Theoret. Chim. Acta (Berl.) 59, 299–307 (1981)

THEORETICA CHIMICA ACTA

Comparative Studies of Static Dipole Polarizabilities of Ionic Crystals on the Basis of Different Self-consistent Potentials

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The static dipole polarizabilities, α^D, have been studied for the ions O^{2-}, F^-, Na^+, Mg^{2+}, Cl^-, K^+ and Ca^{2+} in the crystals NaF, KF, NaCl, KCl, MgO and CaO. The starting zero-order wave functions have been generated using various exchange- and exchange-correlation potentials in order to study the effect of these potentials on α^D. The direct contribution to the dipole polarizability, α_0^D, has been determined by the uncoupled Hartree–Fock method. Self-consistency effects have been included by the geometric approximation. The crystal potential is incorporated using the Watson sphere model. Good agreement between theoretical and experimental results are found for those self-consistent potentials which exclude self-interaction.

Key words: Dipole polarizabilities – Ionic crystals – Density functional theory.

1. Introduction

In the past 15 years potentials for many electron systems deduced from density functional theory have been successfully used for theoretical investigations of the electronic structure of atoms, molecules and solids [1–4]. Physical properties like atomic form factors [5], anti-shielding factors [6], ionization potentials [7], hyperfine interactions [8] and others have been investigated. On the basis of local potentials dipole polarizabilities α^D have been calculated within the X_α-model for free ions and atoms [9–11]. In this paper the influence of the type of the electronic potential V_{xc} on α^D is studied for ions in crystals for various exchange potentials, exchange-correlation potentials and potentials corrected for self-interaction, respectively. For those cases where Hartree–Fock (HF) data are

0040-5744/81/0059/0299/$01.80

available, $\alpha^D(V_{xc})$ is compared with α^D(HF). The direct contribution to α^D, α_0^D, the self-consistency correction α_1^D and the crystal field effect of ions in different crystals have been investigated. The Watson sphere model [12] has been used for the crystal potential. The Watson sphere parameter has been chosen according to the Madelung potential of the crystal considered [13] and α^D has been calculated for the ionic crystals NaF, KF, NaCl, KCl, MgO and CaO.

2. Theory

In this section the exchange-correlation and the external potentials used for the calculation of α^D are reported. Moreover, the method of calculating the polarizability is outlined.

2.1. Exchange-Correlation Potentials

In density functional theory the electronic potential is usually written as [14, 15]

$$V_{el}(r) = V_x(r) + V_c(r) + \int \frac{\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\tau' \tag{1}$$

where $\rho(\boldsymbol{r})$ is the total electron density.

V_x is the Hartree–Fock exchange potential in the Gáspár–Kohn–Sham (GKS) model [14, 16]

$$V_x(r) = -\left(\frac{3}{\pi}\rho(r)\right)^{1/3} \tag{2}$$

and V_c is the correlation potential. A parametrized expression for V_c is given by Hedin and Lundquist [17]

$$V_c(r) = -0.0193 \ln(1 + 39.17\rho^{1/3}(r)). \tag{3}$$

The GKS exchange potential, Eq. (2), is by a factor of $\frac{2}{3}$ smaller than the local exchange potential proposed by Slater in 1951, [18]. In the X_α-method [1] a variable exchange parameter α is used:

$$V_{x,\alpha} = \tfrac{3}{2}\alpha V_x. \tag{4}$$

It is found that the X_α model predicts instability for stable negative free ions, originating from the wrong long range behaviour of the electronic potential [19]. Within the X_α model a far-off electron of an atomic system with N electrons "sees" the repulsion potential of N electrons (V^N-potential) rather than that of N-1 electrons (N^{N-1}-potential). This is due to the self-interaction term in $V_{x,\alpha}$ which does not exactly cancel the self-Coulomb term as in the HF scheme. The Gáspár–Kohn–Sham potential for an electron i corrected for the self-interaction is given by Lindgren [20],

$$V_x^{\mathrm{HS}}(r) = -\int \frac{\rho_i(r')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\tau' - \left[\left(\frac{3}{\pi}\rho(r)\right)^{1/3} - \left(\frac{6}{\pi}\rho_i(r)\right)^{1/3}\right], \tag{5}$$

where ρ_i is the electron density of the electron considered.

