Strictly localized molecular orbitals of compounds containing halogen—copper bond by the EMOA method

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Strictly localized molecular orbitals have been constructed explicitly from directional one-centric wave functions, *i.e.* from hybrid atomic orbitals. The EMOA method has been applied on series of compounds containing fluorine- and chlorine—copper bond. Binding energies and charge distributions have been calculated.

Строго локализованные молекулярные орбитали были составлены в явном виде из направленных одноцентрических волновых функций, т. е. из гибридных атомных орбиталей. Метод ЭМОА был применен для серий соединений фтор- и хлор—медь. Были рассчитаны энергии связи и распределение зарядов.

For a theoretical prediction of the chemical reaction mechanism the knowledge of the total electronic density in the locality of the reaction centre is often important. This problem can be studied by means of the method of molecular orbitals.

Many molecular properties such as binding energies, dipole moments, force constants, charge distributions, bond angles, *etc.,* have been denoted generally as collective molecular properties [1]. These properties are described by the total electronic wave function of the ground state of the molecule. In one-electron approximation this wave function is expressed by means of one-electron wave functions, *i.e.* of molecular spin-orbitals. Molecular orbitals are usually delocalized on all centres of the molecule. However, one can choose also a set of molecular orbitals which are localized on the "covalent bonds" [1—3]. For the construction of a total electronic wave function the use of the delocalized molecular orbitals (MO) or localized molecular orbitals (LMO) is often invariant. Thus the collective molecular properties can be studied in terms of localized molecular orbitals. The importance of LMO, mainly in connection with possibility of their application in the configuration interaction (CI) method, has increased rapidly in the last few years. Due to their localization, LMO include a considerable amount of the correlation energy; so that the LMO CI wave function which gives results comparable with the MO CI wave function may be obtained in an effective way [2].

The most frequently used methods for determining of LMO are: i) application of any localization criteria on MO LCAO SCF wave function [3, 4] and ii) explicit construction of LMO from directional one-centric wave functions, *i.e.* from hybrid atomic orbitals (HAO) [5—8]. From this point of view the proposed method belongs to the second category.

A general method for determination of the HAO in arbitrary molecules has been described in [9]. This extended maximum overlap approximation (EMOA) method has been applied to the series of over 100 polycentric molecules which include H, B, C, N, O, F, P, S, Cl, Br, and I atoms [10, 11]. The calculated total binding energies, dipole moments, bond angles, charge distributions, and carbon 13 — proton nuclear spin—spin coupling constants

are in a remarkable agreement with experimental data [10]. In the present work the applicability of the EMOA method to transition metal compounds was examined.

Method

The EMOA method is based on variational procedure to maximize the weighted sum of overlap integrals between pairs of HAO ψ_i^m and ψ_j^n

$$\varepsilon = \frac{1}{2} \sum_m^G \sum_n^G \sum_i^{N_m} \sum_j^{N_n} K_{m,n} \langle \psi_i^m \mid \psi_j^n \rangle \ (1 - \delta_{m,n}) \ \delta_{f(m,i), f(n,j)}. \qquad (1)$$

In this expression m, $n \in \langle 1, G \rangle$ are indices of atoms; $i \in \langle 1, N_m \rangle$ and $j \in \langle 1, N_n \rangle$ are indices of HAO on given atom; $f(m, i)$ and $f(n, j)$ are discrete topological functions with their values equal to ordering number of localized bond; $K_{m,n}$ are semiempirical weighing parameters which secure the reproduction of the molecular binding energy ε. In [9] a general matrix equation for evaluation of hybridization coefficients has been derived. The hybridization coefficients $a_{i,k}^m$ combine atomic orbitals χ_k^m into hybrid atomic orbitals ψ_i^m

$$\psi_i^m = \sum_k^{R_m} a_{i,k}^m \chi_k^m. \qquad (2)$$

(R_m is the number of basic atomic orbitals.) Resulting HAO are oriented in the directions of the a priori defined localized bonds. This can be exploited for an explicit construction of localized molecular orbitals.

