

MODERN STATE OF MOLECULAR ORBITAL CALCULATIONS FOR COORDINATION COMPOUNDS

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ABSTRACT

The modern state of electronic structure calculations for coordination compounds of non-transition, transition and heavy elements is reviewed. The application of calculations for quantum chemical studies of bonding problems, and for the interpretation of molecular properties [e.g. charge distributions, dipole moments, ionization potentials (validity of Koopmans' theorem)], is discussed.

Modern quantum chemistry methods, and among them various schemes of the MO LCAO SCF theory (exact non-empirical and approximate non-empirical methods, including neglect of atomic orbitals overlap as well as semi-empirical methods), are considered.

Along with this traditional treatment of problems in quantum chemistry the possibilities and the perspectives of alternative approaches to molecular electronic structure studies, such as the scattered wave method, are described briefly.

The consideration of modern quantum chemistry calculations is illustrated with examples taken from the literature and with the authors' own results.

SOME REMARKS ON MOLECULAR ORBITAL THEORY

The molecular orbital method has now become a generally accepted basis for dealing with the electronic structure of coordination compounds. It is not only the most common calculation method used in quantum chemistry, but also the language for discussing the results of experimental studies of the physical properties, structure and bonding of molecules.

The starting point of the MO method is the one-electron approximation based on the concept of 'molecular orbitals' which describe the behaviour of each electron in the effective field determined by the atomic nuclei and other electrons of the molecule. There are several calculation schemes using the MO method¹.

In the *restricted Hartree-Fock method* molecular wave function Ψ is given in the form of a determinant from one-electron molecular spin orbitals (MSO):

$$\Psi = (N!)^{-\frac{1}{2}} \text{Det} |\psi_1(1)\psi_2(2)\dots\psi_N(N)|, \quad \begin{cases} \psi_{2i-1} = \varphi_i\alpha \\ \psi_{2i} = \varphi_i\beta \end{cases} \quad (\text{I})$$

where α, β are spin MSO parts, and φ_i are spatial MSO parts which are the solutions of the equations for a self-consistent field (SCF):

$$\hat{F}\varphi_i = \varepsilon_i\varphi_i \quad (\text{II})$$

Here, \hat{F} is a Hartree-Fock operator defined through φ_i , and ε_i are one-electron energy levels on each of which not more than two electrons may be located. The electronic configuration of a molecule is characterized by a certain occupation of these levels. The molecular wave function Ψ which, similar to one-electron MOs φ_i is transformed by the irreducible representations of a molecular symmetry group, can be written in the form of one determinant only in the case of a closed or half-filled shell (for a term with maximum multiplicity). In other cases, for providing a correct symmetry of the molecular wave function, Ψ is represented as a linear combination of determinants formed of MSOs. The restricted Hartree-Fock method does not allow us to take into account electronic correlations using a one-electron approach; besides, when internuclear distances are large, we shall have wrong behaviour of Ψ due to spin symmetry restrictions. In order to avoid these drawbacks, *configuration interactions* (CI) must be considered through expressing Ψ in the form of a linear combination of determinants $\Psi = C_0\Psi_0 + C_1\Psi_1 + \dots$, each of the determinants corresponding to a certain electronic configuration and having right symmetry. Excited configurations are usually composed of virtual (unfilled) MOs obtained from the calculation of the molecular ground state (Ψ_0), whereas the C_k coefficients are determined from the variational procedure. It is particularly important to take CI into account when considering open-shell systems and excited molecular states, because in such cases there are configurations with nearly the same energies needed to be accounted for. Apart from consideration of CI, the above limitations may also be partially eliminated by using the *unrestricted Hartree-Fock method* whereby the molecular wave function is given in the form of one determinant and different spatial MOs are used for different spins. In this case, φ_i are found by solving two coupled sets of equations:

$$\begin{cases} \hat{F}^\alpha\varphi_i^\alpha = \varepsilon_i^\alpha\varphi_i^\alpha \\ \hat{F}^\beta\varphi_i^\beta = \varepsilon_i^\beta\varphi_i^\beta \end{cases} \quad (\text{III})$$

corresponding to α and β spins. In a general case, $\varphi_i^\alpha \neq \varphi_i^\beta$ and $\varepsilon_i^\alpha \neq \varepsilon_i^\beta$; the molecular wave function Ψ is not associated with any concrete spin state of the system and in the event of spatial degeneration cannot be related to a concrete irreducible representation of the molecular symmetry group, that is strictly speaking, it cannot be used for description of real spectroscopic states of a molecule. Elimination of this drawback requires cumbersome procedures (for example, application of the projection operator technique) and is not generally used. The unrestricted Hartree-Fock method is particularly frequently used for calculating open-shell systems, as the computational

procedure involved in this method is much simpler than that of the restricted Hartree-Fock method with CI.

Apart from the one-electron approximation, molecular calculations usually employ an approximate representation of MOs as a restricted linear combination of atomic orbitals (LCAO) from all the atoms in a molecule:

$$\varphi_i = \sum_p C_{pi} \chi_p \quad (\text{IV})$$

In this case, all SCF equations (II) become (for a closed shell) the matrix Roothaan equations²:

$$\begin{cases} (\hat{F} - \varepsilon_i \hat{S}) \hat{C}_i = 0 \\ \text{Det} | F - \varepsilon_i S | = 0 \end{cases} \quad (\text{V})$$

where \hat{F} and \hat{S} are the matrix of the Hartree-Fock operator and the overlap matrix

$$\begin{aligned} F_{pq} &= H_{pq} + G_{pq}, \\ H_{pq} &= \int \chi_p(1) \left[-\frac{1}{2} \Delta - \sum_A \frac{Z_A}{r_{A1}} \right] \chi_q(1) d\tau_1 \\ G_{pq} &= \sum_r \sum_s C_{ri} C_{si} (2J_{pqrs} - J_{pqrs}) \\ S_{pq} &= \int \chi_p(1) \chi_q(1) d\tau_1 \end{aligned} \quad (\text{VI})$$

and

$$J_{pqrs} = \int \chi_p(1) \chi_q(1) \frac{1}{r_{12}} \chi_r(2) \chi_s(2) d\tau_1 d\tau_2$$

are electron interaction integrals. It can be expected that if the basis set of AOs is sufficiently complete, the obtained Ψ and total molecular energy E must be close to the Hartree-Fock limit.

The main computational difficulties of the Hartree-Fock-Roothaan method (MO LCAO SCF) lie in the necessity of calculating a very large number ($\sim N^4$, where N is the number of basis AOs) of molecular integrals (VI), and also in solution of high-order secular equations (V). This task is made still more difficult if CI must be taken into account: hundreds and thousands of configurations should be considered in order to obtain a satisfactory fit between the calculated total molecular energy and the experimental values³. For this reason, most MO LCAO SCF calculations are carried out using the restricted Hartree-Fock method and take into consideration a rather small number of excited states. However, the unrestricted Hartree-Fock method has been recently more extensively used, though without the spin-projection technique.

We shall now briefly outline what information can in principle be derived from MO calculation results close to the Hartree-Fock limit, and what experimental data can be compared with this information. It should be pointed out at once that calculations using the restricted Hartree-Fock method without full account for CI fail to solve the problem of energetic stability of compounds because electron correlation is neglected. Potential surface calculations also yield unsatisfactory results, though the calculated equilibrium geometry is in most cases in good agreement with experiment.

Therefore, such properties of molecules are not discussed in this paper. It has been found that various quantities characterizing the distribution of electronic density, for instance, dipole moments, magnetic properties and others, may be reproduced with a much higher degree of accuracy.

Strictly speaking, for determining the energy of electronic transitions, separate calculations must be performed for the ground state and each of the excited states of a molecule, consideration of CI being particularly essential for the latter. However, very few such works have yet been published. Usually, virtual MOs from the ground state calculation are employed for obtaining the molecular wave functions of the excited states and for estimating transition energies. This approach is based on the 'frozen orbitals' approximation which implies that no reorganization of molecular MOs occurs when the molecule is excited. In such an approximation, the singlet (1) or triplet (3) transition energy $i \rightarrow j$ is found from the formula:

$$\Delta E_{i \rightarrow j}^{1,3} = \varepsilon_j - \varepsilon_i - (J_{ij} - K_{ij}) \pm K_{ij} \quad (\text{VII})$$

where J_{ij} is a coulomb integral, and K_{ij} is an exchange integral between MO φ_i and φ_j . An elementary approach which does not account explicitly for electron interaction provides calculation of transition energy simply by the difference between MO energies:

$$\Delta E_{i \rightarrow j} = \varepsilon_j - \varepsilon_i \quad (\text{VIII})$$

The development of photoelectron and x-ray photoelectron spectroscopy has led to direct comparison of calculated one-electron energy levels with the experimentally found ionization potentials. Such a comparison is also made possible on the basis of 'frozen orbitals' approximation which gives rise to the well-known Koopmans' theorem⁴.

MO calculations not only enable determination of various physical properties of molecules; they also permit definite conclusions about the nature of bonding. For estimating participation of different AOs in bonding, information about the composition of MOs, i.e. about the AO coefficients C_{pi} of atomic orbitals χ_{pA} of atoms A, is used, as well as data on AO populations usually defined according to Mulliken⁵ as a total number of electrons on atomic orbitals χ_{pA} in all filled MOs of a molecule:

$$Q_{pA} = 2 \sum_I C_{pAi}^2 + k \sum_{qB} Q_{pA} q_B \quad (\text{IX})$$

where $Q_{pA} q_B$ is overlap population corresponding to AO χ_{pA} and χ_{qB} . The total overlap population

$$Q_{AB} = \sum_{p,q} Q_{pA} q_B = 4 \sum_{p,q} \sum_I C_{pAi} C_{qBi} S_{pAqB} \quad (\text{X})$$

is often regarded as a measure of A—B bond strength. For an approximate estimation of electron density distribution in a molecule, effective charges on atoms are usually calculated:

$$Z_A^{\text{eff}} = Z_A - \sum_{pA} Q_{pA} \quad (\text{XI})$$

Serious limitations of Mulliken's calculation scheme ($k = \frac{1}{2}$) are, first, that in the case of non-symmetrical charge distribution in the overlap region,

the overlap population is partitioned equally between the atoms A and B (other population analysis techniques differing in the coefficient k are also available⁶), and, second, that it fails to account for the real spatial distribution of the radial part of AO χ_p . The latter circumstance is particularly important for outer diffuse AOs of the central atom in complex compounds, because a considerable portion of the density of such AOs lies in the ligand region. All the above shows that we should not attach too much importance to the absolute values of effective charges and populations; however, these values may be used when comparing data obtained for related compounds by identical procedures and with the wave functions of the same degree of accuracy. The calculated coefficients of AOs in different MOs are used for comparison with data obtained from ESR and NMR spectra, and also from the Mössbauer spectrum, from estimation of transition intensities in x-ray spectra, etc., calculated effective charges are compared (within the framework of primitive models) with experimental results of studies of chemical shifts in NMR and x-ray photoelectron spectra. MO calculations make it also possible to give, on the basis of the molecular wave function, a descriptive spatial picture of bonding by way of electron density maps. Of particular interest is the possibility of transforming conventional MOs into localized MOs which show electron density distribution in bond directions.

For a long time the computational techniques prevented researches from accomplishing rigorous non-empirical calculations at least for the ground state of complex molecules. Therefore, quantum chemistry of coordination compounds was developing through elaboration and application of various semi-empirical and non-empirical approximation approaches. Most calculations available now have been made using such approximations and served as a basis for conclusions on the bonding nature and electronic structure of the investigated classes of coordination compounds. But the results derived for the same compounds using different approximation techniques may depend appreciably on the accuracy of the methods used.

For this reason, the discussion of concrete results will be preceded by a brief analysis of methodological peculiarities and approximations employed in various calculations. Strictly speaking, the numerous MO calculation schemes may be classified into some basic types, each corresponding to a different approximation used and, consequently, a different degree of accuracy of the results.