This orbital dependent Hartree–Slater (HS) potential is successfully used by Lindgren and Rosén [8] for the study of hyperfine interactions in atoms. Other exchange potentials corrected for self-interaction, which are also studied in this paper, are proposed by Cowan [21] and Gopinathan [22].

2.2. *Crystal Potential*

The crystal potential of the ions considered is simulated by a hollow charged sphere (Watson sphere model [12]). The total charge q of the sphere is taken equal to the charge of the ion but opposite in sign. The radius R_0 of the sphere is chosen in such a way that the model potential is equal to the Madelung potential at the nuclei sites [13]. In this model the crystal potential is given by

$$V_W(a, r) = \begin{cases} q/R_0(a) & \text{for } r \le R_0(a) \\ q/r & \text{for } r > R_0(a) \end{cases};$$

$$R_0(a) = a/M$$

where a is the lattice constant of the crystal and M is the Madelung constant of the structure; $M = 3.49513$ for the crystals considered here. The dipole polarizability is calculated separately for the anions and the cations.

Therefore, the overlap of the wave functions of the ions in the crystals [23] is not taken into account. α^D for a crystal with lattice constant a is simply calculated by adding

$$\alpha^D(a) = \alpha^D_{\text{anion}}(a) + \alpha^D_{\text{cation}}(a).$$

2.3. *Dipole Polarizability* α^D

The method chosen for the calculation of α^D is discussed elsewhere for the case of HF potentials [24]. The direct contribution to α^D, α_0^D, is derived by the simplified uncoupled HF method [25]. From the determinantal wave functions $\Phi_0 + \delta\Phi$ of the one-electron perturbed orbitals $\varphi_m + \delta\varphi_m$ the first order self-consistency contribution to α^D, α_1^D, is determined from the expectation value

$$\alpha_1^D = -2\langle \Phi_0 + \delta\Phi | \mathcal{H}_1 | \Phi_0 + \delta\Phi \rangle \tag{6}$$

where $\mathcal{H}_1$,

$$\mathcal{H}_1 = \sum_{p>m}^{N} v(r_m, r_p) - \sum_{m}^{N} V_m^{\text{SCF}}; \tag{7}$$

$$v(r_m, r_p) = 1/|\boldsymbol{r}_m - \boldsymbol{r}_p|; \tag{8}$$

is the difference in the actual electron-electron potential and the self consistent potential V^{SCF} used for the calculation of the zero order orbitals φ_m.

In terms of φ_m and $\delta\varphi_m$ α_1^D is given by

$$\alpha_1^D = \alpha_{1,\text{HF}}^D + \delta\alpha_1^D, \tag{9}$$

where $\alpha_{1,\text{HF}}^D$ is equal to α_1^D for the case of HF potentials and $\delta\alpha_1^D$ is an additional term for the case of non HF potentials:

$$\alpha^{D}_{1,\mathrm{HF}} = -4 \sum_{m<p} [2\langle \varphi_m \varphi_p | v | \delta\varphi_m \delta\varphi_p \rangle - \langle \delta\varphi_m \varphi_p | v | \delta\varphi_p \varphi_m \rangle - \langle \varphi_p \varphi_m | v | \delta\varphi_m \delta\varphi_p \rangle] \tag{10}$$

$$\delta\alpha^{D}_{1} = -2 \sum_{m} \left[\langle \delta\varphi_m | V^{\mathrm{SCF}}_{xc} | \delta\varphi_m \rangle - \sum_{p} \langle \varphi_p \delta\varphi_m | v | \delta\varphi_m \varphi_p \rangle \right]. \tag{11}$$