Strictly localized molecular orbital (SLMO) $\Phi_{m,n}$ is defined in terms of linear combination of a HAO pair

$$\Phi_{m,n} = b_i^m \ \psi_i^m + b_j^n \ \psi_j^n. \qquad (3)$$

Expanding coefficients b_i^m and b_j^n can be evaluated by solving the following equations

$$\begin{pmatrix} H_{i,i}^{m;m} - \varepsilon_v ; & H_{i,j}^{m;n} - \varepsilon_v \ S_{i,j}^{m;n} \\ H_{i,j}^{m;n} - \varepsilon_v \ S_{i,j}^{m;n}; & H_{j,j}^{n;n} - \varepsilon_v \end{pmatrix} \begin{pmatrix} b_i^m \\ b_j^n \end{pmatrix} = 0, \qquad (4)$$

$$(b_i^m)^2 + (b_j^n)^2 + 2 b_i^m \ b_j^n \ S_{i,j}^{m;n} = 1. \qquad (5)$$

Eqn (4) corresponds to a complete neglect of formally "non-bonding" interactions between HAO. In eqn (4), ε_v denotes orbital energy of the v-th SLMO; $S_{i,j}^{m;n}$ is the overlap integral of HAO; $H_{i,j}^{m;n}$ is the matrix element of one-electron hamiltonian operator of an extended Hückel type method expressed in HAO basis.

The diagonal matrix elements $H_{i,i}^{m;n}$ have been approximated by means of the valence state ionization energy (VSIE) V_k^m

$$H_{i,i}^{m;m} = - \sum_k^{R_m} (a_{i,k}^m)^2 \ V_k^m. \qquad (6)$$

Relations for VSIE have been taken from [12] and for metals from [13, 14]. Off diagonal matrix elements $H_{i,j}^{m;n}$ have been approximated according to *Cusachs* [15]. An iterative calculation is necessary, since VSIE depend on the effective charges of atoms (IEHT method

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is to be used). By means of *Mulliken's* population analysis [16] the gross charges on atoms, Q_m, overlap populations on bonds, $N_{i,j}^{m;n}$, and charge density matrix elements, $P_{i,j}^{m;n}$, have been calculated. These terms are defined as follows

$$P_{i,j}^{m;n} = w_v \, b_i^m \, b_j^n \, \delta_{f(m \cdot i), f(n \cdot j)}, \tag{7}$$

$$N_{i,j}^{m;n} = P_{i,j}^{m;n} \, S_{i,j}^{m;n} (1 - \delta_{m,n}), \tag{8}$$

$$Q_m = Z_m^{\text{core}} - \sum_i^{R_m} \sum_n^{G} \sum_j^{R_n} P_{i,j}^{m;n} \, S_{i,j}^{m;n} \tag{9}$$

(Z_m^{core} is the number of valence electrons of the m-th atom; w_v is the v-th SLMO or lone lobe occupation.)

Results and discussion

The following series of the compounds containing halogen—copper bond has been chosen: CuF, CuCl, CuF_2, $CuCl_2$, CuFCl, $[CuCl_4]^{2-}$, $[CuCl_3F]^{2-}$, cis-$[CuCl_2F_2]^{2-}$, trans-$[CuCl_2F_2]^{2-}$, $[CuClF_3]^{2-}$, and $[CuF_4]^{2-}$ First, it is necessary to describe the bonding situation in the individual molecules and ions, *i.e.* one must decide whether π bonds should be considered. From this point of view, three alternatives are possible.

i) CuX type is described by a model with one σ and two π bonds. 18 valence electrons occupy these three bonds, one lone lobe of the halogen atom and five copper lone lobes (the sixth copper lone lobe is unoccupied).

ii) CuXY type is described by a model with two σ and two π bonds. 25 valence electrons occupy these four localized bonds, four lone lobes of atom X and Y, and 5 lone lobes of the copper atom (the fifth copper lobe is occupied by an unpaired electron).

iii) $[CuX_mY_n]^{2-}$ type (for $m + n = 4$) is described by a model with four σ bonds. 41 valence electrons occupy these localized bonds, further 12 lone lobes of the halogens and 5 lone lobes of the copper atom (the fifth copper lone lobe is occupied by an unpaired electron, again).
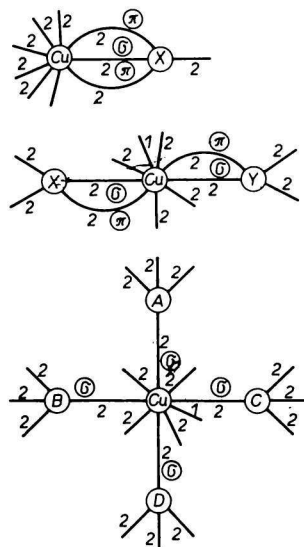

Fig. 1. Schematic representation of the bonding models for some halogen—copper compounds.

As a criterion for determining of the bonding model the bond order has been used; its maximum value corresponds to a minimum of the molecular electronic energy. Possible bonding models for the series of molecules studied are shown in Fig. 1.

