Theoret. Chim. Acta (Berl.) 52, 181–187 (1979)

THEORETICA CHIMICA ACTA

Sternheimer Antishielding Factors of F^-, Cl^-, Br^- and I^-:

Influence of Approximate Free- and Crystal-Ion Potential*

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Sternheimer ionic antishielding factors, γ_∞, have been calculated for F^-, Cl^-, Br^-, and I^- in crystals using the Watson model within the nonrelativistic Hartree–Fock approximation and the perturbation numerical procedure. The free ion calculations of γ_∞ using the Hartree–Fock wave functions have also been carried out in order to ascertain the solid-state effects. The free ion values of γ_∞ change from -22.2, -55.1, -135.106, and -248.1 to -10.3, -34.8, -75.6, and -148.7 in solids for F^-, Cl^-, Br^-, and I^-, respectively. A major part of the discrepancy between the free ionic γ_∞ values based on the Hartree–Fock and Hartree–Fock–Slater wave functions, as noted by the previous workers, is shown to arise from an inaccurate description of the self-interaction potential in the conventional Slater exchange approximation.

Key words: Sternheimer ionic antishielding factors

1. Introduction

The Sternheimer quadrupole ionic antishielding factor [1], γ_∞, plays an important role in the theory of electric field gradients in ionic solids, where it is conventionally assumed that

$$eq = (1 - \gamma_\infty)eq_{\text{ion}}. \tag{1}$$

The negative halogen ions F^-, Cl^-, Br^-, and I^- are expected to undergo significant radial contraction in their electronic charge densities on going from free to the crystalline state. Earlier calculations of γ_∞, which account for the solid state effects,

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* Dedicated to Prof. Dr. H. Hartmann on the occasion of his sixty-fifth birthday.

** Alexander von Humboldt fellow, on leave of absence from the University of Hyderabad, India.

0040–5744/79/0052/0181/$01.40

may be grouped into the following two categories: a) the calculations [2, 3] which are based on the Hartree–Fock (HF) wave functions for the ground state followed by one of the less accurate variation-perturbation methods of Langhoff *et al.* [4] to calculate γ_∞, and b) the calculations wherein [5] γ_∞ is obtained using the more accurate perturbation-numerical (differential equation, DE) approach due to Sternheimer [1] but with ground state functions less accurate than the HF wave functions, usually in terms of the treatment of exchange potential. The purpose of this paper is to report the results of our calculations of γ_∞ for F^-, Cl^-, Br^-, and I^- in ionic solids using the HF wave functions and the DE method, respectively. The Watson model [6] was used to simulate the electrostatic potential due to the crystalline lattice in ionic solids. Further, we have also attempted to understand the cause of the large discrepancy, noted earlier [5, 7], between the free ion calculations of γ_∞ based on the Hartree–Fock–Slater [8] (HFS), and HF wave functions, respectively. In particular, we have studied the effect of treating the self-interaction potential accurately within the Slater-like exchange approximation in atoms as proposed by Gopinathan [9].

In Sect. 2 we describe in brief the method of calculation adopted in the present work. The details about the perturbation-numerical approach and the improved approximation to the HF exchange potential are available in Refs. [1] and [9] respectively. In Sect. 3, we present and discuss the results of our calculations. Finally, the main conclusions are summarized in Sect. 4.

2. Calculations

The one-electron HF equations, in Rydberg units, can be written as

$$[f_1 + V_c(r) + V_s(r) + V_{ex}(r)]u_i(r) = \epsilon_i u_i(r), \tag{1}$$

where u_i's are the spin orbitals with occupancy n_i; $f_1 = -\nabla^2 - 2Z/r$; V_c, V_s, and V_{ex} respectively represent the Coulomb potential, self-interaction, and the characteristic HF exchange-potential for the ith electron and are defined by

$$V_c(r) = \sum n_j \int u_j^*(r')u_j(r')g_{rr'}dr' \tag{2}$$

$$V_s(r) = -n_i \int u_i^*(r')u_i(r')g_{rr'}dr' \tag{3}$$

and

$$V_{ex}(r) = -\sum_{j\neq i}{}' \frac{(n_j \int u_i^*(r)u_j^*(r')u_j(r)u_i(r)g_{rr'}dr')}{u_i^*(r)u_i(r)} \tag{4}$$