Higher order self-consistency contributions are included by the geometric approximation [26],

$$\alpha^{D} = \alpha^{D}_{0} \left(1 - \frac{\alpha^{D}_{1}}{\alpha^{D}_{0}} \right)^{-1}. \tag{12}$$

It shall be pointed out, that Eq. (6) does not include all terms of first order in the perturbing electric field and of first order in self-consistency, if V^{SCF}_{m}, Eq. (7), is a non HF potential. For non HF potentials terms from $\delta\Phi'$ should be included, where $\delta\Phi'$ is the first order perturbed wave function in $\mathscr{H}_1$, Eq. (7). These terms have been neglected in the present work. They have not been studied in the literature for α^D so far. However, Ahmad and Newman [27] have shown by the linked-cluster-many-body-perturbation theory for the case of the antishielding factor of Pr^{3+} that these neglected terms amount to only 5% of the total first order self-consistency effects.

3. Results

In Table 1 the experimental and theoretical results for α^D are listed for various ionic crystals. The agreement between α^D(exp), α^D(HF) and α^D(HS) is quite good taking into consideration the simplicity of the model crystal potential, the omission of correlation effects in the geometric approximation for α^D, the problem of covalency especially for the oxids, and obtaining the experimental results by means of the Clausius–Mossotti relation (see e.g. [31]).

For the V^N potentials α^D(theor) is always larger than the experimental value. It is found that the geometric approximation is less appropriate for V^N-potentials than for V^{N-1}-potentials. Especially for negative free ions $\alpha^D_1(V^N)$ can be larger in size than $\alpha^D_0(V^N)$ and the geometric approximation is probably no suitable method for these systems.

Recently Mahan [30] has studied α^D for alkali halides using a crystal potential similar to the Madelung potential described here. The results of Mahan are given in the last column of Table 1. The differences between his and our results are discussed in the next section.

4. Discussion

Two aspects shall be considered in this section. Firstly the direct contribution to α^D, α^D_0, and the first order self-consistency correction α^D_1 shall be studied for Cl^-.

Table 1. Static dipole polarizability α^D in $Å^3$ for several ionic crystals calculated by different self-consistent procedures

	Gáspár–Kohn–Sham (GKS)			Hedin–Lundquist (HL)			Hartree–Slater (HS)			Hartree–Fock (HF)[a]			exp[b]	Mahan[c]
crystal	cation	anion	sum	cation	anion	sum	cation	anion	sum	cation	anion	sum	sum	sum
NaF	0.267	2.682	2.949	0.239	2.126	2.365	0.148	1.117	1.265	0.147	1.033	1.180	1.163	0.83
KF	1.455	3.448	4.903	1.248	2.617	3.865	0.856	1.258	2.114	0.822	1.144	1.966	2.008	1.69
NaCl	0.246	5.432	5.678	0.222	4.494	4.716	0.146	3.407	3.553	0.146	2.988	3.134	3.263	3.76
KCl	1.333	6.158	7.491	1.157	5.003	6.160	0.832	3.703	4.535	0.808	3.194	4.002	4.173	4.72
MgO	0.140	5.152	5.292	0.130	4.021	4.151	0.073	2.273	2.346				1.743	
CaO	1.035	7.815	8.850	0.922	5.757	6.679	0.500	2.973	3.473				2.910	

[a] Schmidt, Sen and Weiss, Ref. [28].
[b] Tessman, Kahn and Shockley, Ref. [29].
[c] Mahan, Ref. [30].

We have chosen Cl^- as an example because the differences in α^D for different potentials, see Table 1, are most pronounced for negative ions. Secondly the influence of the various crystal potentials on α^D shall be discussed.

In Table 2 $\alpha^D(Cl^-)$ is given for different V^N- and V^{N-1}-potentials. The V^N-potentials used here are the Hedin–Lundquist (HL) potential [17], and potentials including $V_{x,\alpha}$, Eq. (4), with $\alpha = \frac{2}{3}$ (Gasper–Kohn–Sham (GKS) potential [14, 16]) $\alpha = \alpha_{\mathrm{HF}}$ (Hartree–Fock adapted (HFA) potential [32]) and $\alpha = 1$ (Hartree–Fock–Slater (HFS) potential [18]).