The accuracy of *non-empirical (ab initio)* calculations by the MO LCAO SCF method depends on the completeness of the basis set of AOs, which may be 'minimal' (i.e. include only AOs occupied in the ground state of the atoms of a molecule) or extended (i.e. include additionally external AOs), and also on the functional type of the AO. Usually, AOs may be one (single- ζ)-⁸, two (double- ζ)-⁹ and, more rarely, many-component¹⁰ combinations of Slater-type functions (STO) with the radial part $r^{n-1} \exp(-\zeta r)$ (n is the principal quantum number of AOs). The orbital exponents (ζ) are found from calculations of isolated atoms, but, generally speaking, they must be optimized in molecular calculations. A properly selected basis must be well balanced, i.e. the minimal basis set must include AOs of a sufficient accuracy [many-(analytical SCF)- or, at least, double- ζ -AOs] and must be extended by adding external AOs from all the atoms of the molecule. Calculations of some small

molecules have demonstrated that an unbalanced basis set causes a distortion of the wave function and electron density distribution in a molecule (AO populations, effective charges, dipole moments, etc.), as can be seen on SO_2 ¹¹ (Table 1). Since calculations in basis sets composed of analytical SCF AOs are quite laborious, use is often made of mixed basis sets^{12, 13} made up of single- ζ and double- ζ AOs or less accurate basis sets of single- ζ AOs (in these latter sets an unbalanced extension of the basis set is usually made by including outer (vacant) AOs of the central atom only). It has been shown that use of the basis sets composed of single- ζ AOs may give rise to substantial errors due, in particular, to inadmissible errors in energies of $2p$ -AOs of the 1st-row atoms and to still larger errors for $3d$ AOs of the 3d-row atoms, whereas mixed basis sets in which at least these AOs are represented by double- ζ functions yield satisfactory results¹³.

Table 1. Dependence of non-empirical calculation data for SO_2 on AO basis set

Calculations	Basis sets for		E_{total} (a.u.)	3d = AO population		Effective charges		Dipole moment (D)*
	S	O		S	O	S	O	
Ref. 11a, double- ζ AO	<i>sp</i>	<i>sp</i>	-546.63			+1.51	-0.75	2.60
	<i>spd</i>	<i>sp</i>	-546.79	0.59		+0.92	-0.46	
	<i>spd</i>	<i>spd</i>	-546.83	0.55	0.07	+1.05	-0.52	2.17
Ref. 11b single- ζ AO	<i>sp</i>	<i>sp</i>	-540.65			+0.82	-0.41	1.24
	<i>spd</i>	<i>sp</i>	-541.01	1.17		+0.14	-0.07	0.81

* Experimental value 1.63 D, from ref. 11a.

To simplify molecular integral calculations, it has recently become common to represent AOs as linear combinations of Gaussians (GF) $r^K \exp(-\alpha r^2)$ which are selected either by more or less accurate approximation of known AOs or by solving SCF equations for isolated atoms directly in the basis set of GF¹⁴.

Attempts to avoid computational difficulties involved in calculations of complex molecules have resulted in using various approximations with a view to reducing the number of required integrals and facilitating their determination.

Valence approximation which reflects the physical phenomenon of spatial and energy separation of inner and valence electrons permits solution of SCF equations (V) separately for valence electrons which determine the principal physical and chemical properties of a molecule. This approximation does not impair the calculations appreciably if the valence AOs are orthogonalized to the inner AOs of all the atoms and if the potentials set up by the atomic cores¹⁵ are correctly allowed for.

Zero differential overlap approximations (ZDO) based on neglect of values of the type $\chi_p \chi_q d\tau$ in molecular integrals and resulting in a large reduction in the number of integrals that are involved in the calculation can be used in several versions¹⁶⁻¹⁸. The chief of these versions are: (a) neglect of diatomic

differential overlap (NDDO) which is the most rigorous scheme; (b) intermediate neglect of differential overlap (INDO), a technique of intermediate accuracy; and (c) complete neglect of differential overlap (CNDO) which is a technique providing the roughest approximation.

By way of theoretical investigations it has been found possible to show with a certain approximation^{18,19} that calculations with ZDO (as correct to the terms of the S_{pq}^2 order in matrix elements of SCF equations) may be considered as imitation of SCF calculations without ZDO carried out in a symmetrically orthogonalized basis set²⁰ $\hat{\chi}' = \hat{S}^{-\frac{1}{2}}\hat{\chi}$. Therefore, for correct estimation of AO populations and effective charges it is required to deorthogonalize the LCAO coefficients derived in the ZDO approximation, to the 'atomic' basis set²¹.

Calculations by the *non-empirical ZDO technique* involve theoretical determination of required integrals and estimation of scaling factors without turning to experimental data^{22, 23}. Thus, in publications^{22, 24, 27, 29, 30} the matrix elements of SCF equations in the NDDO approximation are calculated rigorously²⁸, with the exception of some non-diagonal elements of the core matrix H_{pq} which are found from comparison with the results of SCF calculation of diatomic fragments of a molecule in valence approximation without ZDO²². If the AO basis set has been correctly selected and the values of S_{pq} are small, good agreement can be attained with *ab initio* SCF calculation results^{29, 30}.

In various *semi-empirical ZDO approximation versions*, separate integrals or whole matrix elements are treated as calculation parameters and are found from experimental (most frequently, spectroscopic) data for isolated atoms or ions. But, according to Coulson, 'the number of sets of parameters is almost equal to the number of researchers working in this field', whereas the results depend significantly on the selected magnitudes of these parameters (see Table 2).

Table 2. Populations of Cl AO and effective charges on atoms in ClF_3 from various calculations

Calculations	SCF CNDO semi-empirical (ref. 31a)		SCF NDDO semi-empirical (ref. 31b)		SCF NDDO non-empirical mixed AO basis set (ref. 31c)		SCF <i>ab initio</i> mixed AO basis set (ref. 31d)		
	AO basis	<i>sp</i>	<i>spd</i>	<i>sp</i>	<i>spd</i>	<i>sp</i>	<i>spd</i>	<i>sp</i>	<i>spd</i>
Cl	3s	1.90	1.90	1.75	1.75	2.00	2.00		
	3p	4.27	3.65	3.86	3.76	4.14	3.89		
	3d		0.94		0.20		0.35		0.66
Z_{eff}	Cl	+0.83	+0.52	+1.49	+1.28	+0.89	+0.75	+1.38	+0.96
	$\text{F}_1(\text{F}_2)$	-0.37	-0.21	-0.53	-0.45	-0.37	-0.34	-0.52	-0.42
	F_3	-0.08	-0.11	-0.34	-0.37	-0.14	-0.07	-0.33	-0.13
Dipole moment D^*		-0.13	-0.62	-0.62	+0.51	-1.00	-0.58	-0.53	-0.46

* Experimental value 0.55 D, from ref. 31a.

The *semi-empirical Wolfsberg-Helmholz* or *extended Hückel method (EHM)* provides the roughest approximation, since it does not explicitly account for interaction even between valence electrons and is based on a purely empirical estimation of the matrix elements of a one-electron energy operator³². In the most sophisticated version^{33, 34}, EHM calculations involve self-consistency of charges and configurations of valence electrons on atoms and employ corrections for ligand field effects introduced in the matrix elements.

It should be emphasized that there is an important difference between approximate non-empirical and semi-empirical calculations. While approximate non-empirical calculations are able to give at least some idea of how different calculated values are going to change if the calculation procedure is made more accurate, such predictions are completely impossible in semi-empirical calculations with uncontrolled approximations and a lack of theoretical justification for selected parameters. Besides, the entire complex of molecular properties cannot be, as a rule, described with one set of empirical parameters. The point is that semi-empirical calculations make it in principle impossible to obtain correctly the molecular wave function. Though it is assumed that this function can be expressed through AOs used for calculating some integrals (overlap and sometimes, electronic interaction), most integrals or matrix elements are estimated from experimental data and do not correspond in any sense to these AOs.

Another approximate MO method has been developed recently—the so-called *scattered wave SCF- X_α method (SW)*³⁵. It is based on simplification of the Hartree-Fock equations by statistical approximation of the exchange potential with the expression $\alpha A\rho(1)^{-1/3}$ where $\rho(1)$ is the density of electrons with a given spin at point (1), and the parameter α may be selected using several ways. Moreover, the SW method assumes that the space of a molecule is divided into zones of the following three types: (1) spherical 'atomic' zones, (2) an interatomic zone and (3) an outer zone lying outside the assumed spherical 'surface' of a molecule. With a view to simplifying calculations, the molecular potential in the zones of the first and third types is averaged over the directions, and that in a zone of the second type over the volume. This permits, unlike conventional representation of MOs in the form of LCAOs, the use of rapidly converging MO expansion in the eigenfunctions of zones, types 1 and 3, with spherically symmetrical potentials (these functions have the same angular components as conventional AOs) and in special functions which account for the exponential asymptotic behaviour of MOs as we move off the atoms (these functions are called 'scattered waves').

The requirement of continuity of MOs (and their derivatives) on adjacent spherical boundaries gives rise to secular equations whose solutions are used for determining the 'scattered wave' amplitudes and new eigenfunctions of first and second type zones, etc., until the self-consistency. Since the calculation procedure does not require computation of many-centre electron interaction integrals, computation time needed for the SCF- X_α SW method is about 100 times less than that necessary for calculations using the *ab initio* SCF MO LCAO method. By applying the SW technique to the consideration of complex ions, the crystal field stabilizing potential can very easily be taken into account through uniform distribution of the compensating charge

of an opposite sign on the complex 'surface' (boundary of zone 3). A special calculation technique for determining orbital energies for the hypothetical states of a molecule allow us to account, with a certain approximation, for the reorganization of MO when the molecule is ionized or excited. Statistical X_α -approximation provides an approach to dealing with many-electron systems without an appreciable increase in the computation difficulties.

Very powerful computers that have appeared within the last few years and the development of effective techniques for calculating molecular integrals have at last made feasible rigorous non-empirical calculation of large coordination compounds. It has also become possible to check the reliability of approximate computation procedures (reliability of various basis sets and semi-empirical sets of parameters) and the validity of approximation approaches to the interpretation of the calculation results.

In this review we shall try to discuss the following problems, restricting ourselves to several most completely investigated classes of coordination compounds:

(1) What results can be obtained through the most rigorous non-empirical calculations on the concrete nature of the electronic structure and bonding in the compounds of non-transition and transition elements (order of MOs; participation in bonding of various AOs, in particular outer vacant AOs; electronic density distribution)?

(2) Are the results of rigorous calculations reproducible by different approximation methods?

(3) Can the 'frozen orbitals' approximation be applied to interpretation of the optical and photoelectron spectra of various classes of coordination compounds?

NON-TRANSITION ELEMENT COORDINATION COMPOUNDS

Molecular orbital investigations of non-transition element compounds have been carried out most extensively for oxyanions and fluorides.

Oxyanions—The electronic structure of tetrahedral oxyanions can be considered taking ClO_4^- as an example (Table 3). The results of non-empirical calculation of ClO_4^- in a double- ζ AO basis set including $3d$ -AO Cl^{36} have shown that bonding in this system depends on MOs $1a_1$ ($3s$ - $2s$ -interaction), $2a_1$ ($3s$ - $2p\sigma$) and $2t_2$ ($3p$ - $2p$), while the upper occupied MOs $1e$, $3t_2$ and t_1 are weakly bonding or non-bonding combinations of $2p$ -AOs on ligands. Vacant d -orbitals of the central atom make a small contribution in almost all the MOs (in particular, some interaction was observed in the upper MOs $1e$ and $3t_2$). Though the total d -orbital population of Cl reaches as much as one electron*, this is not yet two electrons as required in the formal theory of localized pairs.

The use of a single- ζ AO basis set³⁷ in non-empirical calculations has resulted in an exaggerated population of Cl $3d$ -AO ($\sim 2e$), because MOs $1e$ and $3t_2$ have been found to possess a pronounced bonding character with a large transfer of electrons from $2p$ -AOs of ligands to $3d$ -AOs of Cl. This circumstance caused a negative effective charge -0.1 , though more accurate calculations³⁶ estimate a charge of Cl at $+1.5$.

* This value is probably somewhat exaggerated because of the unbalanced basis set which does not include $3d$ -AOs on O atoms.

