RELATIVE SHIFT OF LIGAND VERSUS METAL ORBITALS

Gion CALZAFERRI and Lars FORSS
Institute for Inorganic and Physical Chemistry, University of Bern, Freiestrasse 3, 3000 Bern 9, Switzerland

Received 19 August 1983; in final form 17 November 1983

In extended Hückel calculations on transition-metal complexes, self-consistent charge configuration iteration is in most cases carried out on the central transition metal only. One might ask why this simplification may lead to reasonable results. For highly symmetric compounds, we can prove that the charge distribution depends on the relative value of the Coulomb integral $\alpha_{rel} = \alpha_d/|\alpha_L|$ only. We show that, in the region below $\alpha_{rel} = -1$, the so-called "d* electrons" are transformed into "ligand electrons". In this region, the crystal field model and the angular overlap model break down. Some consequences of this are discussed. We present results on Cu^0, Cu^I and Cu^{II} coordinated by the 4–4 sub-unit of zeolites.

1. Introduction

Extended Hückel calculations on transition-metal complexes are very useful for many applications if the SCCC (self-consistent charge configuration) procedure [1] is applied. In most of these calculations, charge iteration is carried out on the central transition metal only and not on the ligands [1–4]. On applying this method to very different systems, we have observed that it would be desirable to have a better understanding of the interdependence of the Coulomb integrals on the central metal atom and on the ligands. This need became more pronounced when we applied the SCCC procedure to some zeolite compounds. We are interested in zeolites as ligand systems for $Cu^{II,I,0}$ and $Ag^{I,0}$ metals [5].

The most compact three-dimensional surrounding for these metals is the 4–4 sub-unit [6] shown in fig. 1. Assuming $r(O^{2-}) = 1.23$ Å for the radius of oxygen, the radius of the hole is estimated to be 1.34 Å. For comparison, the diameters of the $Cu^{2+,1+,0}$ and $Ag^{1+,0}$ species are $r(Cu^{2+}) = 0.72$ Å, $r(Cu^{+}) = 0.96$ Å, $r(Cu^0) = 1.35$ Å, $r(Ag^0) = 1.60$ Å, $r(Ag^{+}) = 1.26$ Å. This means that, from these five species, all but Ag^0 would fit in the hole of the ligand. This type of coordination has not yet been identified. Nevertheless, one would expect it to be stable. Once the metal ion is in the cage it cannot escape unless an Si–O or Al–O bond is broken or at least stretched.

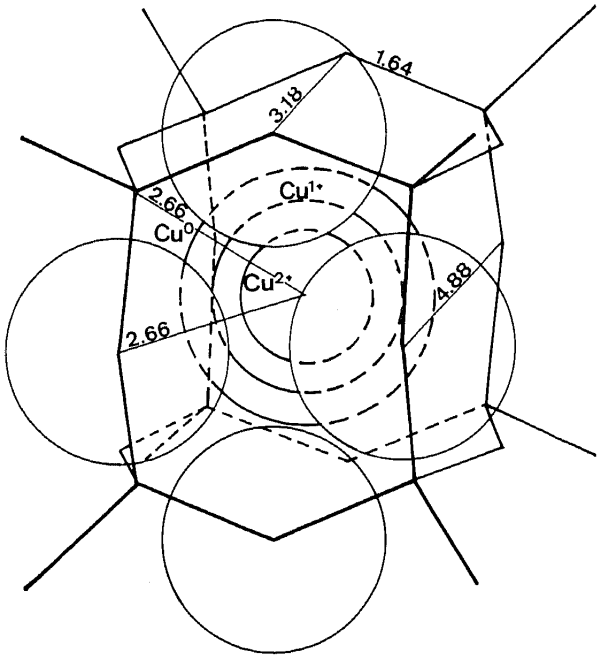


Fig. 1. 4–4 sub-unit of a zeolite framework and comparison of the Cu^{2+}, Cu^{1+} and Cu^0 radii with the opening of the four-membered oxygen ring. The opening corresponds exactly to the radius of Cu^0. The edges of the 4–4 sub-unit are alternately occupied by Si^{IV} and Al^{III}.

