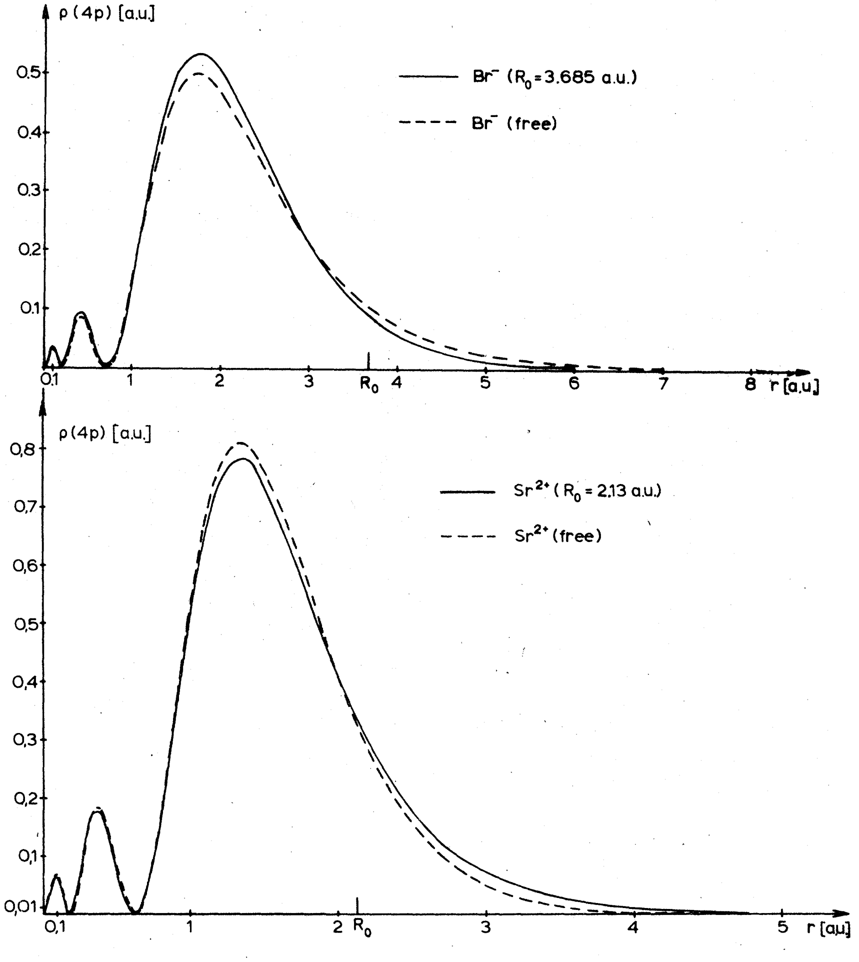

FIG. 3. Charge density ρ for the $4p$ shell for the free ions Br^- and Sr^{2+}, and for the ions Br^- and Sr^{2+} in a Watson sphere. R_0 is the radius of the sphere.

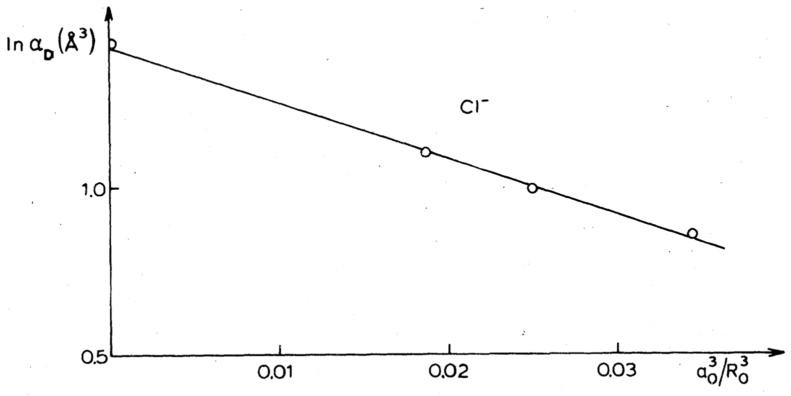

FIG. 4. Dependence of the calculated dipole polarizability for Cl^- as a function of the crystal potential represented by varying R_0, the radius of the Watson sphere. The points shown (0) are the calculated values. We have plotted $\ln\alpha_D$ as a function of $1/R_0^3$ because this is found to be nearly a straight line.

listed to obtain an assessment of the contributions from self-consistency effect by the different procedures.

Considering first the dipole polarizabilities α_D, there is overall very good agreement between our results and those by the EF[29] and FCHF procedure,[13,17,31–34] for the cases where they are available. The only two cases where there is some difference are Ar and Cl^-, our results in these cases being closer to FCHF than to EF. The differences in α_D for these two systems between our work and those from the FCHF procedure is not surprising in view of the significant range of values obtained for the uncoupled α_D^0 with different wave functions (see fourth column of Table III). It is important to note that a comparison of α_D^0 and α_D shows that the consistency

TABLE III. Comparison of polarizabilities α_D, α_D^0, α_Q, and α_Q^0 for free ions and atoms with results by other methods.