Calculation of ClO_4^- in the NDDO approximation²⁷ in a mixed basis set with double- ζ AOs only for $2p$ -AOs of O and with inclusion of vacant $3d$ -AOs of Cl gave populations $3d$ -AOs of Cl close to the results of accurate calculations³⁶. However, due to considerable $3s$ - $2p\sigma$ and $3p\sigma$ - $2p\sigma$ overlap in this system, the NDDO approximation gives a distorted picture of electronic density distribution, leads to exaggeration of Cl AO populations and suggests a conclusion about a too small positive charge on a Cl atom (+0.3).

All the three calculations under consideration^{26, 36, 37} have given the same order of MOs in ClO_4^- .

Table 3. Electronic structure of ClO_4^- from various non-empirical calculations

MO energies (a.u.)	LCAO coefficients				
	Chlorine AOs			Oxygen group AOs	
	3s	3p	3d	2s	2p
$1t_1$	-0.25 ^a				1.00
	-0.11 ^b				1.00
	-0.20 ^c				1.00
$3t_2$	-0.31	0.04	0.07	0.02	0.87
	-0.18	0.00	0.15	0.03	0.82
	-0.39	-0.02	0.20	0.03	0.78
$1e$	-0.36		0.07		0.93
	-0.25		0.25		0.75
	-0.46		0.09		0.91
$2t_2$	-0.53	0.32	0.00	0.21	0.47
	-0.44	0.35	0.04	0.17	0.44
	-0.60	0.45	-0.08	0.26	0.38
$2a_1$	-0.68	0.22		0.53	0.25
	-0.61	0.25		0.55	0.21
	-0.78	0.32		0.59	0.09
$1t_2$	-1.12	0.19	0.03	0.73	0.05
	-1.07	0.20	0.02	0.74	0.03
	-1.28	0.22	0.02	0.74	0.03
$1a_1$	-1.46	0.41		0.47	0.12
	-1.35	0.52		0.41	0.07
	-1.49	0.50		0.47	0.03
Cl AO populations	1.26	3.42	0.88		
	1.54	3.30	2.26		
	1.64	3.90	1.20		
Cl effective charge		+1.44			
		-0.10			
		+0.26			

^aFrom ref. 36. ^bFrom ref. 37. ^cFrom ref. 27.

The same nature of MOs and bonding has been found from calculations of the same accuracy for an SO_4^{2-} ion^{38,39}. The electron density difference map based on the data of the most accurate calculations³⁸, which shows changes in the electronic density distribution caused by the inclusion of Cl $3d$ -AOs

in the basis set (Figure 1), demonstrates that due to this inclusion electronic density in the S—O bond region increases and overlap population rises from 0.35 to 0.86*e*.

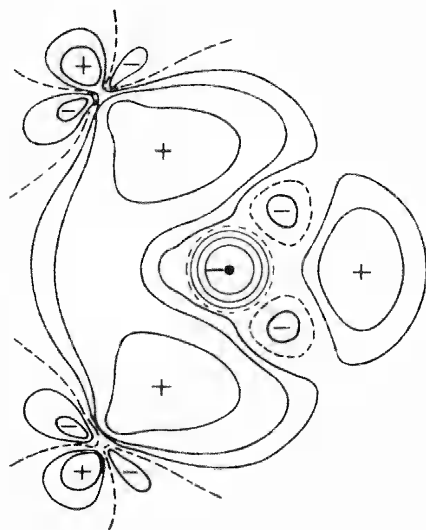


Figure 1. Electron density difference contours for SO_4^{2-} (in a plane O—S—O) showing the effect of S 3*d* = AO. Plotted contours are ± 0.01 , ± 0.02 and ± 0.05 ; broken lines give the zero contours (from ref. 38).

Comparison of data for the entire isoelectronic series of tetrahedral oxyanions AlO_4^{5-} , SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} and ClO_4^- can be carried out only on the basis of non-empirical calculations in the single- ζ AO basis set³⁹, and also in the NDDO approximation with the basis set described above²⁷. The order of MOs is identical in all the ions and agrees with the order found from photo-electron and x-ray photoelectron spectra (assuming Koopmans' theorem is valid)^{39,40}. The series of the investigated anions exhibits broadening of bands formed by MO groups $1a_1-1t_2$ and $2a_1-t_1$ having dominant contributions of oxygen 2*s*- and 2*p*-AOs which is ascribed to successive increase of covalence⁴⁰; at the same time in the left-hand end of the series the above MO groups converge to the respective levels of the ions of the central atom and of ligands (Figure 2). Central atom 3*d*-AO populations are practically the same for all oxyanions, according to the accurate calculation data^{36,38} and calculation in the NDDO approximation²⁷, while according to *ab initio* calculation with single- ζ AOs³⁹ they decrease in the series SO_4^{2-} (2.57), ClO_4^- (2.24), PO_4^{3-} (1.89). It is of interest to note that in the series of ClO_2^- , ClO_3^- , ClO_4^- oxyanions, Cl 3*d*-AO population increases with an increase in the number of ligands and oxidation number of Cl (1.04, 1.55 and 2.24) according to the data of SCF calculations in the single- ζ AO basis set³⁷.

The results of semi-empirical calculations for tetraoxyanions in the CNDO approximation and using the EHM technique depend on the selected parameters so strongly that attempts to derive from these results chemical

information that would be at least qualitatively unambiguous are not promising in our opinion (in particular, they make more vague, rather than clarify, the problem of participation of $3d$ -AOs in bonding⁴¹).

The SCF- X_α SW calculations for ClO_4^- and SO_4^{2-} have given the same order of MOs as *ab initio* calculations⁴².

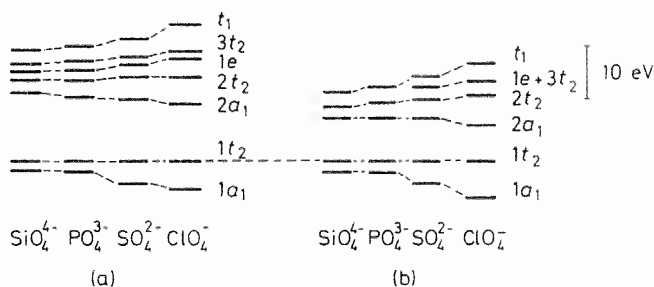


Figure 2. Energy level changes in tetrahedral oxyanions of second row elements: (a) calculated, from ref. 27; (b) experimental, from ref. 40.

Calculations of planar trioxyanions BO_3^{3-} , CO_3^{2-} , NO_3^- using the NDDO approximation with the above mixed basis set²⁷, in good agreement with the results of the *ab initio* calculations for CO_3^{2-} and NO_3^- ^{39,43}, have shown that bonding in compounds of this structural type is accomplished mainly through a formation of a'_1 and e' MOs of σ -character, and also through formation of $1a''_2$ MO corresponding to formation of π -bonds perpendicular to the plane of the molecule. The MO order in the trioxyanions of the first row elements is almost the same; as with tetraoxyanions, in the investigated series an increase in the covalence nature of the bond is observed which is confirmed by a change in the structure of the energy bands of these ions revealed both in calculations and in the photoelectron spectra of these compounds^{39,40} (Figure 3).

The experimentally derived order of the ionization potentials of non-transition element oxyanions coincides with the MO order obtained in non-empirical calculations and in the NDDO approximation. This shows that

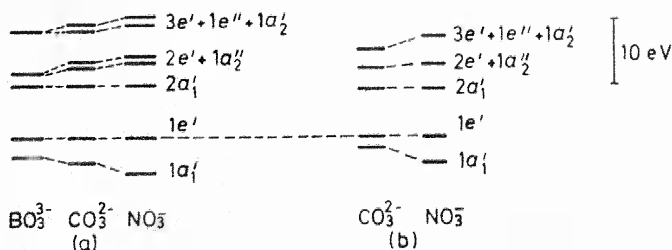


Figure 3. Energy level changes in trigonal oxyanions of first row elements: (a) calculated, from ref. 27; (b) experimental, from ref. 40.

Koopmans' theorem is applicable to this class of compounds. The estimation of intensities in x-ray spectra of non-transition element oxyanions in the MO calculations using the NDDO approximation²⁷ have given good correlation with experiment⁴⁰.

Table 4. Electronic structure of silicon fluorides from SCF MO LCAO calculations in the NDDO approximation²⁶.

MO	Energy (eV)	LCAO coefficients					
		Silicon AOs			Fluorine group AOs		
		3s	3p	3d	2s	2p σ	2p π
SiF ₄							
t ₁	-21.5					1.00	
3t ₂	-22.4		0.50	0.43	-0.48	0.43	-0.72
1e	-23.9			0.01			1.17
2t ₂	-23.0		0.52	0.37	-0.52	0.39	0.67
2a ₁	-27.2	0.74			-0.58	0.51	
1t ₂	-49.9		-0.07	-0.11	1.08	0.18	0.01
1a ₁	-49.9	-0.01			0.97	0.21	
SiF ₆ ²⁻							
3t _{1u}	-4.2		0.27		-0.11	0.56	-0.85
t _{1g}	-4.5						1.00
t _{2u}	-5.0						1.00
2e _g	-6.1			0.81	-0.57	0.72	
1t _{2g}	-8.9			0.02			0.99
2t _{1u}	-10.2		0.46		-0.34	0.51	0.51
2a _{1g}	-13.2	0.67			-0.54	0.56	
1t _{1u}	-32.7		-0.08		1.03	0.12	0.07
1e _g	-33.7			-0.19	1.13	0.11	
1a _{1g}	-34.2	0.01			0.97	0.17	

Fluorides—In the series of non-transition element complex fluorides we shall consider only tetrahedral AlF₄⁻, SiF₄, PF₄⁺ and octahedral AlF₆³⁻, SiF₆²⁻, PF₆⁻, SF₆ and ClF₆⁺ fluorides. Calculations for the entire series of fluorides given above have been made only in the aforementioned non-empirical NDDO approximation in a mixed AO basis set^{25,26}. The reliability of this study will be discussed somewhat later, for an SF₆ molecule for which more rigorous calculation is available⁴⁴.

The electronic structure of typical tetra- and octa-hedral fluorides is illustrated in Table 4 for SiF₄ and SiF₆²⁻. In contrast to oxyanions, fluorine 2s-AOs do not participate in the M—F bonding. Bonding in tetrafluorides is determined by 2a₁- and 2t₂-MOs, and that in hexafluorides by 2a₁- and 2t_{1u}-MOs formed by the interaction of 3s- and 3p-AOs of the central atom with fluorine 2p σ - and 2p π -AOs, and additionally, by 2e_g-MO which is set up exclusively due to interaction of vacant 3d-AOs of the non-transition element with fluorine 2p σ -AOs. Though fluorine 2p π -AOs take part in bonding formation, calculations failed to reveal noticeable 3d π —2p π interaction in fluorides which is so widely discussed in chemical literature. (On the contrary,

oxyanions whose ligands carry unpaired $2p\pi$ -electrons exhibit pronounced $3d\pi-2p\pi$ interaction.) Central atom $3d$ -AO populations in all the studied tetrafluorides are almost identical and do not exceed $0.5 e$; in the hexafluoride series they show a tendency to rise, reaching $1.75 e$ for SF_6 . This suggests a conclusion as to a more marked role of non-transition element $3d$ -AOs in octahedral fluorides as compared with tetrahedral ones. In the isostructural fluoride series the covalence character of bonding increases with transition from Al to Cl. It is interesting to point out that the ClF_6^- system which, unlike the compounds of the investigated isoelectronic series, carries two additional electrons shows a decreased contribution of $3d$ -AOs in bonding and some rise of positive charge on the central atom²⁵.

As follows from comparison of the calculated transition energies in x-ray spectra for octahedral fluorides with the experimental data³⁰ (in the frozen orbital approximation), calculations show correctly all the principal trends in the relative positions of some occupied and vacant levels with a change of the central atom from Al to S⁴⁵.

Calculations of the magnetic shielding constants for ^{19}F nuclei in the framework of the Ramsey-Cornwell theory (but with the estimate of excitation energies from eq. VIII) with due account for changes of the diamagnetic part show, for the studied fluoride series, a satisfactory correlation with the experimental data obtained using NMR spectra⁴⁶.