0 009-2614/84/$ 03.00

2. Relative shift of ligand versus metal orbitals in a one-electron approximation

The absolute value of the expectation energy of a molecular orbital is of minor importance in many applications of one-electron approximations. The orbital splitting (i.e. the orbital stabilisation and destabilisation energy [2,7,8]) is of particular importance in order to get a reasonable behaviour of the frontier molecular orbitals [9]. One might ask why this problem is very often reasonably well treated in extended Hückel calculations with charge iteration on the central metal atom only. In symmetric complexes with non-conjugated ligands, we have found that, in first order, the orbital splitting depends on the relative Coulomb integral

$$\alpha_{rel} = \alpha_d/|\alpha_L|$$

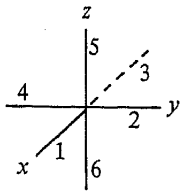
only. α_d is the Coulomb integral of the metal d orbitals and α_L is the Coulomb integral of those ligand orbitals which interact with the central atom. To apply our arguments we shall now study some aspects of mono-atomic-ligand-to-central-atom interactions in an octahedral complex (table 1).

In the following treatment, s,p mixing is neglected and we restrict the discussion to t_{2g} and e_g orbitals. The arguments remain the same for the other orbitals. The metal and ligand orbitals we have to include are summarized in table 2. $S_{d\sigma}$ and $S_{d\pi}$ are the group overlap integrals of the e_g an the t_{2g} orbitals. The problem to be solved is very simple [1]:

(i) problem for e_g,

$$\begin{vmatrix} \alpha_d - \epsilon & \beta_d - \epsilon S_{d\sigma} \\ \beta_{d\sigma} - \epsilon S_{d\sigma} & \alpha_L - \epsilon \end{vmatrix} = 0;$$

Table 1
Coordinates, Coulomb integrals α and atomic orbitals of the central atom M and of the ligand L [1]. α metal: $\alpha_p, \alpha_s, \alpha_d$; α ligand: α_s^L, α_p^L



Metal			Ligands		
$[(n+1)s, (n+1)p, nd]$			σ(s, p)	π(p)	n(p)
(x, y, z)		t_{1u}	$2t_{1u}$		
	s	a_{1g}	$2a_{1g}$		
(z^2, x^2-y^2)		e_g	$2e_g$		
(xy, xz, yz)		t_{2g}		t_{2g}	
					t_{1g}
					t_{2u}

(ii) problem for t_{2g}

$$\begin{vmatrix} \alpha_d - \epsilon & \beta_{d\pi} - \epsilon S_{d\pi} \\ \beta_{d\pi} - \epsilon S_{d\pi} & \alpha_L - \epsilon \end{vmatrix} = 0,$$

and is the same for the e_g and t_{2g} cases. It is important to remember that this simple form applies only to non-conjugated ligands. Conjugated ligand systems are more complex. In the following discussion we use β and S_G for both $\beta_{d\sigma}, \beta_{d\pi}$ and $S_{d\sigma}, S_{d\pi}$. It is convenient to divide the resulting determinant by $|\alpha_L|$ and to introduce α_{rel}, ϵ_{rel} and β_{rel} in the following way:

$$\alpha_{rel} = \alpha_d/|\alpha_L|, \quad \epsilon_{rel} = \epsilon/|\alpha_L|, \quad \beta_{rel} = \beta/|\alpha_L|,$$

$$\begin{vmatrix} \alpha_{rel} - \epsilon & \beta_{rel} - \epsilon_{rel} S_G \\ \beta_{rel} - \epsilon_{rel} S_G & -1 - \epsilon_{rel} \end{vmatrix} = 0. \qquad (1)$$

Table 2
Metal and ligand orbitals for the t_{2g} and e_g molecular orbitals in an octahedral complex

Representation	Metal orbitals	ligand orbitals	
		σ	π
e_g	$d_{x^2-y^2}$	$(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)/2$	
	d_{z^2}	$(2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)/2\sqrt{3}$	
t_{2g}	d_{xy}		$(y_1 + x_5 + x_3 + y_5)/2$
	d_{yz}		$(x_2 + y_5 + y_4 + x_6)/2$
	d_{xy}		$(x_1 + y_2 + y_3 + x_4)/2$