For V^{N-1} potentials the results for the HF potential, the Hartree–Slater (HS) potential of Rosen and Lindgren [20, 8], the potential of Cowan [21] and the potential of Gopinathan [22] are chosen. It is found that the Cowan and Gopinathan potentials give nearly the same results for α^D. Calculating α^D as a function of the exchange parameter α in the Cowan or Gopinathan approach ($\alpha^D(C, G)$), it is found that $\alpha = 0.5$ gives results for $\alpha^D(C, G)$ which are close to the corresponding HF results.

Considering first α_0^D it can be seen from Table 2 that α_0^D depends sensitively on the chosen exchange parameter α. The results $\alpha_0^D(\mathrm{HFA})$, $\alpha_0^D(\mathrm{HL})$, $\alpha_0^D(\mathrm{HS})$ and $\alpha_0^D(C, G;\ \alpha = 0.5)$ are nearly equal, which means that the smooth attractive correlative potential $V_c(\mathrm{HL})$, Eq. (3), has nearly the same effect as the increase of the exchange parameter α in the X_α-method from $\alpha = \frac{2}{3}$ to $\alpha = \alpha_{\mathrm{HF}}$ (=0.72325 for Cl) and the same effect as the exclusion of self repulsion. $\alpha_0^D(\mathrm{HFA})$, $\alpha_0^D(\mathrm{HL})$ and $\alpha_0^D(\mathrm{HS})$ are larger than $\alpha_0^D(\mathrm{HF})$, because the outermost orbitals of negative ions are slightly more diffuse in the HFA-, HL- and HS-approximations than in the HF approach. As α_0^D also $\alpha_{1,\mathrm{HF}}^D$ is nearly the same for the methods given above, however, $\delta\alpha_1^D$ is quite different for the V^N- and the V^{N-1}-potentials. This is due to the self-energy terms in $\delta\alpha_1^D(p = m$ in Eq. (11)). In contrast to the V^{N-1}-potentials one gets a net self-energy term in $\delta\alpha_1^D$ for the V^N-potentials, which is positive in sign and which is the dominant contribution to α_1^D. Therefore, $\delta\alpha_1^D(V^N)$ and $\delta\alpha_1^D(V^{N-1})$ are different in size and in sign. The differences in $\delta\alpha_1^D$ cause quite different results for the total α^D (last row in Table 2) gained from the geometric approximation. There is some doubt whether the self-consistency effects on α^D are described correctly by the geometric approximation for V^N potentials.

Next the results of Mahan [30], last column in Table 1, shall be discussed. For his calculations Mahan has taken an exchange-correlative potential without self-interaction. Because the correlation potential used by Mahan is a smooth attractive function like Eq. (3), his values for α^D should be smaller than $\alpha^D(\mathrm{HS})$, 10th column of Table 1, for which the potential V_c is omitted. However Mahan has not included self-consistent effects in the calculation of α^D and therefore $\alpha^D(\mathrm{Mahan}) < \alpha^D(\mathrm{HS})$ does not hold for all alkali halides. As can be seen from Table 2 these self-consistent effects are very important for negative ions and α_1^D decreases the total α^D. Therefore the inclusion of self-consistent effects would lower $\alpha^D(\mathrm{Mahan})$ below $\alpha^D(\mathrm{HS})$ and also below $\alpha^D(\exp)$ for all alkali halides. It may be that a more realistic function for the electron correlation potential V_c

Table 2. Dipole polarizability α^D in Å^3 for Cl$^-$ within a Watson sphere ($R_0 = 1.81$ Å) α_0^D is the direct contribution to α^D and $\alpha_{1,\mathrm{HF}}^D$ and $\delta\alpha_1^D$ are the first order self-consistency corrections to α^D

