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CHARGE DENSITIES AT THE IRON NUCLEUS IN IRON HALIDES (*)

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Résumé. — On a calculé la densité totale de charge sur le noyau de fer, $\rho(0)$, dans les halogénures ferreux FeX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) à l'aide d'un modèle de cluster semi-empirique incluant l'orthogonalisation des orbitales moléculaires aux orbitales centrées sur l'ion fer. La décroissance du déplacement isomérique ($\sim 0,4 \text{ mm/s}$) lorsqu'on passe de FeF_2 à FeI_2 est due à un accroissement de la contribution à $\rho(0)$ des orbitales 4s du fer ; cet accroissement est supérieur à la décroissance de la contribution de recouvrement.

Abstract. — On the basis of semiempirical cluster calculations and a subsequent orthogonalization of iron core orbitals to molecular orbitals the total charge density at the iron nucleus $\rho(0)$ is investigated for iron halides FeX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). The decrease in isomershift from FeF_2 to FeI_2 by about 0.4 mm s^{-1} is explained by an increase in Fe-4s contribution to $\rho(0)$ which is pronounced enough to overcompensate the decrease in overlap contribution to $\rho(0)$.

1. Introduction. — Within the approximation of the semiempirical MO cluster approach [1] and the procedure [2] for calculating the total charge density at the iron nucleus, $\rho(0)$, we investigate the iron halides FeX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). The change in the isomershift, $\Delta\delta = \delta_A - \delta_B$, from compound A to compound B is related to a change in electron density $\Delta\rho(0) = \rho_A(0) - \rho_B(0)$:

$$\Delta\delta = \alpha \Delta\rho(0), \quad (1)$$

with the isomershift calibration constant having a value [3-7] of about, $-0.2 (\pm 0.1) a_0^3 \text{ mm s}^{-1}$ in the case of Fe^{57} . The aim of this work is not to derive α quantitatively, but to elucidate the trends within the electronic structure related with the considerable decrease in isomershift [8] from the fluorine to the iodine compound.

2. Theoretical background. — The compounds under study are represented by $[\text{FeX}_6]^{4-}$ -clusters, the geometry of which are taken from literature [9, 10].

Within the semiempirical MO cluster approach [1] the diagonal elements of the Fockmatrix $F_{\mu\mu}$ are represented by charge dependent valence ionization potentials which are described in terms of two empirical parameters α_μ and $\Delta\alpha_\mu$:

$$F_{\mu\mu} = -(\alpha_\mu + q_A \Delta\alpha_\mu). \quad (2)$$

q_A is the effective charge of atom A where the atomic orbital (AO) $|\mu\rangle$ is localized. The AO basis set consists of Slater type orbitals (STO's) Fe-3d, -4s and -4p and ligand-ns and -np with $n = 2$ for F, $n = 3$ for Cl, $n = 4$ for Br and $n = 5$ for I (Table I). The α_μ

TABLE I

Empirical parameters used in the LCAO-MO cluster calculations

		$\xi(^*)$	α	$\Delta\alpha$
Ligand parameters		—	—	—
F	2s :	2.600	34.0	18.0
	2p :	2.600	18.5	15.0
Cl	3s :	2.033	29.0	15.5
	3p :	2.033	13.0	10.0
Br	4s :	2.054	26.0	14.0
	4p :	2.054	11.5	9.0
I	5s :	1.900	25.0	14.0
	5p :	1.900	10.5	8.0
Iron parameters for model I and model II (**)				
Fe	3d :	2.870	7.0	8.0
	4p :	1.400	6.5	8.0
Iron 4s parameter for model I (**)				
	4s :	1.400	7.5	8.0
Iron 4s parameter for model II				
	$[\text{FeF}_6]^{4-}$:	1.400	7.5	8.0
	$[\text{FeCl}_6]^{4-}$:	1.400	11.1	8.0
	$[\text{FeBr}_6]^{4-}$:	1.400	14.7	8.0
	$[\text{FeI}_6]^{4-}$:	1.400	20.1	8.0

(*) Taken from Pople, J. R., Beveridge, D. L., « *Approximate Molecular Orbital Theory* » (McGraw-Hill Book Company) 1970.

(**) Taken from ref. [1].