As in most semi-empirical treatments, we assume that β is proportional to the overlap integral. It is interesting that, with this assumption, β_{rel} depends on α_{rel} only. This is true for the approaches published by Ballhausen and Gray [10], Cusachs [11], Wolfsberg and Helmholz [12] and also for the weighted Wolfsberg–Helmholz formula [13]. The solution of eq. (1) is

$$\epsilon^{\pm}_{rel} = [(\alpha_{rel} - 1 - 2\beta_{rel}S_G)/2(1 - S_G^2)] \times \left[1 \pm \left(1 + 4(1 - S_G^2)\frac{\alpha_{rel} + \beta_{rel}^2}{(\alpha_{rel} - 1 - 2\beta_{rel}S_G)^2}\right)^{1/2}\right]. \quad (2)$$

The molecular orbitals can be written as

$$\Psi^{\pm} = C_d^{\pm}\Phi_d + C_L^{\pm}\Phi_L = C_d^{\pm}\,[\Phi_d + (C_L^{\pm}/C_d^{\pm})\Phi_L]\,. \quad (3)$$

Choosing $C_d^{\pm} > 0$ and introducing

$$\beta_{rel} = fS_G\,,$$

we get

$$v^{\pm} = C_d/C_L = -S_G(f - \epsilon^{\pm})/(\alpha_{rel} - \epsilon^{\pm})\,. \quad (4)$$

For the abovementioned approximations of β, these equations prove that the wavefunction depends only on the overlap integral and on the relative Coulomb integral α_{rel}.

We can now understand why charge iteration on the central metal atom only can lead to a reasonable description of the frontier molecular orbitals. We also deduce from this result that convergence problems can arise if α_L and α_d are iterated at the same time. In popular models such as the crystal field model or the angular overlap model [14], it is assumed that the so-called d* electrons are localized on the metal atom. By applying a Mulliken population analysis [15], it is now easy to show the limits of such an assumption. The partial gross population is defined as

$$N(i,r_k) = N(i)\,C_{ir_k}\left(C_{ir_k} + \sum_{l\neq k} C_{is_l}\,S_{r_k s_l}\right). \quad (5)$$

$N(i)$ is the occupation of the ith orbital and C_{ir_k} and C_{is_l} are the coefficients of the atomic orbitals r and s on atoms k and l. $S_{r_k s_l}$ is the overlap integral. It is convenient to put two electrons in the orbital Ψ^-. Ψ^- corresponds to the orbitals treated in the crystal field and in the angular overlap description:

$$N^-(M) = 2C_d^-(C_d^- + C_L^- S), \quad N^-(L) = 2C_L^-(C_L^- + C_d^- S)\,. \quad (6)$$

Fig. 2 shows the relative orbital energies ϵ^-_{rel} and ϵ^+_{rel} as well as $N^-(M)$ and $N^-(L)$ versus α_{rel} for two different overlap integrals $S = 0.05$ and 0.3. β_{rel} has been approximated by the Wolfsberg–Helmholz formula [12] with $K = 1.75$: $\beta_{rel} = \frac{1}{2}KS(\alpha_{rel} - 1)$. From the result shown in fig. 2 it is obvious that the very popular idea of the so-called d* electrons being localized on the central metal atom breaks down suddenly as soon as α_{rel} passes the value -1. As a consequence, the classical arguments used in transition-metal chemistry become wrong in the region $\alpha \leqslant -1$.

In the picture presented in this paper, oxidation and reduction may cause a change in α_{rel}. One has to be aware of the fact that redox reactions can lead to a sudden change from "d* electrons" in the HOMO to "ligand electrons" or vice versa. This situation has some similarity to the charge jump observed in tautomerism in dithioglyoxal between a pair of thiocarbonyl groups and an S–S bond [16], but seems to be of far greater importance. The cause of the charge jump described here is different. In dithioglyoxal it is due to an n,π^* orbital crossing and in the present case it is due to a change of the relative Coulomb integral α_{rel}. Such a change in α_{rel} is the reason for the very different reactivity of isoelectronic Ni^{II} and Co^{I} porphine-type complexes [4]. The arguments can be applied because of the σ,π separability in these compounds. A change from α_{rel} smaller than -1 to α_{rel} larger than -1 seems to occur as well in the reduction of Co^{III} porphine-type complexes to Co^{I} compounds [4].