Hybrid atomic orbitals and binding energies

In a CuF_2 molecule equivalent Cu—F bonds are considered; thus both parameters $K_{m,n}$ in eqn (1) have equal values. Then, by comparing the calculated sum of overlap integrals between the optimum HAO with the experimental molecular binding energy *via* eqn (1), we obtain parameter $K_{Cu,F}$. In a similar way we obtain parameter $K_{Cu,Cl}$ from a $CuCl_2$ molecule. Calculated parameters $K_{Cu,F}$ and $K_{Cu,Cl}$ can be used for reproduction of the binding energies in the other molecules with Cu—F and Cu—Cl bonds.

Table 1

Calculated total binding energies

Molecule	Symmetry	Interatomic distances[a]		Binding energy[b]
		Cu—F	Cu—Cl	
CuF	$C_{\infty v}$	1.743	—	442.80
CuCl	$C_{\infty v}$	—	2.051	370.85
CuF_2	$D_{\infty h}$	1.72	—	753.12[c]
$CuCl_2$	$D_{\infty h}$	—	2.09	589.94[c]
CuFCl	$C_{\infty v}$	1.72	2.09	671.21
$[CuCl_4]^{2-}$	D_{4h}	—	2.22	794.02
$[CuCl_3F]^{2-}$	C_{2v}	1.72	2.22	882.61
cis-$[CuCl_2F_2]^{2-}$	C_{2v}	1.72	2.22	974.83
trans-$[CuCl_2F_2]^{2-}$	D_{2h}	1.72	2.22	975.28
$[CuClF_3]^{2-}$	C_{2v}	1.72	2.22	1069.9
$[CuF_4]^{2-}$	D_{4h}	1.72	—	1166.5

a) Values are given in 10^{-10} m [20].
b) Values are given in 10^3 J mol^{-1}. Semiempirical parameters $K_{Cu,F}=596.0878$, $K_{Cu,Cl}=328.4285$ (10^3 J mol^{-1}) were used.
c) Experimental value [17].

In all calculations *Slater* AO [18] with exponents for metals proposed by *Gouterman* [19] have been used. The calculated total binding energy (Table 1) for CuCl molecule is 370 kJ mol^{-1}. This value is in a good agreement with experimental data (347 ± 25 kJ mol^{-1}) [21]. The calculated binding energy for CuF molecule, 443 kJ mol^{-1} does not agree with experiment (339 ± 70 kJ mol^{-1}), however, according to [21] this experimental value is too small. Experimental binding energies for other derivatives are not available.

Calculated HAO and particular binding energies are listed in Table 2. Values of the particular binding energies are in a good agreement with estimated strengths of individual bonds ($\sigma_{Cu-F}=277$—306, $\pi_{Cu-F}=68$—71, $\sigma_{Cu-Cl}=198$— 4°, $\pi_{Cu-Cl}=62$—65 kJ mol^{-1}).

Table 2

Hybrid atomic orbitals and particular binding energies

Molecule	Bond Cu—X	Total hybridization coefficient					Binding energy kJ mol$^-$
		$S^2(Cu)$	$P^2(Cu)$	$D^2(Cu)$	$S^2(X)$	$R^2(X)$	
CuF	Cu—F	0.286	0.679	0.035	0.861	0.139	306.28
	Cu—F (π)	—	0.927	0.073	—	1.0	68.26
CuCl	Cu—Cl	0.348	0.632	0.019	0.697	0.303	239.95
	Cu—Cl (π)	—	0.963	0.037	—	1.0	65.45
CuF$_2$	Cu—F	0.442	0.500	0.058	0.860	0.140	305.93
	Cu—F(π)	—	0.920	0.080	—	1.0	70.63
CuCl$_2$	Cu—Cl	0.475	0.500	0.025	0.681	0.319	232.77
	Cu—Cl (π)	—	0.966	0.034	—	1.0	62.20
CuFCl	Cu—F	0.453	0.494	0.053	0.861	0.139	305.58
	Cu—F (π)	—	0.920	0.080	—	1.0	70.63
	Cu—Cl	0.469	0.504	0.028	0.681	0.319	232.89
	Cu—Cl (π)	—	0.966	0.034	—	1.0	62.20
[CuCl$_4$]$^{2-}$	Cu—Cl	0.247	0.500	0.253	0.634	0.366	198.50
$\begin{bmatrix} Cl_b \\ | \\ Cl_a{-}Cu{-}F \\ | \\ Cl_b \end{bmatrix}^{2-}$	Cu—F	0.189	0.438	0.373	0.826	0.174	276.96
	Cu—Cl$_a$	0.217	0.555	0.227	0.635	0.365	200.97
	Cu—Cl$_b$	0.290	0.503	0.207	0.636	0.364	202.34
$\begin{bmatrix} Cl \\ | \\ Cl{-}Cu{-}F \\ | \\ F \end{bmatrix}^{2-}$	Cu—F	0.232	0.451	0.317	0.832	0.168	283.36
	Cu—Cl	0.258	0.548	0.194	0.637	0.363	204.06
$\begin{bmatrix} Cl \\ | \\ F{-}Cu{-}F \\ | \\ Cl \end{bmatrix}^{2-}$	Cu—F	0.163	0.500	0.337	0.830	0.170	282.06
	Cu—Cl	0.239	0.500	0.171	0.638	0.362	205.58
$\begin{bmatrix} F_b \\ | \\ Cl{-}Cu{-}F_a \\ | \\ F_b \end{bmatrix}^{2-}$	Cu—F$_a$	0.273	0.457	0.270	0.838	0.162	288.88
	Cu—F$_b$	0.202	0.502	0.296	0.834	0.166	287.11
	Cu—Cl	0.298	0.537	0.165	0.639	0.361	206.79
[CuF$_4$]$^{2-}$	Cu—F	0.242	0.500	0.258	0.839	0.161	291.63