Type of potential	V^N				V^{N-1}			
method[a]	$X_\alpha(GKS)$	X_α(HFA)	X_α(HFS)	HL		C, G	HS	HF
exchange parameter	2/3	0.72325	1		1	0.5		
α_0^D	6.446	5.851	3.822	5.871	2.865	5.040	5.793	5.146
$\alpha_{1,\mathrm{HF}}^D$	−3.634	−3.284	−2.113	−3.351	−1.589	−2.981	−3.359	−3.083
$\delta\alpha_1^D$	3.377	2.708	0.781	2.370	−0.845	−0.313	0.128	—
α^D	6.198	5.327	2.835	5.031	1.549	3.048	3.719	3.218

[a] GKS=Gáspár–Kohn–Sham; HFA=Hartree–Fock adapted; HFS=Hartree–Fock–Slater; HL=Hedin–Lundquist; C, G=Cowan, Gopinathan; HS=Hartree–Slater; HF=Hartree–Fock.

Table 3. Relative change of the dipole polarizability α^D for several ions as a function of the crystal potential of the crystals given in Table 1, e.g. for $\mathrm{F}^- \Delta V/V = (V_M(\mathrm{NaF}) - V_M(\mathrm{KF}))/V_M(\mathrm{NaF})$ and $\Delta\alpha^D/\alpha^D = (\alpha^D_{\mathrm{anion}}(\mathrm{NaF}) - \alpha^D_{\mathrm{anion}}(\mathrm{KF}))/\alpha^D_{\mathrm{anion}}(\mathrm{NaF})$, where V_M is the lattice potential

		$\Delta\alpha^D/\alpha^D \cdot 100$[a]			
Ion	$\frac{\Delta V}{V}100$	GKS	HL	HS	WC
Na^+	−17.8	−8.5	−7.7	−1.4	−1.8
K^+	−15.0	−9.2	−7.9	−2.9	−0.9
F^-	13.4	22.2	18.8	11.2	10.1
Cl^-	10.4	11.8	10.2	7.8	6.7
O^{2-}	12.3	34.1	30.2	23.5	

[a] GKS = Gáspár–Kohn–Sham potential; HL = Hedin–Lundquist potential; HS = Hartree-Slater potential; WC = semiempirical results of Wilson and Curtis [33].

has nodes as found for the helium atom [15]. However to investigate all aspects of correlative effects more quantitatively, the model for the crystal has to be improved simultaneously, because our results α^D(HS), which exclude correlative effects, are already close to the experimental results.

Finally in this section the influence of the crystal potential on α^D shall be considered. Table 3 shows for different ions the percentage change of the lattice potential V_W and α^D(HS) and α^D(HL) for the crystals given in Table 1. As expected the change in α^D is mostly pronounced for the weakly bonded electrons of O^{2-}. The changes $\Delta\alpha^D/\alpha^D$ for the HS (and HF) procedure for the alkali halides are in agreement with semi empirical calculations of Wilson and Curtis [33] which are listed in Table 3, too.

5. Conclusions

From the investigations reported here it can be seen that:

(a) The calculated values of α^D depend strongly on the model chosen for the self-consistent potential; especially α^D varies drastically as a function of the exchange parameter α.

(b) The V^N-exchange-correlative potentials lead to values α^D, which are mostly larger than the corresponding Hartree–Fock (HF)- and experimental values.

(c) Besides HF the Hartree–Slater (HS) approximation gives good results for α^D in ionic crystals. On the basis of the Watson sphere model the difference in α^D(exp) and α^D(HS) is less than 10% for the alkali halides.

Acknowledgements. The authors are grateful to Prof. Dr. Al. Weiss for his continuing interest in this work and helpful discussions. We are indebted to the "Deutsche Forschungsgemeinschaft" for financial support.