3. Model calculations on Cu^{2+}, Cu^{1+} and Cu^{0} in the zeolite 4–4 sub-unit

Fig. 3 summarizes the most important results from extended Hückel calculations on the system shown in fig. 1. The orbital diagram of the "empty" 4–4 sub-unit, calculated on the basis of "H_{ii} standard" and "H_{ii} iterated", is drawn on either side. The Coulomb parameters for the left diagram have been taken from ref. [17]. The Coulomb parameters on the right-hand side have been obtained by a VOIE charge iteration on all atoms [1] using the parameters published in ref. [18]. The same Slater exponentials as in ref. [17] have been used. Interestingly enough, the important qualitative features of the molecular orbital diagram for the 4–4 sub-unit is the same for both H_{ii} parameter sets.

The only important differences are that the levels of the hatched occupied frontier orbital region shift to a significantly higher energy and that the splitting is somewhat larger. This large hatched region consists of more than 40 molecular orbitals which are localized on the oxygen atoms. The interaction between the oxygen atoms is very small so that no real band structure is formed.

We have found that inclusion of d orbitals on Si does not change any results discussed in this paper.

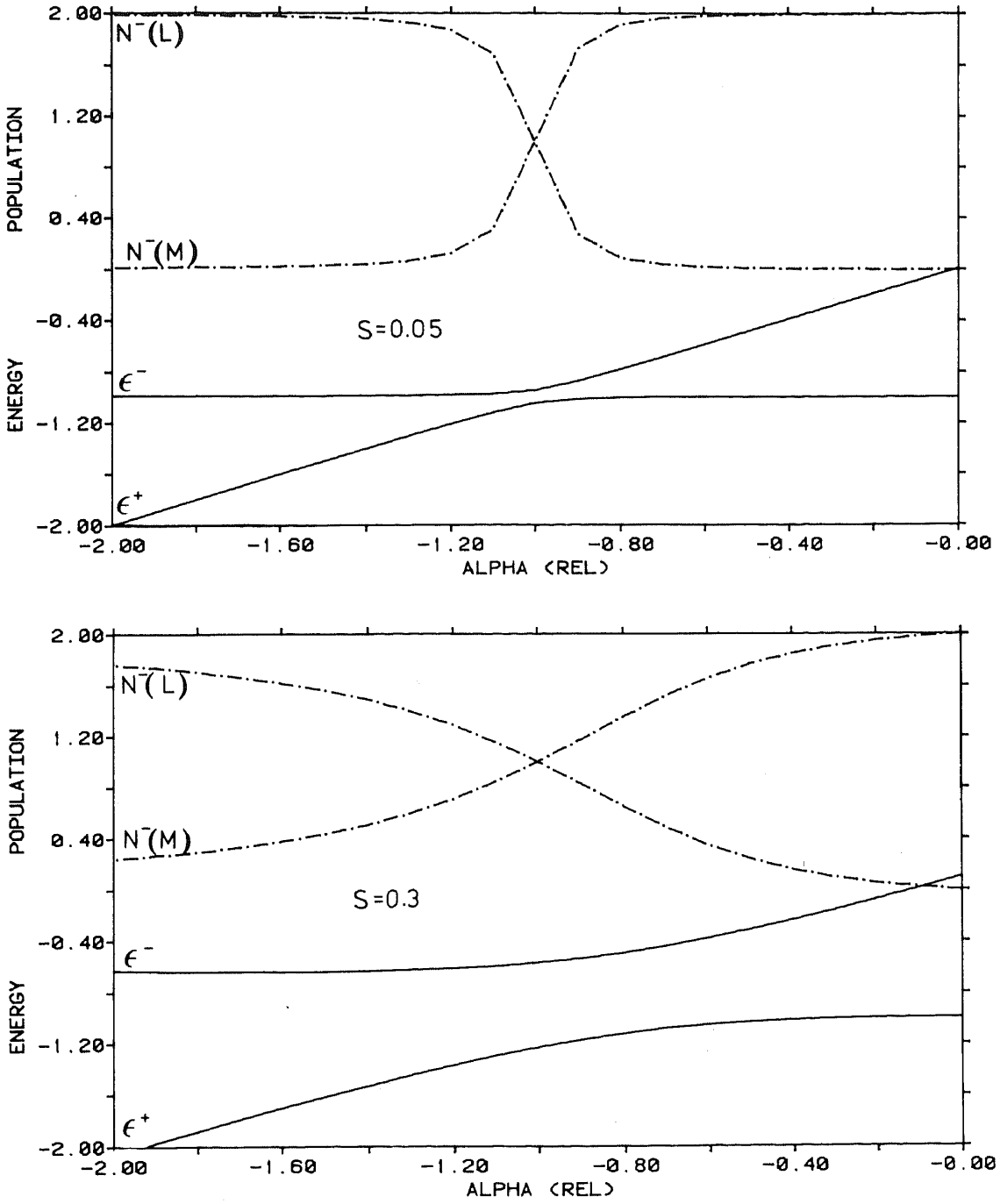


Fig. 2. Orbital energy $\epsilon^{\pm}_{rel}$ according to eq. (2) and partial gross population of Ψ^- for $N(i) = 2$ according to eqs. (5) and (6) versus $\alpha_{rel} = \alpha_d/|\alpha_L|$ for two different overlap integrals ($S = 0.3$ and 0.05).