The reliability of the calculations for fluorides^{25, 26} is illustrated with SF_6 (Table 5) as an example by comparing them with the results of rigorous calculations in a double- ζ AO basis set including S $3d$ -AOs⁴⁴, and also with the data of x-ray photoelectron spectroscopy⁴⁷ on MO energies (assuming Koopmans' theorem is valid). The same table shows the results of calculations of SF_6 ionization potentials using the SCF- X_α SW method which took into account (approximately) reorganization of MOs caused by ionization of a molecule⁴⁸. It can be seen that SF_6 calculation in the NDDO approximation not only allows us to correctly reproduce the valence MO order (except for the inversion of $1e_g$ and $1t_{1u}$ which is of no great importance), but also estimates their energies so that it is quite sufficient to interpret an X-ray photoelectron spectrum on the basis of Koopmans' theorem. At the same time, comparison

Table 5. Energy levels of SF_6 (eV) from various calculations and experimental data

MO	SCF LCAO <i>ab initio</i> (ref. 44)	SCF LCAO non-empirical NDDO (ref. 26)	SCF- X_α SW (ref. 48)	X-ray photoelectron spectrum (ESCA) (ref. 37)
$1t_{1g}$	-18.2	-19.9	-15.9	16.0
$3t_{1u}$	-18.9	-20.0	-16.8	17.3
$1t_{2u}$	-19.4	-20.8	-16.8	
$2e_g$	-19.4	-22.7	-17.5	18.7
$1t_{2g}$	-22.2	-25.4	-18.8	19.9
$2t_{1u}$	-24.6	-27.9	-21.8	22.9
$2a_{1g}$	-29.6	-33.5	-26.7	27.0
$1e_g$	-45.4	-49.1	-35.6	39.3
$1t_{1u}$	-46.9	-48.4	-36.5	41.2
$1a_{1g}$	-50.5	-52.0	-39.3	44.2

of the calculated data on S 3*d*-AO population indicates that at large overlap between 3*d*-AOs with ligand AOs the NDDO approximation may result in a considerable overestimation of the contribution of 3*d*-AOs in bonding.

In general, the most reliable calculations of non-transition element coordination compounds permit the following general conclusions. The 3*d*-orbitals show a definite involvement in bonding in compounds with an enlarged formal valence of the central atom, the contribution of these orbitals increasing with the number of ligands. Thus, bonding in these compounds cannot be accounted for only through ionic valence structures without *d*-orbitals, but in all cases the role of the *d*-orbitals is much smaller than that required by the localized hybrid orbitals concept.

TRANSITION ELEMENT COORDINATION COMPOUNDS

Oxyanions—The transition element complexes that have been most extensively studied are tetrahedral oxyanions MnO_4^- , CrO_4^{2-} and VO_4^{3-} . Modern quantum chemistry of coordination compounds started actually in 1952 when Wolfsberg and Helmholz carried out calculations for MnO_4^- and CrO_4^{2-} ³² intended primarily for interpreting their optical spectra. Today about 20 calculations for MnO_4^- of an increasing order of complexity are available (see, for example, references in publication⁴⁹). It is noteworthy that the task of interpreting the spectrum of this compound has been gradually overshadowed by the attempts to find such a version of the theory that would guarantee the reliability of the electronic structure obtained and its stability in the course of further specifications. Finally, permanganate has become a sort of 'touchstone' for inorganic quantum chemistry. A stable picture of its electronic structure was impossible to obtain until Johansen's work in 1972⁴⁹. It would be instructive to see how the results of this exact study are reproduced in various simplified versions of the calculations performed.

Table 6 presents the result of non-empirical SCF calculations for MnO_4^- carried out as follows: (1) in the basis set of Hartree-Fock AOs approximated by thorough expansions in GF⁴⁹; (2) in a mixed basis set common in calculations of transition element compounds (with double- ζ 3*d*-AO for Mn¹², and in a mixed basis set of single- ζ 1*s*- and 2*s*-AOs and Hartree-Fock 2*p*-AO for O, with rough approximation of the basis AOs by small expansions in GF⁵⁰); (3) in a basis set of single- ζ AOs for Mn and O roughly approximated by GF expansions⁵¹. It can be seen that calculation⁵⁰ in which account is taken of the necessity to describe Mn 3*d*-AOs and O 2*p*-AOs by sufficiently exact functions quite satisfactorily gives the picture of the electronic structure of MnO_4^- obtained in exact calculation⁴⁹. According to the result of these calculations, the main contribution in bond formation in MnO_4^- is made by 3*d*-2*p* interaction in 5*t*₂- and 1*e*-MOs, while the upper occupied 1*t*₁, 6*a*₁ and 6*t*₂ may be regarded as non-bonding combinations of 2*p* π -AOs of ligands*.

* Unlike ClO_4^- in which bonding is due to 3*s*-2*p* and 3*p*-2*p* interactions in 6*a*₁ and 5*t*₂ MOs, and weakly bonding 1*e* MO involving vacant Cl 3*d*-AOs is destabilized (6*a*₁ MO in MnO_4^- including vacant Mn 4*s*-AOs is similarly destabilized).

Table 6. Electronic structure of MnO_4^- from various non-empirical SCF MO LCAO calculations

MO, energy (a.u.) composition (%)	Hartree-Fock AO basis set (ref. 49)	Double- ζ Mn 3d- O 2p-AO (ref. 50)	Single- ζ AO basis set (ref. 51)	
$1t_1$ 100% 2p O	-0.280	-0.211	-0.107	
$6a_1$	-0.295	-0.244	-0.073	
4s Mn/2p O	8/88	1/95	5/89	
$6t_2$	-0.333	-0.268	-0.157	
4p Mn/2p O	7/88	3/93	9/81	
$1e$	-0.422	-0.418	-0.230	
3d Mn/2p O	29/71	44/56	22/78	
$5t_2$	-0.471	-0.438	-0.320	
3d Mn/2p O	53/40	51/40	44/44	
$4t_2$	-1.082	-1.020	-0.969	
3d Mn/2s O	7/88	9/86	5/90	
$5a_1$	-1.103	-1.041	-0.989	
4s Mn/2s O	8/92	7/90	9/88	
E_{total} (a.u.)	-1448.7571	-1435.4853	-1433.3820	
Mn	3d	4.94	5.45	4.17
electron	4s	0.32	0.15	0.28
configuration	4p	0.74	0.52	1.29
Total overlap population	0.652	0.694	0.493	
Atomic charges	Mn	+0.90	+0.93	+1.29
	O	-0.50	-0.48	-0.57

The data on the composition of MnO_4^- MOs contradict the commonly accepted qualitative ideas of a significant involvement of vacant 4p-AOs of a metal in the bonding. The charge distribution calculated for MnO_4^- is in satisfactory agreement with the experimental estimate (+1.2 on Mn⁵²).

In the calculations for MnO_4^- made in the single- ζ AO basis set⁵¹, charges on atoms are exaggerated, the order of the upper occupied MOs is incorrectly determined, the role of Mn 3d-AOs in the strongly bonding $5t_2$ -MO is underestimated, Mn 4p-AO population is overestimated and the total overlap population is put too low.

On the other hand, the non-empirical CNDO approximation version (Table 7) using a mixed AO basis set for Mn and a single-AO basis set for the oxygen AOs^{16,53} gives a wrong sequence of valence MOs, exaggerates too much the role of Mn 4s- and 4p-AOs and at the same time underestimates the contribution of Mn 3d-AOs in the bonding $5t_2$ -MO which leads to a distortion in the Mn valence configuration and a completely unreal charge distribution. Semi-empirical calculations for MnO_4^- using the CNDO approximation⁵⁴ have demonstrated that variation of the parameters causes a change in the order of valence MOs and absolute arbitrariness in estimating charges on atoms (from +1.10 to -0.35 for Mn), so that a certain solution version was selected by comparison with the spectral data on the basis of

MODERN STATE OF MOLECULAR ORBITAL CALCULATIONS

 Table 7. Electronic structure of MnO_4^- from rigorous and approximate MO calculations

MO, energy (a.u.) composition (%)	<i>Ab initio</i> Hartree- Fock AO basis set (ref. 49)	Non-empirical SCF CNDO, double- ζ Mn 3d-AO (ref. 53)	Semi-empirical SCF CNDO single- ζ AO basis set (ref. 54)	Modified EHM (ref. 34)	SCF- X_x SW (ref. 55)	
$1t_1$ 100% 2p O	-0.280	-0.440	-0.137	-0.343	-0.341	
$6a_1$	-0.295	-0.660	-0.163	-0.486	-0.387	
$4s$ Mn/2p O	8/88	51/13	7/93			
$6t_2$	-0.333	-0.520	-0.197	-0.414	-0.381	
$4p$ Mn/2p O	7/88	16/72	2/98			
$1e$	-0.422	-0.510	-0.392	-0.600	-0.450	
$3d$ Mn/2p O	29/71	48/52	54/46		38/30	
$5t_2$	-0.471	-0.880	-0.412	-0.602	-0.457	
$3d$ Mn/2p O	53/40	23/37	75/25		43/33	
$4t_2$	-1.082	-1.300		-1.082	-0.893	
$3d$ Mn/2s O	7/88	14/76				
$5a_1$	-1.103	-1.360		-1.056	-0.906	
$4s$ Mn/2s O	8/92	35/63				
Mn	3d	4.94	5.12	6.71	4.42	
electron	4s	0.32	1.72	0.10	0.26	
Configuration	4p	0.74	3.18	0.02	0.48	
Atomic charges	Mn	+0.99	-3.00	+0.17	+1.85	+0.64
	O	-0.50	+0.50	-0.29	-0.71	-0.41

rather indirect assignments associated with discussion of magnetic circular dichroism.

The data of calculation for MnO_4^- in the most elaborate EHM version³⁴ are at variance with the results of accurate calculated data⁴⁹, both with respect to MO order and charge distribution.

The calculation of MnO_4^- by the SCF- X_x SW method yields an inversion of $6a_1$ - and $6t_2$ -MOs, but suggests a qualitatively correct inference on the formation of bonding due to $3d$ - $2p$ interaction in $5t_2$ - and $1e$ -MOs and a satisfactory estimation of charge distribution⁵⁵.

Table 8. Energies of occupied MOs (a.u.) in transition metal tetraoxyanions from various non-empirical calculations

	VO_4^{3-} Calculations			CrO_4^{2-} Calculations			MnO_4^- Calculations				
	a	b	c	a	b	c	a	b	c		
$1t_1$	0.32	0.43	0.05	$1t_1$	0.08	0.19	-0.19	$1t_1$	-0.21	-0.11	-0.44
$6t_2$	0.25	0.36	0.08	$6t_2$	0.02	0.12	-0.21	$6a_1$	-0.24	-0.07	-0.66
$6d_1$	0.22	0.37	-0.12	$6a_1$	0.01	0.17	-0.39	$6t_2$	-0.27	-0.16	-0.52
$1e$	0.19	0.38	-0.09	$1e$	-0.10	0.08	-0.30	$1e$	-0.42	-0.23	-0.51
$5t_2$	0.18	0.30	-0.38	$5t_2$	-0.11	0.00	-0.63	$5t_2$	-0.44	-0.32	-0.88

^a *Ab initio* SCF, double- ζ Mn 3d-, O 2p-AO (ref. 56).

^b *Ab initio* SCF, single- ζ -AO basis set (refs. 51, 56).

^c SCF CNDO non-empirical, double- ζ Mn 3d-AO (refs. 53, 57).