In the HFS approximation,

$$V_s + V_{ex} = -6C\alpha\rho^{1/3}(r), \tag{5}$$

where α is the Slater exchange parameter, $C = (3/4\pi)^{1/3}$, and the electronic density $\rho(r) = \sum n_i u_i^*(r)u_i(r)$. One of the main drawbacks of the HFS approximation is that the potential in Eq. (5) vanishes at large r as against the correct HF limit of

$-2/r$ as $r \to \infty$. This is due to the fact that V_s is under-estimated in the HFS approximation. In order to overcome this defect one usually employs the Latter tail-correction [10] in the HFS approximation. Using the characteristic properties of the Fermi-hole and assuming that the density varies linearly over the Fermi-sphere, Gopinathan [9] has derived that

$$V_{\mathrm{ex}}(r) = -9\frac{C\alpha}{2}\left(2\rho_i'(r)\rho^{-2/3}(r) - \tfrac{2}{3}\rho^{-5/3}(r)\sum_{\mathrm{spin}} n_i u_i(r) u_i(r) \rho_i'(r)\right) \tag{6}$$

with

$$\alpha = \frac{8}{(2\pi)^{2/3}} \frac{\left(\dfrac{1}{n}+\dfrac{1}{2}\right)}{\left(\dfrac{1}{n}+\dfrac{1}{3}\right)^{2/3}}, \tag{7}$$

where n gives the number of electrons of a given spin.

ρ_i' gives the total charge density, ρ_i, less the ith electron density. The use of Eqs. (6) and (7) lead to the correct asymptotic behaviour of $(V_s + V_{\mathrm{ex}})$ as $r \to \infty$, since the self-interaction is exactly evaluated for each orbital. Also, the theoretical values of α rather than the empirical ones can be used in the calculations. The wave functions obtained from Eqs. (1), (5) and (6) will be respectively denoted by HF, HFS, and HFG wave functions.

In the Watson model [6] for ions in crystals, the electrostatic potential due to the crystalline lattice is realized by superimposing around a given ion, a uniformly charged hollow sphere carrying a total charge equal and opposite to the ion in question. The radius of the sphere r_{ion}, is taken as the Pauling ionic radius [11] of the central ion. Thus, the crystal-ion wave functions are generated self-consistently using the following additional potential, V_{w}, in Eq. (1), due to the Watson sphere,

$$\begin{aligned} V_{\mathrm{w}} &= \frac{2n_{\mathrm{ion}}}{r_{\mathrm{ion}}} \quad \text{for} \quad r_i \leqslant r_{\mathrm{ion}} \\ &= \frac{2n_{\mathrm{ion}}}{r_i} \quad \text{for} \quad r_i \geqslant r_{\mathrm{ion}}. \end{aligned} \tag{8}$$

The calculations of γ_∞ require the knowledge of the first-order perturbed wave functions, $u'(nl \to l')$, due to the nuclear quadrupole moment and these are obtained by solving the following inhomogeneous differential equation:

$$\left[\frac{d^2}{dr^2} + \frac{l'(l'+1) - l(l+1)}{r^2} + \frac{1}{u(nl)}\,\frac{d^2 u(nl)}{dr^2}\right] u'(nl \to l') = u(nl)\left[\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl}\right], \tag{9}$$

where the unperturbed radial wave functions $u(nl)$ satisfy the orthonormality conditions

$$\int_0^\infty u^2(nl)\,dr = 1 \tag{10}$$

and

$$\int_0^\infty u(nl)u'(nl \to l')\, dr = 0. \tag{11}$$

Finally, γ_∞ is calculated according to

$$= \sum_{nl} c(nl \to l') \int_0^\infty u(nl)u'(nl \to l')r^2\, dr, \tag{12}$$

where the angular integrals corresponding to the various radial ($l = l'$) and angular ($l \neq l'$) excitations have been calculated by Sternheimer [1]. The numerical methods of solving Eq. (9) and evaluating the various radial integrals have been described elsewhere [12].