References

1. Slater, J. C.: Quantum theory of molecules and solids, Vol. 4. New York: McGraw-Hill 1979
2. Johnson, K. H.: Intern. J. Quantum Chem. **15**, 361 (1967); **45**, 153 (1971)
3. Morazzi, V. L., Williams, A. R., Janak, J. F.: Calculated electronic properties of metals, Chap. V. New York: Pergamon Press 1978
4. Hedin, L., Lundquist, S.: Solid State Physics **23**, 1 (1969)
5. Schwarz, K., Schulz, H.: Acta Crystallogr. **A34**, 994 (1978)
6. Sen, K. D., Narasimhan, P. T.: Phys. Rev. **B16**, 107 (1977); Lauer, S., Marathe, V. R., Trautwein, A.: Phys. Rev. **A19**, 1852 (1979)
7. Schwarz, K.: J. Phys. **B11**, 1339 (1978)
8. Lindgren, I., Rosén, A.: Case studies in atomic physics **4**, 93 (1974)
9. Feiock, F. D., Johnson, W. R.: Phys. Rev. **187**, 39 (1969)
10. Talman, J. D., Ganas, P. S., Green, A. E. S.: Intern. J. Quantum Chem. **S13**, 67 (1979)
11. Hameed, S.: Phys. Rev. **A4**, 543 (1971)
12. Watson, R. E.: Phys. Rev. **111**, 1108 (1958)
13. Paschalis, E., Weiss, Al.: Theoret. Chim. Acta (Berl.) **13**, 381 (1969)
14. Kohn, W., Sham, L. I.: Phys. Rev. **140A**, 1133 (1965)
15. Smith, D. W., Jagannathan, S., Handler, G. S.: Intern. J. Quantum Chem. **S13**, 103 (1979)
16. Gáspár, R.: Acta Phys. Acad. Sci. Hung. **3**, 263 (1954)
17. Hedin, L., Lundquist, S.: J. Physique **33 (C3)**, 73 (1972)
18. Slater, J. C.: Phys. Rev. **81**, 385 (1951)
19. Schwarz, K.: Chem. Phys. Letters **57**, 605 (1979); Sen, K. D.: Phys. Letters **74**, 201 (1980); Zunger, A., Perdew, I. P., Oliver, G. L.: Solid State Commun. **34**, 933 (1980)
20. Lindgren, I.: Intern. J. Quantum Chem. **5**, 411 (1971)
21. Cowan, R. D.: Phys. Rev. **163**, 54 (1967)
22. Gopinathan, M. S.: Phys. Rev. **A15**, 2135 (1977)
23. Löwdin, P. O.: Adv. Phys. **5**, 3 (1956)
24. Schmidt, P. C., Sen, K. D., Weiss, Al., Das, T. P.: Phys. Rev. **B19**, 5525 (1979); Sen, K. D., Schmidt, P. C.: Intern. J. Quantum Chem., 373 (1981)
25. Langhoff, P. W., Hurst, R. P.: Phys. Rev. **139A**, 1415 (1965); method d in : Langhoff, P. W., Karplus, M., Hurst, R. P.: J. Chem. Phys. **44**, 505 (1966)
26. Hirschfelder, J. O., Byers Brown, W., Epstein, S. T.: Adv. Quant. Chem. **1**, 255 (1964); Epstein, S. T., Johnson, R. E.: J. Chem. Phys. **47**, 2275 (1967); Kelly, H. P.: Adv. Chem. Phys. **14**, 129 (1969); Kelly, H. P.: Atomic Phys. **2**, 227 (1971)
27. Ahmad, S., Newman, D. I.: J. Phys. **C12**, 1245 (1979)
28. Schmidt, P. C., Sen, K. D., Weiss, Al.: Ber. Bunsenges. Phys. Chem. **84**, 1240 (1980)
29. Tessman, I. R., Kahn, A. H., Shockley, W.: Phys. Rev. **92**, 890 (1953)
30. Mahan, G. D.: Solid State Ionics **1**, 29 (1980)
31. Claro, F. H.: Phys. Rev. **B18**, 7058 (1978)
32. Schwarz, K.: Phys. Rev. **B5**, 2466 (1972)
33. Wilson, I. N., Curtis, R. M.: J. Phys. Chem. **74**, 187 (1970)

Received August 25, 1980/February 3, 1981