Table 9. Composition of the valence MOs (%) for transition metal tetraoxyanions from non-empirical calculations (1) in mixed AO basis set, ref. 56; (2) in single- ζ AO basis set, refs. 51, 56; (3) in the CNDO approximation, refs. 53, 57

MO	Calculation	Metal AOs												Oxygen group AOs						
		3d			4s			4p			2s			2p						
		VO ₄ ³⁻	CrO ₄ ²⁻	MnO ₄ ⁻	VO ₄ ³⁻	CrO ₄ ²⁻	MnO ₄ ⁻	VO ₄ ³⁻	CrO ₄ ²⁻	MnO ₄ ⁻	VO ₄ ³⁻	CrO ₄ ²⁻	MnO ₄ ⁻	VO ₄ ³⁻	CrO ₄ ²⁻	MnO ₄ ⁻				
1r ₁	(1)	1	1	2													100	100	100	
	(2)	12	5	6														88	92	93
	(3)	7	13	16														75	78	81
6t ₂	(1)																	90	80	72
	(2)				5	1												92	96	95
	(3)				24	7	5											70	87	89
6a ₁	(1)				44	47	51											7	8	13
	(2)																	65	61	56
	(3)																	91	80	78
1e	(1)	35	39	44														75	72	52
	(2)	9	20	22																
	(3)	25	28	48																
5t ₂	(1)	32	40	51				4	5	3								63	52	40
	(2)	19	32	44				21	14	10								60	54	44
	(3)	12	18	23				53	45	40								36	36	37
4t ₂	(1)	5	7	9				5	4	3								87	86	1
	(2)	4	4	5				9	3	2								91	90	2
	(3)	18	14	14				9	11	10								74	76	1
5a ₁	(1)				11	9	7											88	89	90
	(2)					11	9											87	88	2
	(3)				51	46	35											49	53	63

MODERN STATE OF MOLECULAR ORBITAL CALCULATIONS

Comparison of various MnO_4^- calculations shows that approximate, in particular semi-empirical, calculations do not in any way guarantee the reliability of the results obtained. Unfortunately, the same refers to non-empirical SCF calculations with single- ζ AO basis sets. The latter remark is especially important, because it is sometimes claimed that calculations with limited but identically selected basis sets are apt to, at least, reproduce chemical trends in related compound series.

Table 10. Electronic structure of transition metal tetraoxanions from non-empirical MO calculations

Overlap populations	<i>Ab initio</i> , in mixed AO basis sets (ref. 56)			<i>Ab initio</i> , in single- ζ AO basis sets (refs. 51, 56)			
	VO_4^{3-}	CrO_4^{2-}	MnO_4^-	VO_4^{3-}	CrO_4^{2-}	MnO_4^-	
4s-2s	0.058	0.066	0.049	-0.056	0.016	0.013	
4s-2p	0.051	0.020	0.018	0.081	0.051	0.047	
3d-2s	0.033	0.004	-0.050	0.011	0.017	0.007	
3d-2p	0.483	0.493	0.477	0.165	0.228	0.219	
4p-2s	0.090	0.097	0.076	-0.120	-0.058	-0.021	
4p-2p	0.219	0.177	0.124	0.252	0.254	0.228	
Total overlap populations	0.934	0.857	0.694	0.333	0.508	0.493	
Metal electronic configuration	3d	3.57	4.43	5.45	2.35	3.26	4.17
	4s	0.32	0.20	0.16	0.71	0.36	0.28
	4p	1.19	0.82	0.52	2.24	1.75	1.29
Atomic charges	Mn	-0.08	+0.58	+0.93	-0.29	+0.63	+1.29
	O	-0.73	-0.64	-0.48	-0.68	-0.66	-0.57

The incompetence of this view is obviously illustrated in Table 8 which gives the comparison of the results of two *ab initio* and one approximate non-empirical calculations for the isoelectronic series of tetraoxanions VO_4^{3-} , CrO_4^{2-} and MnO_4^- using the basis sets described above for Mn^{53, 56, 57}. *Ab initio* calculations with a single- ζ AO basis set and also calculations using the CNDO approximation do not allow us to reproduce for at least one oxyanion a sequence of valence MOs obtained in reliable calculations⁵⁶ with an extended AO basis set (these sequences have been found to be far from identical for different oxyanions as could be expected from the general postulates of the crystal field theory). Comparative data (Tables 9 and 10) on the composition of valence MOs indicate that apart from drawbacks pointed out for MnO_4^- as an illustration, calculations with single- ζ AO basis sets in the series VO_4^{3-} , CrO_4^{2-} , MnO_4^- yield an exaggerated change of the central atom AO contribution in $5t_2$ -, $1e$ - and $6a_1$ -MOs, with changes of the contribution of 3d-AOs in the $6t_2$ -MO and 4p-AO in the $5t_2$ -MO completely distorted. Moreover, such calculations give underestimated total overlap populations which do not follow a systematic trend of these values in the series MnO_4^- , CrO_4^{2-} , VO_4^{3-} predicted by more reliable calculations. Also,

it follows from calculations with a single- ζ AO basis set that the main contribution in bonding in all the investigated oxyanions depends on the $4p-2p$ overlap population, whereas according to reliable calculations⁵⁶, the $3d-2p$ overlap population is two or three times bigger and dominates.

Approximate calculations of oxyanions^{53, 57} by the CNDO method yield results which are still less accurate.

The attempts to confirm the correctness of calculations of the electronic structure of transition metal oxyanions, by comparing with the experimental optical spectrum calculated in various approximations which have been made almost in all works, have met with failure. This is probably due to the fact that the first vacant MOs in these compounds are located very close to each other, as was revealed in the accurate calculations for the ground state of MnO_4^- ⁴⁹. In such conditions, account of configuration interaction and direct calculation of excited states are absolutely indispensable for estimation of transition energies. However, even in the best works⁵⁰ devoted to the discussion of the optical spectrum of transition metal oxyanions, the wave functions of excited states were derived using virtual ground-state MOs and the effect of Cl was not fully taken into consideration. The only conclusion which can be made on the basis of the calculations for transition metal oxyanions available at present is that the first optical transitions in these complexes are, most probably, associated with a transfer of charges from the ligands to the metal atom.

Additional correlation between the calculated and experimental data on the position of energy levels could be established if well-resolved valence x-ray photoelectron spectra were available. The spectra that have been resolved so far permit only an approximate estimation of the width of a band formed by a group of the upper five valence $1t_1-5t_2$ MOs (1.5 eV for CrO_4^{2-} and 3.0 eV for MnO_4^- according to calculations⁵⁸) which has an order of magnitude in good agreement with the results of the reliable non-empirical calculations (5.2 and 6.2 eV, respectively⁵⁰), but is highly exaggerated in some semi-empirical calculations.

By combining x-ray-photoelectron and x-ray spectra and analysing the intensities in the x-ray spectra on the basis of MO calculations, it has become possible to plot the empirical order of valence MOs for VO_4^{3-} and CrO_4^{2-} ⁵⁶: $5a_1 < 4t_2 < 5t_2 < 6t_2 < 1t_1 < 1e$ (the position of $6a_1$ has not yet been found) which differs from that obtained in non-empirical calculations in the position of the $1e$ -MO only. The reason for this difference may be either insufficient accuracy of the MO calculated composition which must affect spectrum assignment, or inapplicability of the 'frozen orbitals' approximation to these compounds.

Fluorides—The transition metal fluoride that has been studied in greatest detail is NiF_6^{4-} (an arbitrarily isolated cluster in a KNiF_3 crystal). Unlike the complexes considered above, NiF_6^{4-} has an open electron shell which permits making use of ESR and NMR spectra providing information about the composition of the MO on which an unpaired electron is located, for discussion of its structure. The crystal field splitting parameter $10Dq$, a fractional occupancy by unpaired spins f_s and f_o of the ligand AOs, and the A_s and A_o components of the hyperfine interaction tensor in ESR and NMR spectra have been discussed in the calculations of NiF_6^{4-} . The pioneering approximate

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non-empirical calculations⁵⁹ in a Hartree-Fock analytical AO basis set for Ni^{2+} and F^- showed good agreement with the experiment for $10Dq$, f_s , f_σ and A_s , A_σ and demonstrated the crucial importance of covalence effects in the $\text{Ni}^{2+}-\text{F}^-$ bond, and also of the π -bond in hyperfine interactions and optical intensities; however, this agreement was later shown to be accidental⁶⁰. Reliable data on the electronic structure of NiF_6^{4-} were obtained as recently as 1971 in work^{61*} based on restricted and unrestricted Hartree-Fock calculations for the ground state (${}^3A_{1g}$) and two excited states ($3T_{2g}$ and ${}^3T_{1g}$) in sufficiently extended GF basis sets for the Ni^{2+} ion (including $4s$ and $4p$ AOs) and for F^- ions. Table 11 illustrates the energies and composition of NiF_6^{4-} MOs. Two unpaired electrons are located on the antibonding e_g -MO.

Table 11. Electronic structure of NiF_6^{4-} from *ab initio* RHF SCF calculations, ref. 61

MO	Energy (a.u.)	Composition (%)				Character
		Ni^{2+}	AO	F^-	AO	
e_g	0.664	98	$3d$	2	$2p$	Antibonding
t_{2g}	0.265	77	$3d$	23	$2p$	Antibonding
t_{1g}	0.222			100	$2p$	Non-bonding
t_{1u}	0.211			100	$2p$	Non-bonding
t_{2u}	0.204			100	$2p$	Non-bonding
e_g	0.197	2	$3d$	98	$2p$	Bonding
t_{1u}	0.166			100	$2p$	Non-bonding
t_{2g}	0.151	23	$3d$	77	$2p$	Bonding
a_{1g}	0.137	2	$4s$	98	$2p$	Antibonding
e_g	-0.713			100	$2s$	Non-bonding
t_{1u}	-0.717	1	$4p$	99	$2s$	Non-bonding
a_{1g}	-0.728	2	$4s$	98	$2s$	Non-bonding

One of the most interesting calculation results is that Ni AO populations in the complex differ little from populations in a free Ni^{2+} ion, and that fluorine may be regarded with approximation as an F^- ion. The total overlap population for the Ni-F bond is close to zero which corresponds to an ionic model. Covalence arises mainly due to Ni $3d$ -AO interaction with F $2p$ -AO with a very small contribution from Ni $4s$ - and $4p$ -AOs. This disproves common hypotheses about strong involvement of $4s$ - and $4p$ -AOs of nickel in the bonding which are based on the results of calculations with unsatisfactory basis sets.

The calculated values of the hyperfine interaction parameters A_s , A_σ from ligands correlate with the experimental data. The fractional occupancy by the unpaired spins f_s and f_σ of the ligand $2s$ - and $2p\sigma$ -AOs, which defined the degree of covalence, is small. Despite, however, this circumstance, covalence effects in NiF_6^{4-} strongly influence such electronic structure details as the crystal field splitting parameter $10Dq$ and the energies of other electronic

* The same results were obtained in a later calculation⁶² made with a somewhat less complete AO basis set (this paper gives detailed references to NiF_6^{4-} calculations).

transitions (Table 12). It is evident that estimations of the energies of transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ($10Dq$) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ within the crystal field model are at great variance with the experimental data. Estimation of the parameter $10Dq$ within the restricted Hartree-Fock theory using ground state virtual MOs (in the 'frozen orbitals' approximation) yields a result which is 5 times exaggerated. It is only estimation of the parameter $10Dq$ from the energy difference for the excited and ground states based on direct calculations of the excited state that shows good agreement with the experimentally derived value. And, nevertheless, similar calculations for the second electronic transition ${}^3A_{2g} \rightarrow {}^3T_{1g}$ gave a value exaggerated by a factor of 2. It was believed⁶¹ that this was due to the fact that the calculations do not take into account CI which is particularly important because of possible coupling of the ${}^3T_{1g}$ ($t_{2g}^5 e_g^3$) state to the ${}^3T_{1g}$ state arising from the configuration $t_{2g}^4 e_g^4$.

Table 12. Estimates of electronic transition energies in NiF_6^{4-} from *ab initio* calculations, ref. 61

Transition	From crystal field model	From eq. VII	From excited complex calculations	Experimental data
${}^3A_{2g}(t_{2g}^6 e_g^2) \rightarrow {}^3T_{2g}(t_{2g}^5 e_g^3)$ ($10Dq$)	1512	33250	6089	7250
${}^3A_{2g}(t_{2g}^6 e_g^2) \rightarrow {}^3T_{1g}(t_{2g}^5 e_g^3)$	17214		21203	12530

It should be remembered that comparison with experiment for perovskite KNiF_3 is based on the calculations for the model cluster NiF_6^{4-} . However, as has been shown⁶², the inclusion of successive layers of positive point charges (K^+) in a calculation of approximately the same accuracy does not produce any appreciable effect on the value of $10Dq$ which proves the acceptability of the NiF_6^{4-} model cluster.