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and $\Delta\alpha_\mu$ for the ligand AO's are derived from ionization potentials of neutral and ionized halides, which are available from experimental work [11, 12] as well as from Hartree-Fock calculations [13-15]. Experimental ionization potentials I_X for neutral halides X (in eV) are $I_F=17.43$, $I_{Cl}=13.02$, $I_{Br}=11.85$ and $I_I=10.45$; and the increase in I_X for a X^+ -ion is largest for F and less pronounced in the order Cl, Br, I. It is further known from the definition of the electronegativity [16], χ , that an atom (halide) preferably takes up an electron from its bonding neighbour (Fe) if the difference $\Delta\chi = \chi_{\text{halide}} - \chi_{\text{Fe}}$ is large. Since $\Delta\chi$ decreases [17] from FeF_2 (2.2) to FeCl_2 (1.2), FeBr_2 (1.0), and FeI_2 (0.7) it is obvious that the ionization potential I_{X^-} for X^- ions decreases from I_{F^-} to I_{I^-} (Table I).

For iron we used two different parameter sets (Table I). The first, denoted as model I, already has been used for a variety of similar iron containing compounds to derive electron densities, electric field gradients and magnetic properties [1, 2, 18-20]. Because of reasons described in the discussion, we were not able to get results which are qualitatively consistent with the decrease in δ from FeF_2 to FeI_2 . Model II takes qualitatively account of Hartree-Fock results [13-15] for various $3d^n 4s^m$ -configurations, namely that the Fe $3d^n 4s^{m+1}$ configuration is energetically preferable compared to the Fe $3d^{n+1} 4s^m$ configuration for $n = 6, 7$ and $m = 0, 1$ (Table II).

TABLE II

Hartree-Fock energies for various $3d^n 4s^m$ configurations in atomic units (taken from ref. [15])

Fe^{2+}	$3d^6$	- 12 616.55
	$3d^5 4s$	- 12 612.98
	$3d^4 4s^2$	- 12 609.81
Fe^{1+}	$3d^7$	- 12 620.77
	$3d^6 4s$	- 12 622.12
	$3d^5 4s^2$	- 12 619.57
Fe^0	$3d^8$	- 12 620.96
	$3d^7 4s$	- 12 623.76
	$3d^6 4s^2$	- 12 624.42
Fe^{1-}	$3d^9$	- 12 617.75
	$3d^8 4s$	- 12 620.74
	$3d^7 4s^2$	- 12 622.89

The total calculated charge density $\rho(0)$ consists in our scheme [2] of the valence-contribution (Fe-4s- and direct ligand-AO-contribution at the iron nucleus) and of the iron core contribution :

$$\rho(0) = \rho_{\text{val}}(0) + \rho_c(0). \quad (3)$$

$\rho_c(0)$ results from the iron core functions φ_{ns} ($n = 1, 2, 3$) :

$$\rho_c(0) = 2 \sum_{n=1}^3 |\varphi_{ns}(0)|^2, \quad (4)$$

where the φ_{ns} are orthogonalized to the M occupied cluster MO's φ_j :

$$\varphi_{ns} = N_{ns} \left(\psi_{ns} - \sum_{m=n+1}^3 \langle \varphi_{ms} | \psi_{ns} \rangle \varphi_{ms} - \sum_{j=1}^M \langle \varphi_j | \varphi_{ns} \rangle \varphi_j \right). \quad (5)$$

N_{ns} is the normalization constant for the orbital φ_{ns} .

From known charge densities for various $3d^n 4s^m$ configurations [2, 21] of the free iron ion one may calculate by linear interpolation (this has been proved to give valuable results [2]) the charge density $\rho_p(0)$, the iron ion would have if it were free but have the $3d^x 4s^y$ configuration which results from the MO cluster calculation :

$$\rho_p(0) = 2 \sum_{n=1}^3 |\psi_{ns}(0)|_{3d^x 4s^y}^2. \quad (6)$$

With $\rho_p(0)$ we define an overlap contribution

$$\rho_{\text{ov}}(0) = \rho_c(0) - \rho_p(0). \quad (7)$$

Using the LCAO definition of the cluster MO's ($\varphi_j = \sum_{\mu} c_{j\mu} \psi_{\mu}$) and the definition of the bond order

matrix elements ($P_{\mu\nu} = \sum_{j=1}^M n_j c_{j\mu} c_{j\nu}$; $n_j = 0, 1, 2$)

it is obvious from eqs (5) and (7) that the main contribution to ρ_{ov} is due to nondiagonal bond order matrix elements $P_{\text{Fe}-4s, \text{lig}-ns}$ and $P_{\text{Fe}-4s, \text{lig}-np}$ and to overlap integrals $S_{\text{Fe}-ns, \text{lig}-ns}$ and $S_{\text{Fe}-ns, \text{lig}-np}$.