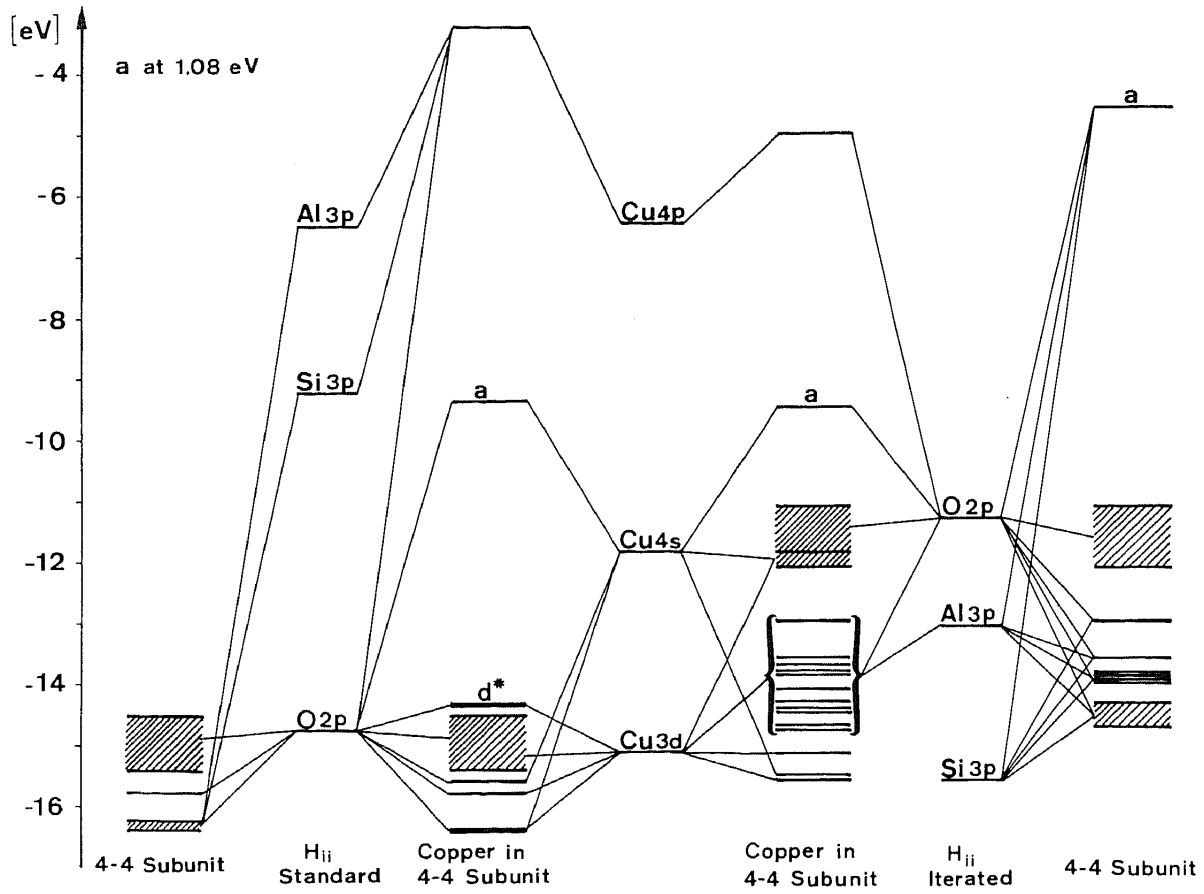


Fig. 3. Molecular orbital diagram. The large hatched regions are the occupied frontier orbitals of the 4–4 sub-unit. They consist of more than 40 orbitals localized mainly on the oxygen atoms. In case of the Cu^0 complex, the orbital with symmetry a is filled with one electron.

Therefore, no calculations which include d orbitals on the Si atoms are reported. It turned out that the really important parameter is the Coulomb integral of the oxygen p orbitals. The interaction between the copper central atom and the 4–4 sub-unit is almost completely determined by the oxygen atoms. Because of this fact, the main features of the molecular orbital diagram of the copper complex can be interpreted in the O_h point group. This means that we can apply the results reported in section 2 without change. $|\alpha_L|$ corresponds approximately to $|H_{pp}|$ of the oxygen and α_d to H_{dd} of the copper. We have found that the H_{dd} levels for Cu^0, Cu^I and Cu^{II}, calculated by an SCCC procedure on the copper atom only with the A, B, C parameters from ref. [19] ‡, are in each case approximately equal to −15.3 eV.

‡ The double-zeta d orbitals for Cu(I), Cu(II) and Cu(III) published in ref. [20]. The Slater coefficients for the 4s and 4p orbitals have been taken from ref. [21].

This situation is very different from that observed in Co^I and Co^{III} porphine-type complexes [4]. It means that the molecular orbital diagram shown in fig. 3 is valid for all three oxidation states. As a reference for the occupation, it is sufficient to know that, in the case of the Cu^0 complex, the orbital with symmetry a is filled with one electron. In the non-iterated case, α_{rel} is approximately −1, which means that we are situate just in the crossing region of fig. 2.