For the entire series of octahedral hexafluoride complexes MF_6^{n-} non-empirical approximate calculations have been carried out with a mixed basis set (with double- ζ M $3d$ -AOs and F $2p$ -AOs) partially neglecting some many-centre integrals and roughly estimating the rest of these integrals^{63, 65}, and also semi-empirical calculations in the INDO-type⁶⁶ and CNDO⁶⁷ approximations and using the Wolfsberg-Helmholz method^{68, 69}. Calculations⁶³ have shown a satisfactory correlation with the experimental transition energies (with partial inclusion of CI) and with the data of ESR spectra; however, M $4s$ - and $4p$ -AO populations are exaggerated too much. In semi-empirical calculations^{66, 67} for NiF_6^{4-} , $4s$ - and $4p$ -AO populations are greatly exaggerated, and the fractional occupancy by the unpaired spin of the ligands is underestimated. Calculations⁶⁷ give underestimated values of the central atom effective charge (Table 13); in calculations⁶⁹ by the Wolfsberg and Helmholz method the compositions of e_g - and t_{2g} -MOs are not correct which leads to unsatisfactory values of f_s and f_g . Therefore, systematic studies of the transition element hexafluoride series with the aid of

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 Table 13. Electronic structure of NiF_6^{4-}

Calculations :	Modified EHM (ref. 69)	UHF approximated		Ab initio		
		CNDO (ref. 67)	INDO-type (ref. 66)	RHF (ref. 61)	UHF (ref. 61)	
Ni AO	3d	8.36	8.08	8.04	8.06	8.02
populations	4s	0.09	0.55	0.36	0.07	0.07
	4p	0.10	0.49	0.02	0.06	0.04
Ni Z_{eff}	+1.64	+0.88*	+1.54	+1.82	+1.82	
f_s (%) (experim. 0.54)	0.48†	0.15		0.36	0.44	
f_p (%) (experim. 3.78)	8.3†	1.4	0.46	4.80	6.32	

* Ni net charge in ref. 67 is given as -0.19 . Here we give Ni gross charge $+0.88$, calculated from AO populations as given in ref. 67.

† Our estimation from MO composition, given in ref. 69.

approximate calculations do not seem reliable and make it impossible to discuss chemical trends on the basis of their results.

Square planar complexes—Interesting and rather unexpected results have been obtained recently for square planar transition metal complexes. In earlier studies, interpretation of the optical and magnetic properties of such compounds as CuCl_4^{2-} , PtCl_4^{2-} , $\text{Ni}(\text{CN})_4^{2-}$ involved various MO schemes based on qualitative consideration (as in the crystal field theory) or on semi-empirical calculations by the Wolfsberg–Helmholz method^{70, 71}. According to such schemes, the upper occupied MOs in square planar complexes are almost pure metal 3d-AOs, and the set of lower MOs consists of non-bonding combinations of the ligand σ - and π -orbitals.

Table 14. Electronic structure of transition metal square planar complexes

Crystal field theory	Empirical by Figgis	PtCl_4^{2-} EHM (ref. 70)	CuCl_4^{2-} ab initio SCF MO LCAO (ref. 72)	CuCl_4^{2-} SCF- X_g SW (ref. 77)	PtCl_4^{2-} SCF- X_g SW (ref. 78)
$d_{x^2-y^2}$	$d_{x^2-y^2}$	$b_{1g}^* d_{x^2-y^2}$	$b_{1g} d_{x^2-y^2}$	$b_{1g} d_{x^2-y^2}$	$b_{1g}^* d_{x^2-y^2}$
d_{xy}	d_{z^2}	$b_{2g} 50\% d_{xy}$	$a_{2g} 3pCl$	$a_{2g} 3pCl$	$b_{2g} 50\% d_{xy}$
d_{z^2}	$d_{xz, yz}$	$e_g 50\% d_{xz, yz}$	$e_u 3pCl$	$e_u 3pCl$	$e_g 45\% d_{xz, yz}$
$d_{xz, yz}$	d_{xy}	$a_{1g} d_{z^2}$	$b_{2u} 3pCl$	$e_g d_{xz, yz}$	$a_{2g} 3pCl$
3pCl	3pCl	$b_{2u} 3pCl$	$e_g 3pCl$	$b_{2u} 3pCl$	$e_u 3pCl$
3pCl	3pCl	$a_{2g} 3pCl$	$b_{1g} 3pCl$	$b_{2g} d_{xy}$	$a_{1g} 60\% d_{z^2}$
3pCl	3pCl	$e_u 3pCl$	$a_{2u} 3pCl$	$a_{2u} 3pCl$	$b_{2u} 3pCl$
3pCl	3pCl	$a_{2u} 3pCl$	$b_{2g} 3pCl$	$a_{1g} d_{z^2}$	$a_{2u} 3pCl$
3pCl	3pCl	$e_g 50\% d_{xz, yz}$	$e_u 3pCl$	$e_u 3pCl$	$e_u spCl$
3pCl	3pCl	$e_u 3pCl$	$a_{1g} 3pCl$	$e_g 50\% d_{xz, yz}$	$e_g 50\% d_{xz, yz}$
3pCl	3pCl	$b_{2g} 50\% d_{xy}$	$a_{1g} d_{z^2}$	$b_{2g} 50\% d_{xy}$	$b_{2g} 50\% d_{xy}$
3pCl	3pCl	$a_{1u} 3pCl$	$e_g d_{xz, yz}$	$b_{1g} 50\% d_{x^2-y^2}$	$a_{1g} 50\% d_{z^2}$
3pCl	3pCl	$b_{1g} 3pCl$	$b_{2g} d_{xy}$	$a_{1g} 50\% d_{z^2}$	$b_{1g} 50\% d_{x^2-y^2}$

However, the non-empirical restricted Hartree-Fock calculations (in a mixed basis set) carried out later for CuCl_4^{2-} which is an open-shell system⁷² suggested quite the opposite conclusions. Except for the half-filled b_{1g}^* MO, with the dominant contribution from the Cu $3d_{x^2-y^2}$ -AO, the entire set of the upper MOs consists exclusively or almost exclusively of Cl $3p$ -AOs, and under these MOs are located MOs which are almost pure Cu $3d$ -AOs. The energy of the half-filled b_{1g}^* (entered at the top of Table 14) is less than that for MOs consisting of Cl $3p$ -AOs and is located in the same energy region with the other MOs including the Cu $3d$ -AO. The whole sequence of MOs including $3d$ -AOs is in accordance with the empirical scheme given by Figgis⁷¹.

Calculations of CuCl_4^{2-} and PtCl_4^{2-} by the X_α -SW method^{73, 74} have given an electronic structure which agrees neither with the empirical schemes nor with the MO LCAO SCF calculation data. According to calculations using the X_α -SW technique, levels corresponding to pure p -AOs on ligands and those including metal d -AOs form alternating sets.

Contrariwise, conclusions about the CuCl_4^{2-} MO sequence made in one of the INDO approximation versions⁷⁵ agree, on the whole, with those inferred from accurate calculations⁷² probably due to properly selected semi-empirical parameters). Using the same approximation, a qualitatively similar MO scheme was obtained⁷⁵ for palladium and platinum halogen complexes isostructural with CuCl_4^{2-} . These complexes have one valence electron less than CuCl_4^{2-} , and their b_{1g} MO is unoccupied. According to the calculations, the upper filled MOs of these complexes, similar to CuCl_4^{2-} , have a composition close to ligand p -orbitals, and MOs including metal d -AOs are located under the aforementioned MOs. However, it has been found from the photoelectron spectrum of PtCl_4^{2-} that the ionization energy for levels corresponding to metal d -AOs is lower than for levels corresponding to Cl $3p$ -AOs. Such a discrepancy between the calculated and experimental values might be accounted for either by an error in the non-empirical calculations or by the fact that Koopmans' theorem is inapplicable in this particular case on account of reorganization of MOs caused by ionization of the complex. An answer to this question can be given only after performing non-empirical calculations for the ground as well as for excited states of the ionized complex. Such studies have been made for a square planar $\text{Ni}(\text{CN})_4^{2-}$ complex whose ground state was found to exhibit^{77, 78} an MO sequence identical with that obtained for CuCl_4^{2-} . Calculations of the excited states of a monocharged $\text{Ni}(\text{CN})_4^-$ have demonstrated that ionization energies due to a removal of an electron from MOs corresponding to the Ni $3d$ -AO are lower as compared with the energies of MOs corresponding to almost pure ligand σ - and π -orbitals⁷⁹ which is associated with considerable reorganization of the MOs during ionization of $\text{Ni}(\text{CN})_4^{2-}$.

According to the results of the calculations, such reorganization of MOs occurs not only during ionization, but also in the case of electron excitations in $\text{Ni}(\text{CN})_4^{2-}$. Judging by estimation of transition energies simply from MO energy differences, transitions with the lowest energy in the optical spectrum of $\text{Ni}(\text{CN})_4^{2-}$ should be assigned to π - π^* , rather than to d - d^* transitions, which contradicts the experimental assignment (Table 15). The use of the 'frozen orbitals' approximation for estimating the energy of an excited complex also fails to provide agreement with experiment. Correlation

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 Table 15. Various estimates of electronic transition energies (cm^{-1}) for $\text{Ni}(\text{CN})_4^{2-}$ from *ab initio* calculations, ref. 81

Transitions	From eq. VIII	From eq. VII	From energy difference of excited and ground states	Experimental data and assignment
$1a_{2g}(\pi) \rightarrow 4a_{2u}(\pi)$	112 400	75 170	71 700	
$9a_{1g}(d_{z^2}) \rightarrow 4a_{2u}(\pi)$	129 000	80 330	33 900	35 200($d \rightarrow \pi$)
$1a_{2g}(\pi) \rightarrow 3b_{2g}(\pi)$	141 000	108 000	106 000	
$9a_{1g}(d_{z^2}) \rightarrow 3b_{2g}(\pi)$	152 500	103 600	58 500	
$1a_{2g}(\pi) \rightarrow 6b_{1g}(d_{x^2-y^2})$	152 800	111 000	69 700	
$9a_{1g}(d_{z^2}) \rightarrow 6b_{1g}(d_{x^2-y^2})$	164 000	62 770	20 600	23 000($d \rightarrow d$)

between the calculated and experimental data can be attained only by means of direct calculations of the excited states of $\text{Ni}(\text{CN})_4^{2-}$. In this case, the calculated energies of transitions originating or terminating on MOs which are predominantly Ni 3d-AOs are found to be 2 or 3 times lower, due to considerable reorganization of these MOs. In an excited $\text{Ni}(\text{CN})_4^{2-}$ complex MOs including Ni 3d-AOs become almost pure Ni 3d-AOs, whereas MOs which are predominantly ligand orbitals preserve their composition unchanged in any excited state (Table 16).

Thus, MOs in square planar transition metal complexes may be considerably reorganized in the course of electron excitation or ionization.

 Table 16. Reorganization of occupied and unoccupied MOs in $\text{Ni}(\text{CN})_4^{2-}$ at certain one-electron excitations from *ab initio* calculations, ref. 81

MO	States*	LCAO coefficients†
$1a_{2g}(\pi)$	A	$0.32 2p_C + 0.22 2p'_C + 0.71 2p_N$
	B	
	$1a_{2g}(\pi) \rightarrow 4a_{2u}(\pi)$	$0.32 2p_C + 0.22 2p'_C + 0.71 2p_N$
	$1a_{2g}(\pi) \rightarrow 3b_{2g}(\pi)$	$0.31 2p_C + 0.24 2p'_C + 0.70 2p_N$
$9a_{1g}(d_{z^2})$	A	$0.36 4s_{\text{Ni}} - 0.23 2p_C + 0.42 2p_N + 0.72 3d_{z^2\text{Ni}}$
	B	
	$9a_{1g}(d_{z^2}) \rightarrow 6b_{1g}(d_{x^2-y^2})$	$0.95 3d_{z^2\text{Ni}}$
	$9a_{1g}(d_{z^2}) \rightarrow 3b_{2g}(\pi)$	$0.97 3d_{z^2\text{Ni}}$
$3b_{2g}(\pi)$	A	$0.29 2p_C - 0.58 2p'_C + 0.82 2p_N + 0.25 3d_{xy\text{Ni}}$
	$1a_{2g}(\pi) \rightarrow 3b_{2g}(\pi)$	$-0.31 2p_C - 0.55 2p'_C + 0.75 2p_N + 0.28 3d_{xy\text{Ni}} - 0.25 3d'_{xy\text{Ni}}$
$6b_{1g}(d_{x^2-y^2})$	A	$-0.24 2s_C + 0.26 2s_N + 0.23 2p_C + 0.38 2p'_C - 0.28 2p_N + 0.85 3d_{x^2-y^2\text{Ni}} + 0.53 3d_{x^2-y^2\text{Ni}}$
	$1a_{2g}(\pi) \rightarrow 6b_{1g}(d_{x^2-y^2})$	$-0.49 2s_C + 0.99 3d_{x^2-y^2\text{Ni}}$

* A—from ground state calculation;

B—from calculations for the excited states.