3. Results and discussion. — The MO results which are interesting with respect to the evaluation of charge densities $\rho(0)$ are summarized in table III. It is common to both models, I and II, that the effective charge of the iron q_{Fe} , (which is a formal charge [22], consisting of the core charge of the Fe atom, of the Fe valence population, and to some degree of the overlap charge) decreases from FeF_2 to FeI_2 . Concerning model I this is mainly due to an increasing 3d-population from FeF_2 to FeI_2 . This situation, however, is not consistent with the Hartree-Fock results for various $3d^n 4s^m$ configurations in table II. Model II takes account of these results and describes the decrease of q_{Fe} from FeF_2 to FeI_2 mainly in terms of an increase in the Fe-4s population.

Table IV contains the total charge density $\rho(0)$ and the contributions $\rho_{\text{val}}(0)$, $\rho_p(0)$ and $\rho_{\text{ov}}(0)$ for the two models and the four clusters. The overlap contribution $\rho_{\text{ov}}(0)$ does not explain the experimental decrease in isomershift from FeF_2 to FeI_2 , since the change in $\rho_{\text{ov}}(0)$ goes in the wrong direction (in both models). From a consideration of the overlap integrals only (Table III) one would expect a nearly constant overlap contribution for all four compounds; the inclusion of the bond order matrix elements $P_{\text{Fe}-4s, \text{lig}-ns}$ and $P_{\text{Fe}-4s, \text{lig}-np}$ in eq. (5), however, accounts for the change in $\rho_{\text{ov}}(0)$. The contribution $\rho_p(0)$ which is

TABLE III
Summary of LCAO-MO cluster calculations

		FeF ₂	FeCl ₂	FeBr ₂	FeI ₂
Model I	q_{Fe}	0.082	- 0.133	- 0.238	- 0.337
	3d-population (*)	6.592	6.474	6.622	6.875
	4s-population (*)	0.148	0.144	0.052	0.034
	4p-population (*)	0.410	0.403	0.245	0.345
	$q_{4s}\text{-P}_{4s,4s}$	0.155	0.206	0.184	- 0.161
	$P_{\text{Fe}-4s,\text{lig}-ns}$	0.089	0.049	0.013	- 0.104
	$P_{\text{Fe}-4s,\text{lig}-np}$	- 0.185	- 0.169	- 0.109	- 0.001
Model II	q_{Fe}	0.094	- 0.147	- 0.291	- 0.430
	3d-population (*)	6.615	6.375	6.403	6.413
	4s-population (*)	0.099	0.353	0.479	0.772
	4p-population (*)	0.431	0.346	0.168	0.303
	$q_{4s}\text{-P}_{4s,4s}$	0.099	0.273	0.398	0.470
	$P_{\text{Fe}-4s,\text{lig}-ns}$	0.072	0.057	0.079	0.039
	$P_{\text{Fe}-4s,\text{lig}-np}$	- 0.147	- 0.232	- 0.198	- 0.181
	$R_{\text{Fe-X}}$	2.122 (**)	2.587 (**)	2.654	2.879
	$S_{\text{Fe}-3s,\text{lig}-ns}$ (***)	0.012 03	0.012 35	0.014 52	0.015 99
	$S_{\text{Fe}-3s,\text{lig}-np}$ (***)	- 0.060 68	- 0.058 54	- 0.064 81	- 0.063 09
	$S_{\text{Fe}-2s,\text{lig}-ns}$ (***)	0.001 53	0.001 88	0.002 33	0.002 68
	$S_{\text{Fe}-2s,\text{lig}-np}$ (***)	- 0.011 48	- 0.010 22	- 0.012 57	- 0.012 27
	$S_{\text{Fe}-1s,\text{lig}-ns}$ (***)	0.000 20	0.000 26	0.000 32	0.000 37
	$S_{\text{Fe}-1s,\text{lig}-np}$ (***)	- 0.001 59	- 0.001 42	- 0.001 74	- 0.001 70

(*) Open-shell populations ($S = 2$).

(**) Numbers given for ligands which are oriented perpendicular to the tetragonal axis of the cluster.

(***) Integral are given for the case that the iron-ligand bond is oriented along the positive x -axis with Fe at $x = 0$.