Distribution of the electronic density

Gross charges on atoms, overlap populations on bonds, and density matrix elements give a very good characterization of the distribution of total electronic density in a molecule. The corresponding values are listed in Table 3.

Values of overlap populations and off-diagonal matrix elements $P_{i,j}^{Cu, X}$ in molecules CuF and CuCl show that the electronic density in the middle of the σ bond is too small; an extreme polarity of σ_{Cu-X} bond is indicated, which comes up to a pure ionic bond. The polarity of π_{Cu-X} bond is not so high.

Table 3

Distribution of the electronic density[a]

| Molecule	Bond Cu—X	Density matrix elements			Overlap population	Charge	
		$P^{Cu,Cu}_{i,i}$	$P^{Cu,X}_{i,i}$	$P^{X,X}_{i,i}$		X	Cu
CuF	Cu—F	003	075	1920	075	−367	+367
	Cu—F (π)	226	608	1634	139		
CuCl	Cu—Cl	001	608	1989	010	−238	+238
	Cu—Cl (π)	255	618	1499	246		
CuF_2	Cu—F	020	189	1786	193	−336	+673
	Cu—F (π)	454	786	1360	186		
$CuCl_2$	Cu—Cl	030	223	1647	323	−242	+484
	Cu—Cl (π)	420	735	1287	293		
CuFCl	Cu—F	014	160	1822	163	−397	+568
	Cu—F (π)	416	764	1403	181		
	Cu—Cl	052	285	1544	404	−170	
	Cu—Cl (π)	434	746	1283	283		
$[CuCl_4]^{2-}$	Cu—Cl	233	516	1143	624	−455	−179
$\begin{bmatrix} Cl_b \\ | \\ Cl_a—Cu—F \\ | \\ Cl_b \end{bmatrix}^{2-}$	Cu—F	121	423	1489	394	−682	−058
	Cu—Cl$_a$	250	526	1107	643	−429	
	Cu—Cl$_b$	258	530	1089	653	−415	
$\begin{bmatrix} Cl \\ | \\ Cl—Cu—F \\ | \\ F \end{bmatrix}^{2-}$	Cu—F	130	434	1457	413	−663	+070
	Cu—Cl	289	546	1023	679	−372	
$\begin{bmatrix} Cl \\ | \\ F—Cu—F \\ | \\ Cl \end{bmatrix}^{2-}$	Cu—F	126	430	1468	407	−670	+070
	Cu—Cl	293	547	1022	685	−365	
$\begin{bmatrix} F_b \\ | \\ Cl—Cu—F_a \\ | \\ F_b \end{bmatrix}^{2-}$	Cu—F$_a$	145	453	1416	439	−635	+214
	Cu—F$_b$	145	453	1419	437	−637	
	Cu—Cl	338	566	948	713	−306	
$[CuF_4]^{2-}$	Cu—F	170	481	1359	471	−595	+378

a) Values are given in 10^3 e.

The electronic density in the middle of the Cu—X bond in linear molecules CuF_2 and $CuCl_2$ is much higher than in a CuF or CuCl molecule. Values of gross charges on atoms indicate that electronegative halogens compete with each other on electron-withdrawing effect.

Distribution of the electronic density in a CuFCl molecule shows that individual π bonds retain their properties referring to CuF_2 and $CuCl_2$ molecules. However, the $\sigma_{Cu—F}$ bond in CuFCl is more polar than in CuF_2 molecule. Density matrix elements indicate that the

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minimum electronic density is in the locality of the Cu—F bond on Cu atom; this locality is preferentially disposed to the nucleophilic attack.