† Only coefficients bigger than 0.2 are included.

Confusions that may arise in interpreting the experimental data will then be associated with incorrect methods of estimating excitation or ionization energies, rather than with errors in non-empirical calculations.

The above allows us to place reliance on the results of rigorous computations for the ground state of the investigated square planar complexes and to discuss the bonding picture obtained for these complexes. Calculations⁷² suggested a conclusion about a comparatively small covalence of the CuCl_4^{2-} complex (overlap population is 0.2; the charges are shown in Table 17) and a comparatively low contribution of Cu 4s- and 4p-AOs in the bonding. Similar results are obtained also for NiF_4^{2-} ⁸⁰ and CuF_4^{2-} ⁸¹. (It is noteworthy that bonding in nickel tetrafluoride is, according to calculations, more covalent than that in hexafluoride.)

Table 17. Electronic structure of some transition metal complexes from *ab initio* calculations

AO populations and atomic charge	CuCl_4^{2-} (from ref. 72)	NiF_4^{2-} (from ref. 80)	$\text{Ni}(\text{CN})_4^{2-}$		$\text{Ni}(\text{CO})_4$		$\text{Ni}_5\text{H}_5\text{NO}$ (from ref. 77)
			(from ref. 77)	(from ref. 78)	(from ref. 82)	(from ref. 81)	
3d	9.14	8.13	8.75	8.76	9.23	9.23	9.05
4s	0.34	0.02	0.21	0.52	-0.03	0.00	0.00
4p	0.24	0.49	0.26	0.41	0.35	0.57	0.15
Z_M	+1.28	+1.12	+0.81	+0.46	+0.47	+0.24	+0.82

It should be noted that, as shown by approximate calculations by the scattered wave method^{73, 74}, CuCl_4^{2-} and PtCl_4^{2-} possess considerable covalence and have a number of rather bonding MOs which does not seem to be likely in the light of the results of the exact calculations described above.

In contrast to square planar complexes with halogen ligands, bonding in the $\text{Ni}(\text{CN})_4^{2-}$ complex, according to non-empirical calculations^{77, 78}, has a more covalent character and is determined mainly by the interaction of ligand σ -AOs with Ni 3d- and also 4s- and 4p-AOs, involving a transfer of carbon 2s-electrons to metal. No bonding due to ligand π -AOs in $\text{Ni}(\text{CN})_4^{2-}$ has been revealed. The effective charge on Ni is estimated at about +0.5.

Carbonyls—Two calculations for a tetrahedral $\text{Ni}(\text{CO})_4$ complex^{81, 82} (identical with those^{77, 78} for $\text{Ni}(\text{CN})_4^{2-}$) have permitted a general conclusion that bonding in this complex (Table 18) is accomplished mainly due to interaction of Ni 4p-AOs (despite their low total population) with C 2s-AOs rather than due to 3d-2p interaction (4p-2s interaction makes a major contribution to the total overlap population of the Ni—C bond). At the same time it was found that 3d-2p π overlap population makes a small positive contribution, whereas in $\text{Ni}(\text{CN})_4^{2-}$ it is a small negative value. By comparing electronic density distribution in a free CO molecule and in an $\text{Ni}(\text{CO})_4$ complex it can be noted that an increase in the 2p-AO population of the C atoms is larger than a decrease in the 2s-AO population of these atoms which causes a small resultant charge transfer from Ni to CO (a charge on

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 Table 18. Ni(CO)₄ electronic structure from *ab initio* calculations, ref. 82

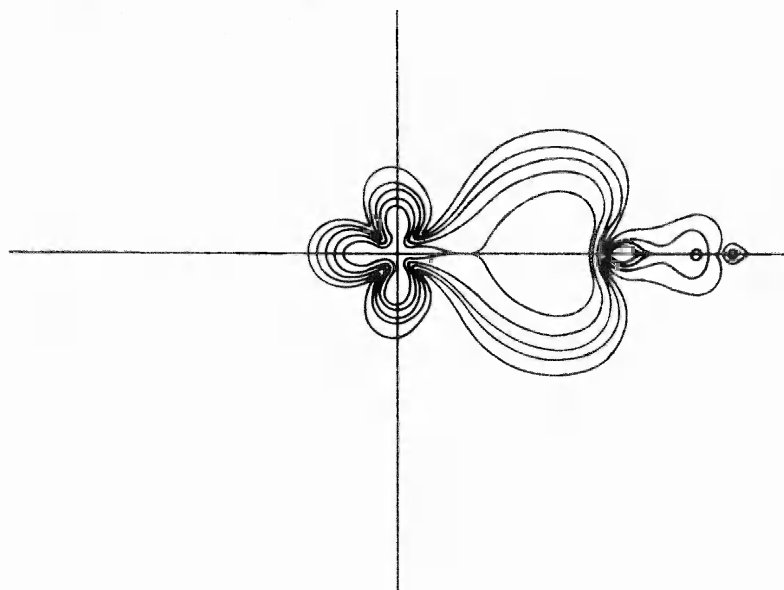
Energy levels (a.u.)	MO composition (%)							
	Oxygen AOs			Carbon AOs		Metal AOs		
	3d	4s	4p	2s	2p	2s	2p	
9t ₂	-0.429	65		9	11	7		8
2e	-0.496	90				1		9
8t ₂	-0.679	21		2	23	29	3	21
1t ₁	-0.687					27		73
1e	-0.697	4				31		66
7t ₂	-0.697	2		-2		32		68
8a ₁	-0.720		1		16	37	8	39
6t ₂	-0.830	3		-2	29	1	23	46
7a ₁	-0.855		-3		46	9	18	29
6a ₁	-1.574				14	10	66	10
5t ₂	-1.575			-1	14	11	65	10
AO populations	9.231	-0.034	0.352		1.56	2.21	1.83	4.52
Atomic charges		+0.466			+0.234		-0.350	

Ni is estimated at $+0.47 e^{82}$ or at $+0.24^{81}$ (Table 13)). However, main changes in C—O bonding overlap population are not due to a decrease in the π -component because of acceptance of electrons on carbon oxide 2π -MOs; they are caused by an increase in the σ -component on account of a transfer of carbon 2s-electrons from the antibonding 5σ -MO of the ligand to the metal. A similar picture of bonding in Cr(CO)₆ obtained in calculations⁸² (effective charge on Cr is +0.7, experimental estimate of work⁵² is +0.4), indicates that from the viewpoint of the contribution to the bond, the CO ligand must be defined rather as a σ -donor, whereas from the viewpoint of charge transfer it acts as a π -acceptor.

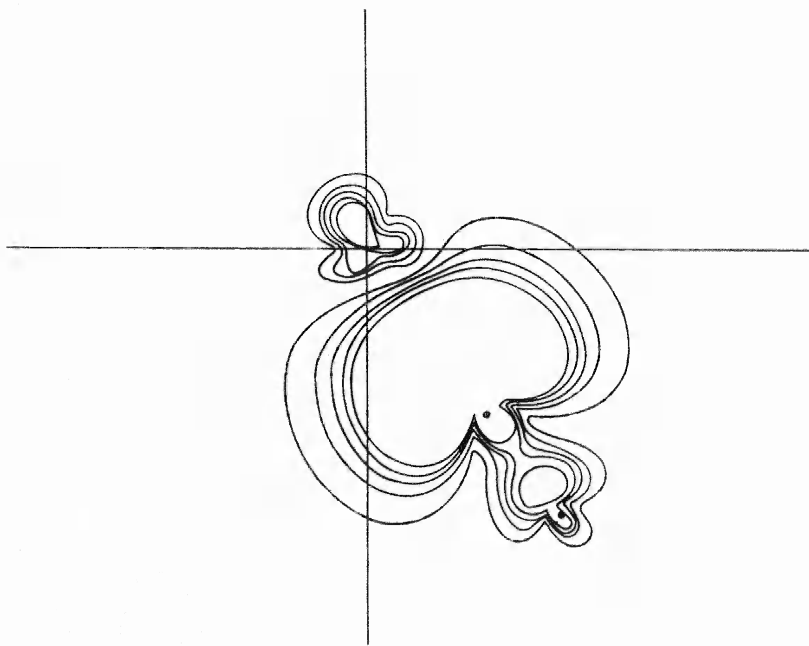
Differences in coordination of CN⁻ and CO become most pronounced if we consider localized MOs (LMOs) corresponding to Ni—C σ -bonds (Figure 4) and unshared pairs of carbon 2s-electrons. The picture of the σ -type of LMO shows that Ni 3d-AOs in Ni(CN)₄²⁻ are much more involved in the bonding than in Ni(CO)₄, where an important contribution is made by Ni 4p-AOs. The Ni—C overlap population in LMO for Ni(CN)₄²⁻ is 0.49 and for Ni(CO)₄ 0.07. The shift of the gravity centre of the LMO charge in the unshared carbon pair reaches 0.16 a.u. in Ni(CN)₄²⁻ and 0.09 a.u. in Ni(CO)₄.

Unlike Ni(CN)₄²⁻, in which the upper filled MOs have a π -ligand orbital character, the five upper occupied MOs (*t*₂ and *e*) in an Ni(CO)₄ complex are predominantly Ni 3d-AOs. Interpretation of the photoelectron spectrum of Ni(CO)₄ also leads to a conclusion that its first two ionization potentials are due to the removal of electrons mainly from Ni *d*-AOs. This testifies that Koopmans' theorem is valid for Ni(CO)₄, though final conclusions can be made only after calculation of the (NiCO₄)⁺ ion.

It should be pointed out that although the MO sequence calculated for Ni(CO)₄ using the SCF-X_z SW technique⁷⁷ correlates in its main features



(a)



(b)

Figure 4. Electron density contours for Ni—C localized orbital: (a) in $\text{Ni}(\text{CN})_4^{2-}$, (b) in $\text{Ni}(\text{CO})_4$ (from ref. 81).

with the sequence found in exact calculations, it gave rise to a wrong conclusion about formation of a strong covalent Ni—C bond (principally through interaction between the Ni 3d-AO and the ligand 5 σ -MO), and also failed to reveal a transfer of electrons from the metal atom to the unoccupied ligand 2 π -MO*.

π -Complexes

The use of the MO technique has played a decisive role in explaining the electronic structure of transition metal π -complexes in which the bond concept is totally inconsistent with classical valence theory. Studies of reactivity, redox reactions, magnetic susceptibility, fine structure in ESR spectra, optical and photoelectron spectra⁸³ enabled one to conclude that the two upper occupied MOs and the first vacant MO in all the complexes with aromatic rings must be predominantly metal 3d-AOs and be arranged in the order $a_{1g} \approx e_{2g} < e_{1g}^*$; the metal atom must carry a positive charge, but the bond must be covalent so that it cannot be described with the aid of a purely ionic $M^{2+}-(C_5H_5^-)_2$ model. The use of the extended Hückel method^{84,85} and the CNDO approximation^{86,87} gave different MO sequences (Table 19) and different estimates of the effective charges; only calculations⁸⁷ correlated with the above empirical MO sequence (assuming Koopmans' theorem is valid) and with the estimates of the effective charges. However, the most recent non-empirical calculation for ferrocene $Fe(C_5H_5)_2$ ⁸⁸ in the near-minimal basis set with double-AO only for Fe 3d-AO revealed a quite different picture of its electronic structure which, similar to square planar complexes, prevented correct interpretation of the experimental data with the aid of Koopmans' theorem. Orbitals e_{2g} and a_{1g} MOs which are predominantly metal 3d-AOs have been found to be much lower than e_{1g} and e_{1u} consisting of almost pure p -ligand orbitals. However, the calculation of the ionization potentials from the total energy differences of the ferricinium ground and excited states and ferrocene ground state showed correlation with experiment, so that although e_{2g} and a_{1g} MOs are lower than e_{1u} and e_{1g} MOs, the first two ionization potentials are due to removal of electrons from e_{2g} and a_{1g} MOs. In this case too, the invalidity of Koopmans' theorem is accounted for by considerable reorganization of e_{2g} and a_{1g} MOs which contain some contributions of π -ligand orbitals in $Fe(C_5H_5)_2$, and are almost pure Fe 3d-AOs in $Fe(C_5H_5)_2^+$.