TABLE IV

Relativistic charge densities (in a_0^{-3}) at the iron nucleus in $[\text{FeX}_6]^{4-}$

		$[\text{FeF}_6]^{4-}$	$[\text{FeCl}_6]^{4-}$	$[\text{FeBr}_6]^{4-}$	$[\text{FeI}_6]^{4-}$
Model I	$\rho_p(0)$	15 062.299	15 062.479	15 062.199	15 061.796
	$\rho_{\text{val}}(0)$	0.608	0.635	0.209	0.116
	$\rho_{\text{ov}}(0)$	4.084	2.898	2.849	1.497
	$\rho(0)$	15 066.989	15 066.013	15 065.259	15 063.409
Model II	$\rho_p(0)$	15 062.235	15 062.748	15 062.774	15 062.919
	$\rho_{\text{val}}(0)$	0.400	1.641	2.192	3.514
	$\rho_{\text{ov}}(0)$	3.855	3.276	3.399	2.587
	$\rho(0)$	15 066.491	15 067.665	15 068.363	15 069.021

associated with shielding effects of Fe-3d population upon Fe- ns core orbitals remains in both models nearly the same. The change in valence contribution (which is mainly due to Fe-4s population), $\rho_{\text{val}}(0)$, explains for model II the change in isomershifts qualitatively correct; this change is pronounced enough to overcompensate the change of $\rho_{\text{ov}}(0)$. In figure 1 the isomershift of FeX_2 -compounds are plotted with respect to the calculated overall electron density $\rho(0)$. The slope of the solid line in figure 1 ($-0.14 \text{ mm s}^{-1} a_0^3$)

FIG. 1. — Experimental isomer shift versus relativistic electron charge density at the iron nucleus for iron-halides, (experimental isomer shifts at 300 K relative to metallic iron are taken from ref. [8]).

we do not consider as quantitative result of the calibration constant α in eq. (1), since the Fe-4s valence ionization potentials entering the semiempirical Fockmatrix have been estimated only on the qualitative basis described above.

The present study shows the limitation of semiempirical MO cluster calculations at least with respect

to an estimate of electron densities; clusters containing different elements require different parameter sets, and it is extremely difficult to find a parameter set which is consistent within a whole series of different compounds. The main reason for this limitation is due to the specific iteration procedure in the LCAO-MO scheme on which all our subsequent calculations are based, since all diagonal Fockmatrix elements $F_{\mu\mu}$ of atom A in eq. (2) are corrected with the same effective charge q_A . (A more sophisticated iteration procedure with specific corrections due to orbital charges is in preparation.)

In cases within which the semiempirical parameter set remains consistent, we may consider the numerical results as quantitative results with respect to the evaluation of differences of charge densities. Such cases are for example the change of isomer shift within two iron-flourine-clusters [2], the pressure dependence of the isomer shift [23, 24] (Fig. 2) in FeF_2 , and the change

FIG. 2. — Experimental pressure dependent isomer shift at 300 K relative to metallic iron (taken from ref. [23]) versus calculated electron charge density of FeF_2 (taken from ref. [24]).

FIG. 3. — Experimental isomer shift at 300 K relative to metallic iron versus calculated electron charge density of iron-oxygen compounds (taken from ref. [25]): 1) $\text{Fe}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$; 2) BiFeO_3 ; 3) bipyramidal Fe-site in $\text{BaFe}_{12}\text{O}_{19}$; 4) Fe^{II} in MgO ; 5) $\alpha\text{-FeSO}_4$; 6) FeTiO_3 ; 7) GdFeO_3 ; 8) Fe_2TiO_5 ; 9) FeCO_3 ; 10) Fe^{III} in MgO ; 11) SrFeO_3 ; 12) KFeO_2 ; 13) $\text{BaFeSi}_4\text{O}_{10}$; 14) V_2FeO_4 .

in isomer shifts among fourteen different iron oxygen compounds [25] (Fig. 3). For these cases we derive α -values of $-0.26 \pm 0.02 \text{ mm s}^{-1} a_0^3$,

$$-0.22 \pm 0.02 \text{ mm s}^{-1} a_0^3,$$

and $-0.195 \pm 0.02 \text{ mm s}^{-1} a_0^3$ respectively. Thus, we believe that the actual value of α is in the range $-0.18 \text{ mm s}^{-1} a_0^3$ to $-0.28 \text{ mm s}^{-1} a_0^3$.

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