The free ion wave functions for F^- and Cl^- have been obtained within the HFS and HFG approximation respectively in order to estimate the extent of disagreement between γ_∞ values based on the HF and HFS wave functions arising from the incorrect description of the self-interaction term in the latter. We have used a substantially modified Herman–Skillman program [13] with the option of 441-point mesh to generate the ground state wave functions within the HFG and HFS approximations respectively. The α values for the HFG approximation have been taken according to Eq. (7). The HF wave functions for the free and crystal ions of F^-, Cl^-, Br^-, and I^- have been generated over the 441-point mesh using the analytic wave functions calculated by Paschalis and Weiss [3].

3. Results and Discussion

The shellwise contributions to γ_∞ for the free ions of F^- and Cl^- using HF, HFG, and HFS wave functions are listed in Tables 1 and 2 respectively. Our total γ_∞ values using HF wave functions are -22.2 and -55.1 for F^- and Cl^- respectively which are in exact agreement with the $(\gamma_\infty)_0$ values reported recently by Beri *et al.* [14] using the HF functions of Clementi *et al.* [15]. The γ_∞ values based on HFS wave functions are known [5, 7] to be nearly twice as large as the corresponding

Table 1. The shell-wise contributions to γ_∞ for the free F^- ion using the Hartree–Fock (HF), modified Hartree–Fock–Slater (see Eqs. 6–7 of text) (HFG), and Hartree–Fock–Slater (HFS) wave functions, respectively

Perturbation	HF	HFG	HFS
$1s \to d$	0.079	0.080	0.078
$2s \to d$	0.324	0.316	0.313
$2p \to f$	0.512	0.456	0.510
Tot. Ang.	0.92	0.851	0.901
$2p \to p$	−23.022	−15.773	−41.998
Tot. Rad.	−23.022	−15.773	−41.998
Total	−22.106	−14.921	−41.098

Table 2. The shell-wise contributions to γ_∞ for the free Cl^- ion using Hartree–Fock (HF), modified Hartree–Fock–Slater (HFG), and the HFS wave functions, respectively

Perturbation	HF	HFG	HFS
$1s \to d$	0.041	0.041	0.041
$2s \to d$	0.119	0.119	0.119
$3s \to d$	0.443	0.381	0.381
$2p \to f$	0.159	0.155	0.156
$3p \to f$	0.719	0.658	0.701
Tot. Ang.	1.481	1.345	1.398
$2p \to p$	−1.522	−1.528	−1.5389
$3p \to p$	−55.027	−47.422	−81.903
Tot. Rad.	−56.549	−47.513	−83.442
	−55.068	−46.028	−82.0445

HF estimates. As is evident from the results in Tables 1 and 2, the accurate treatment of self-interaction in the HFG approximation substantially improves the γ_∞ values within the Slater-like exchange approximation. For F^-, the HFG wave functions result in $\gamma_\infty = -15$ to be compared with the HF and HFS estimates of -22 and -41 respectively. Similarly for Cl^-, the HFG, HF, and HFS estimates of γ_∞ are -46, -55, and -82 respectively. We therefore conclude that the major part of discrepancy noted previously between the γ_∞ results based on HF and HFS wave functions is due to the inaccurate treatment of self-interaction (see Eq. (3)). The numerically smaller magnitudes of γ_∞ obtained within the HFG approximation are due to the overemphasis of the exchange potential for the outer orbitals. Nevertheless, with respect to the calculations of γ_∞, the nonlocal HFG potential provides a significantly improved approximation to the HF potential as compared to the more popular HFS potential without any additional computing efforts. Similar conclusions have also been obtained in the recent calculations of spin densities [9] in 3*d* ions. It would be worthwhile to try HFG wave functions in the calculations of polarizabilities [16] and of hyperfine interaction constants [17] in alkali atoms.