In the series $[CuCl_4]^{2-}$, $[CuCl_3F]^{2-}$, cis-$[CuCl_2F_2]^{2-}$, trans-$[CuCl_2F_2]^{2-}$, $[CuClF_3]^{2-}$, and $[CuF_4]^{2-}$ the positive charge on Cu atom increases and simultaneously negative charges on Cl and F atoms decrease; so that the inductive effect of electronegative substituents is perfectly reproduced. Distribution of the electronic density in a $[CuCl_3F]^{2-}$ ion indicate that different reactivity of the "trans" Cu—Cl$_a$ and "cis" Cu—Cl$_b$ bonds in the substitution nucleophilic reactions may be expected (see Table 3); a "trans influence" of the ligands is indicated. From this point of view, the "trans" influence" of fluorine is somewhat larger so that the reaction of $[CuCl_3F]^{2-}$ with F$^-$ gives rather trans-$[CuCl_2F_2]^{2-}$. In the $[CuClF_3]^{2-}$ ion the slight difference between electronic density on "trans" Cu—F$_a$ and "cis" Cu—F$_b$ bond does not allow of an unambiguous prediction of the reaction product. The following reaction schemes are to be considered
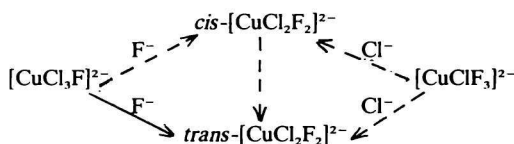
Similar calculations with a systematic variation of some ligands, mainly in connection with study of non-polar spliting of the halogen—metal bond [22] might be certainly interesting.

It may be concluded that the explicit construction of the strictly localized molecular orbitals using hybrid atomic orbitals can be applied also to transition metal compounds. This proved to be an effective way for examination of some collective molecular properties, such as binding energies and distribution of the electronic densities, further force constants, dipole moments, molecular quadrupole moments, bond angles, etc.

References

1. Dewar, M. J. S., *The Molecular Orbital Theory of Organic Chemistry.* McGraw-Hill, New York, 1969.
2. Diner, S., Malrieu, J. P., and Claverie, P., *Theor. Chim. Acta 13,* 18 (1969).
3. Ruedenberg, K., in *Modern Quantum Chemistry.* (O. Sinanoğlu, Editor.) Academic Press, New York, 1965.
4. Polák, R., *Int. J. Quantum Chem. 4,* 271 (1970).
5. Del Re, G., *Int. J. Quantum Chem. 1,* 293 (1967).
6. Del Re, G., *Theor. Chim. Acta 1,* 188 (1963).
7. Vielard, A. and del Re, G., *Theor. Chim. Acta 2,* 55 (1964).
8. Esposito, U. and Carpentieri, M., *Theor. Chim. Acta 6,* 36 (1966).
9. Boča, R., Pelikán, P., Valko, L., and Miertuš, S., *Chem. Phys. 11,* 229 (1975).
10. Miertuš, S., Boča, R., Pelikán, P., and Valko, L., *Chem. Phys. 11,* 237 (1975).
11. Pelikán, P., Boča, R., and Valko, L., unpublished results.
12. Carroll, D. G., Armstrong, A. T., and McGlynn, S. P., *J. Chem. Phys. 44,* 1865 (1966).
13. Bash, H., Viste, A., and Gray, H. B., *J. Chem. Phys. 44,* 10 (1966).
14. Johansen, H. and Ballhausen, C. J., *Mol. Phys. 10,* 175 (1966).
15. Cusachs, L. C., *J. Chem. Phys. 43,* S-157 (1965).
16. Mulliken, R. S., *J. Chem. Phys. 23,* 1833, 1841, 2338, 2343 (1955).

17. Brewer, L., Somayajulu, G. R., and Brackett, E., *Chem. Rev. 63,* 111 (1963).
18. Slater, J. C., *Phys. Rev. 36,* 57 (1930).
19. Zerner, M. and Gouterman, M., *Theor. Chim. Acta 4,* 44 (1966).
20. Krasnov, K. S., Timonishin, V. S., Danilova, T. G., and Khandozhko, S. V., *Molekulyarnye postoyannye neorganicheskikh soedinenii.* Izd. Khimiya, Leningrad, 1968.
21. Gaydon, A. G., *Dissociation Energies and Spectra of Diatomic Molecules,* 3rd Ed., London, 1968.
22. Gažo, J., *Proceedings XIIIth ICCC,* p. 293. Cracow—Zakopane, 1970.

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