Ion (atom)	Dipole polarizabilities[a]						Quadrupole polarizabilities[b]				
	α_D^0			α_D			α_Q^0		α_Q		
	This work	Litt[c]	Langhoff-Hurst[d]	This work	EF[c]	FCHF[e]	This work	Litt[c]	This work	EF[c]	FCHF[e]
He	0.220	0.220	0.220	0.195	0.195	0.196[f,g,h]	0.0981	0.0979	0.0967	0.0962	0.0967[g,h]
Li^+	0.0304	0.0303	0.0304	0.0280	0.0280	0.0281[g]	0.00470	0.00469	0.00466	0.00464	0.00466[g]
F^-	1.884	1.806	1.953-1.893	1.541	1.283	1.40[i]	2.757	2.765	2.359	2.939	2.937[i]
Ne	0.423	0.414	0.473-0.418	0.357	0.348	0.350[i,h]	0.269	0.268	0.244	0.251	0.268[i,h]
Na^+	0.166	0.163	0.166-0.165	0.143	0.139	0.140[i]	0.0645	0.0641	0.0601	0.0590	0.0632[i]
Mg^{2+}	0.0809		0.0812	0.0706		0.0697[i]	0.0218	0.0218	0.0207	0.0200	0.0215[i]
Al^{3+}	0.0452		0.04525	0.0400		0.0393[i]	0.00917	0.00909	0.00878	0.00835	0.00895[i]
Cl^-	6.527	6.217	7.772-6.605	4.198	3.187	3.760[j]	11.65	11.77	9.73	13.17	11.92[j]
Ar	2.591	2.291	1.441-2.829	1.943	1.430	1.594[k,h]	2.216	2.059	1.992	2.069	2.084[h,l]
K^+	1.146	1.077	1.135	0.773	0.728	0.789[j]	0.725	0.718	0.669	0.698	0.674[j]
Ca^{2+}			0.652				0.311	0.308	0.291	0.292	
Br^-							18.96	18.916	15.69	20.96	
Rb^+							1.855	1.627	1.688	2.078	

[a] Units of Å^3, α_D^0 referring to uncoupled result and α_D including consistency.

[b] Units of Å^5, α_Q^0, and α_Q having similar meaning as α_D^0 and α_D.

[c] Refers to Effective Field approach (see Ref. 29).

[d] Reference 24.

[e] Refers to Fully Coupled Hartree-Fock approach (see for example Ref. 1).

[f] Cohen, Ref. 31.

[g] Langhoff *et al.*, Ref. 17.

[h] McEachran *et al.*, Ref. 33.

[i] Lahiri and Mukherji, Ref. 32.

[j] Lahiri and Mukherji, Ref. 13.

[k] Kaneko and Arai, Ref. 34; Lahiri and Mukherji, Ref. 13 have found $\alpha_D = 1.494$ Å^3.

[l] Lahiri and Mukherji, Ref. 13 have found $\alpha_Q = 1.957$ Å^5.

effect in all cases leads to a decrease in the polarizability by all three procedures, as one expects from physical considerations discussed earlier in this section. This similarity in trend and the good agreement in α_D is remarkable, considering the fact that consistency effects are included by very different procedures in the three cases.

For α_Q, again the overall agreement between our results and those by the other two procedures, wherever available, is satisfactory. A few exceptions are the cases of F^-, Cl^-, Br^-, and Rb^+. Of these, only F^- and Cl^- results are available in the case of FCHF,[13,32] our result for Cl^- being somewhat closer to the FCHF result than to EF.[29] What is noteworthy, is that except for these four cases, the consistency effect by the EF and FCHF procedures, obtained by comparison with uncoupled results, give the same trend of decrease as found from our results. Since the EF procedure, from considerations of flexibility of the variational approach used is expected to be somewhat less accurate than the FCHF procedure,[1,17] especially for α_Q, it would be desirable to have FCHF results for Rb^+ and Br^- to see if the trend in the direction of self-consistency contribution agrees with the present work or with the EF results.[29] Also, since in those cases where self-consistent one-electron results are available from many-body perturbation-theoretical calculations[12,15,18,19] good agreement has been found with the results of the present procedure, it would be helpful to have values of α_Q by the former for F^-, Cl^-, Br^-, and Rb^+ to check how they agree with the results from present work and the EF and FCHF procedures.

However, except for these few ions in the case of α_Q, the good agreement between α_D and α_Q by our procedure and the EF and FCHF procedure for the free ion systems, leads us to expect that similar agreement would be obtained between the different procedures for ions in crystals. It would however be interesting to check this expectation when results from FCHF and other procedure for α_D and α_Q for ions in crystals are available in the future.

IV. CONCLUSION

The results of the present work have demonstrated that both self-consistency effects and effects of the crystal environment have important influence on the dipole and quadrupole polarizabilities of ions in crystals, and have to be explicitly included in making quantitative comparisons with experimental data. Good agreement with experimental data for dipole polarizabilities has been obtained in cases where they are available. Many-body effects have not been included in the present analysis, but calculations by the many-body perturbation-theoretic procedure in a number of atomic systems[15] have shown that such effects are not important for polarizabilities. The physical reason for this is that polarizabilities usually arise from the outer regions of the ions, where the electron density is relatively small and so many-body effects are less pronounced. In addition, it should be remarked that the Watson sphere model[7] provides an approximate procedure for the incorporation of environment effects in the solid state including covalency. The present work has demonstrated that, at least for properties like the polarizabilities which do not depend explicitly on the departure from spherical symmetry in the ground state, the Watson sphere model does give a good representation of the influence of the crystal environment. It would however be desirable in the future to carry out, at least in a few ionic crystals, polarizability calculations using band wave functions as representation of the electronic distribution in the crystals. Such a calculation would avoid the use of the additivity approximation[4,30] involving the component ions, as has been done in analysis of experimental data[4,30] and the present work. A comparison of results of such an analysis with those of the present work would therefore provide a test of the adequacy of the additivity approximation. The importance of self-consistency effects found here indicates that in a band polarizability calculation as well these effects will have to be explicitly incorporated.

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[†] Permanent address: Dept. of Phys., State Univ. of New York, Albany, N.Y. 12222.

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