The net γ_∞ results for F^-, Cl^-, Br^-, and I^- ions in the free and solid state, obtained in the present work using HF wave functions, are given in Table 3. For comparison we have also listed there the γ_∞ values for these ions obtained so far by the other workers. The crystal-ion γ_∞ values, given in column 4 in Table 3, pertain to the radius of the Watson sphere equal to the Pauling ionic radius. Due to the presence of the stabilizing potential for the ion in the solid, the total radial charge density undergoes a net contraction relative to the free ion case. This amounts to nearly 40–50% reduction in γ_∞ as the halogen negative ions are stabilized in ionic solids.

In Table 4 we have studied the variation of γ_∞ for F^- and Cl^- as a function of the radius, r_{ion}, of the Watson sphere. Near the Pauling radius (shown as starred), the γ_∞ values do not change very significantly due to the small changes ($\leqslant 0.1$ Å) in

Table 3. Total γ_∞ values for the free ions and ions in crystals using HF wave functions. The crystal ion values correspond to the Pauling ionic radius of 1.33, 1.81, 1.95 and 2.16 Å for F^- Cl^-, Br^- and I^-, respectively

	Free ion		Crystal ion	
Ion	This work	Others	This work	Others
F^-	−22.106	−66.86, −23.22, −25.71, −21.11[a]; −22.53[b], −23.03, −22.15, −22.12, −22.0[c], 29.88[d], −37.61[e], −41.109[f]; −42.190[g], 19.29[h]	−10.306	−14.583[f], −10.62[o], −10.16[p]
Cl^-	−55.068	−53.91[c], −101.116[e], −82.047[f]; −83.50[g], −56.58[h], −56.6[i], −49.28[j]; −78.3[k]; −63.21[l]	−34.801	−27.04[a], −54.99[f] −37.64[o] −33.64[p]
Br^-	−135.106	−123.0[b]; −244.3[e]; −195.10[f]; −210.0[g]; −140.83[h]; −99.0[j]; −100.0[m]	−75.586	−97.424[f] −73.41[p]
I^-	−248.052	−331.633[f]; −396.10[g]; −178.75[j]; −175[m]; −138.4[n]	−148.710	−177.732[f] −141.91[p]

[a] See Ref. [2] of text.

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Table 4. Variation of γ_∞ values for F^- and Cl^- as a function of the radius of Watson sphere, r_{ion} (in Å units). The Pauling ionic radii have been shown as starred

F^-		Cl^-	
r_{ion}	γ_∞	r_{ion}	γ_∞
∞	−22.106	∞	−55.068
1.40	−10.895	1.99	−37.781
1.36	−10.554	1.81*	−34.801
1.33*	−10.306	1.63	−29.908

r_{ion}. We recommend the use of theoretical values of -10, -35, -76, and -149, respectively, for F^-, Cl^-, Br^-, and I^- in ionic solids with a conservative accuracy limit of ~15% due to the self-consistency effects [14]. Calculations including such effects within the Watson model are presently in progress.

4. Summary

The Sternheimer antishielding factors, γ_∞, have been calculated for the negative halogen ions F^-, Cl^-, Br^-, and I^- using Hartree–Fock wave functions for the free ions and ions in solids. The Watson model for ionic solids has been assumed as simulating the electrostatic potential due to the crystalline lattice. In solids, the γ_∞ values decrease in magnitude by 40–50% relative to the free ion. The serious discrepancy observed between the free ion calculations of γ_∞ for the negative halogen ions using Hartree–Fock and Hartree–Fock–Slater wave functions, has been found to arise mostly due to under-estimation of self-interaction potential in the Slater exchange approximation.

Acknowledgement. K. D. S. is grateful to the Alexander von Humboldt Foundation for an award of a junior fellowship during which this work has been carried out. Thanks are due to Dr. P. C. Schmidt for his interest in this work.

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Received March 19, 1979