If we proceed from the electron configuration of d^8 of Fe and $(C_5H_5)_2$, then according to non-empirical calculations⁸⁸, bonding in $Fe(C_5H_5)_2$ can be explained by covalent, donor-acceptor and dative interactions [(a) unpaired Fe d_{xz} , d_{yz} electrons and the e_{1g} MO of the rings accompanied by a transfer of about 1.14 e from Fe to $(C_5H_5)_2$; (b) electrons of filled e_{1u} MOs of the rings and vacant Fe 4p-AOs (donation of 0.24 e from the rings to Fe); (c) unshared pairs of Fe d_{z^2} , $d_{x^2-y^2}$ and d_{xy} electrons with vacant σ - and π -MOs of the rings {back-donation of 0.35 e from Fe to $(C_5H_5)_2$ }. It results in a net balance shift of 0.62 e from Fe to each ring so that the bonding is not

* It must be pointed out that earlier approximate calculations of carbonyls and also cyanides of transition metals (see references 77-79) gave a distorted picture of the electronic structure with large negative charges on the metal atom.

Table 19. Electronic structure of ferrocene from various MO calculations

	EHM, ref. 85		CNDO, ref. 87a ^c		CNDO, ref. 87b ^d		<i>Ab initio</i> calc., ref. 88		Experimental data (from ref. 88)
	Ionization potentials (from Koopmans' theorem)	Ionization potentials (from Koopmans' theorem)	Ionization potentials (from Koopmans' theorem)	Ionization potentials (from Koopmans' theorem)	IP (from Koopmans' theorem)	IP (from Koopmans' theorem)	IP (from ion and molecule total energy differences)		
Ionization potentials (eV)^b									
I	7.7 (a_{2p}^* , M)	6.0 (e_{2p}^* , ML)	8.0 (e_{2p}^* , ML)	11.7 (e_{1s} , L)	8.3 (e_{2p}^* , M)			6.8 (e_{2p}^* , M)	
II	11.0 (e_{2p}^* , M)	8.1 (a_{1g}^* , M)	10.3 (a_{1g}^* , M)	11.9 (e_{1g} , L)	10.1 (a_{1g}^* , M)			7.2 (a_{1g}^* , M)	
III	13.5 (e_{1s} , L)	9.8 (e_{1s} , LM)	10.8 (e_{1s} , LM)	14.4 (e_{2p}^* , M)	11.1 (e_{1s} , L)			8.8 (L)	
IV	15.5 (e_{1s} , ML)	12.5 (e_{1s} , LM)	11.0 (e_{1s} , LM)	16.0 (a_{2p} , L)	11.2 (e_{1g} , L)			9.3 (L)	
V	18.5 (a_{2p} , L)	13.5 (a_{2p} , LM)	13.0 (a_{2p} , LM)	16.6 (a_{1g} , M)	15.5 (a_{2p} , L)				
Fe AO populations									
4s	— ^c	0.48	0.34	0.01					
4p _x	— ^c	0.00	0.00	0.00					
4p _{x,y}	— ^c	0.70	0.51	0.12					
3d _{x²-y²}	2.00	2.00	2.00	1.93					
3d _{xy}	0.77	0.36	0.43	0.43					
3d _{x²-y²,xy}	1.72	1.40	1.78	1.86					
Fe effective charge	+1.02	+0.60	+0.24	+1.23					

^c In calc. ref. 87b more rigorous account for central atom core potential was made comparing to calc. ref. 87a.^b MOs marked with asterisks correspond to experimental assignment of first two ionization potentials; M and L mean the dominant metal or ligand MO components.^c 4s- and 4p-AOs were not included in calc. ref. 85; if they are included unrealistic populations result ($3d^{6.87} 4s^{-0.19} 4p^{-1.56}$).

quite ionic. Notice should be taken that according to the calculation results, the σ -system of the rings does not remain unchanged.

A similar picture of the electronic structure has been obtained in the non-empirical calculations⁸⁹ for bis(π -allyl)nickel ($\text{Ni}(\text{C}_3\text{H}_5)_2$) (Table 20). Ionization of this complex also causes appreciable reorganization of MOs containing Ni 3d-AOs. The experimentally derived sequence of ionization potentials can be reproduced only in calculations of the excited states of a bis(π -allyl)nickel cation; the ionization potentials calculated using Koopmans' theorem have an incorrect sequence and in some cases differ from the experimental values by an order of 10 eV. Nickel-allyl bonding is mainly due to interaction of 4s- and 4p-AOs, rather than of 3d-AOs, with the radical π -orbitals. A low total overlap population and the effective charge on Ni close to 2+ testify to the fact that the bonding is markedly ionic. Note that within the extended Hückel approximation⁸⁵ for $\text{Pd}(\text{C}_3\text{H}_5)_2$ the effective charge on Pd is estimated at -0.3 which seems hardly probable when compared with the charge of +2.0 for Ni in $\text{Ni}(\text{C}_3\text{H}_5)_2$ obtained in exact calculations.

As to π -complexes of more heavy metals, we shall refer to the non-empirical calculations of the $\text{Ag}(\text{C}_2\text{H}_4)^+$ complex ion found in solutions⁹⁰. The calculations have shown that a structure with Ag located on the C_2 symmetry axis perpendicular to the C_2H_4 plane is more probable than a structure with Ag lying on the C_2 axis in the C_2H_4 plane. The AO populations calculated for the former structure as well as chemical shifts of core electron binding energies as compared with free Ag^+ and C_2H_4 demonstrate that the bonding in this structure is mainly due to donor-acceptor interaction of electrons on the filled π -MO of ethylene with the unoccupied Ag^+ 4s-AO. When complexing occurs, the C—C bond overlap population decreases, the principal reason for this decrease being electron donation from the π -bonding MO of C_2H_4 rather than electron acceptance on the antibonding π^* -MO.

Table 20. Electronic structure of $\text{Ni}(\text{C}_3\text{H}_5)_2$ and $\text{Ni}(\text{C}_3\text{H}_5)_2^+$ from *ab initio* calculations, ref. 89.

MO	MO energy (eV)	State of the ion	Ionization potential (IP)	Experimental IP	IP number	MO composition in $\text{Ni}(\text{C}_3\text{H}_5)_2$		MO composition in $\text{Ni}(\text{C}_3\text{H}_5)_2^+$			
						Ni3d	Ligand		Ni3d	Ligand	
							σ	π		σ	π
7a _u	-9.5	² A _u	8.92	9.48	V	94	6	94	6		
6b _g	-11.1					34	56	10			
13a _g	-13.8	² B _u	13.6			27	53	20			
11b _u	-14.2						93	7	94	6	
12a _g	-15.8						8	26	66		
5b _u	-15.9						42	1	57		
6a _u	-15.9	² A _u	15.7				100		100		
10b _u	-16.1	² B _u	15.8			3	97		4	96	
11a _g	-16.3	² A _g	8.21	(8.17)	III	83	4	13	98	2	
4b _g	-16.5						25	75			
10a _g	-17.5	² A _g	8.52	(8.59)	IV	69	2	29	99	1	
5a _u	-17.9							100			
9a _g	-18.2	² A _g	7.92	(7.85)	I	62	12	26	96	2	2
3b _g	-18.8					² B _g	8.03		II	38	62

Finally, we shall consider the results of non-empirical calculation for the C_5H_5NiNO complex⁷⁷, using double- ζ functions only for the Ni $3d$ -AO, C $2p$ -AO (but not for the oxygen $2p$ -AO). This calculation resulted in the conclusion that the main contribution in the Ni—NO bond is made by MO e_1 of π -type. The N—O π -bond overlap population was shown to increase despite some transfer (about 0.1) of the charge from Ni to the antibonding NO 2π -MO, which is probably caused by an increase in the covalent character of the bonding 1π -MO. The donor-acceptor Ni—NO σ -bond has proved ineffective (the overlap population is a small negative value). The total N—O bond overlap population in the complex is higher than in nitrosyl. The effective charge of the NO group is close to zero. In the Ni— C_5H_5 bond the total overlap population is small and negative which means that this bond is rather ionic than covalent. The resultant charge on the ring is -0.8 , and on Ni, $+0.8$.

The discussed series of non-empirical calculations for Ni with CO, NO, CN^- , C_3H_5 and C_5H_5 ligands carried out with similar accuracy shows that the bond between nickel and cyclopentadienyl and allyl is predominantly ionic, while the bond of Ni with other ligands is covalent. The cyanide ion forms a donor σ -bond with a transfer of electrons from the ligands to the metal. Nitrosyl forms a π -bond without noticeable electron transfer, and carbon oxide acts as a σ -donor and π -acceptor.

In general, considering the peculiar features of the electronic structure of transition metal complexes with different types of ligands, it may be stated that the vacant $4p$ -AOs of the metal are in some cases involved in the bonding, particularly in oxyanions, carbonyls and, to a lesser extent, in halogenides.

In a number of cases correlation can be established between the calculated changes in the overlap population in a diatomic A—B ligand upon complexing and the experimental data derived on a change in the A—B bond strength (for instance, for NO in NiC_5H_5NO , for C—C in $AgC_2H_4^+$), though for carbonyls such correlation cannot be obtained⁸². It should be mentioned at this point that theoretically this comparison is not quite substantiated.

The 'frozen orbitals' approximation is inapplicable to many transition metal compounds (for example, square planar complexes and π -complexes). This shows that a simple one-electron ground-state level scheme is not sufficient for interpreting experimental data involving electron transfer processes. Unfortunately, the available results do not allow us to predict in what cases this situation is possible.

IV. CONCLUSION

What general conclusions can be made (on the basis of this review) about the state of molecular orbital calculations of coordination compounds?

The studies that have been carried out convincingly show that in order to obtain a reliable picture of the electronic structure of coordination compounds, sufficiently rigorous calculations are needed. Inorganic quantum chemistry is decisively turning to this course which has been made possible by rapid progress in the computational technique.

On the other hand, development of chemistry requires theoretical in-

vestigations of more complex objects (heavy element compounds, polynuclear clusters, etc.) and, most important, consideration of whole series of such compounds. Expensive and laborious *ab initio* calculations for a tremendous number of complex systems are not feasible at the present time and can hardly be made in future. (We should not forget that the *ab initio* calculation of the electronic structure of such a molecule as $\text{Ni}(\text{CO})_4$ required several dozens of computation hours on a powerful modern computer⁸².) It can be understood why the major part of molecular orbital calculations of coordination compounds are performed using various approximations. Unfortunately, many techniques used nowadays employ rough approximations and simplifications which result in wrong information about the electronic structure and bonding nature of the investigated compounds.

We believe that in order to be able to carry out mass calculations of coordination compounds, it is necessary to elaborate new techniques and use the best of the available approximation methods employing substantiated simplifications (mixed basis sets, valence approximation and others) and to verify these methods by comparison with rigorous calculations. At the same time, for the most interesting compounds whose studies involve crucial problems of the bonding, we think it imperative to perform rigorous calculations using all the facilities offered by modern computers.

Finally, it is possible that future progress of theoretical chemistry of coordination compounds may call for elaboration of quite new quantum chemistry approaches and this is what we must persistently strive to develop in our research.

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