Therefore, the ligand field picture becomes very uncertain. It seems doubtful whether the Cu^I complex can safely be described as a d^{10} system and the Cu^{II} complex as a d^9 system. In the iterated case, α_{rel} is about −1.3. Any description which is derived from a crystal field picture breaks down in this α_{rel} region. Although there exists some spectroscopic information concerning copper zeolite systems [22], we do not have any valid information that could tell us which of the two molecular orbital diagrams more reflects the

electronic structure of this system. What we need is spectroscopic information on single zeolite crystals. These crystals are in general not more than a few micrometers in diameter.

Acknowledgement

This work is part of grant 4.399.0.80.04 financed by the Swiss National Science Foundation. We would like to thank Ciba-Geigy AG for financial support.

References

[1] C.J. Ballhausen and H.B. Gray, Molecular orbital theory (Benjamin, New York, 1965);
S.P. McGlynn, L.G. Vanquickenborne, M.K. Kinoshita and D.G. Carroll, Introduction to applied quantum chemistry (Holt, Rinehart and Winston, New York, 1972).
[2] R. Hoffman, B.F. Beier, E.L. Muetterties and A.R. Rossi, Inorg. Chem. 16 (1977) 511;
T.A. Albright, P. Hofmann and R. Hoffmann, J. Am. Chem. Soc. 99 (1977) 7546, and references therein.
[3] G. Calzaferri and F. Felix, Helv. Chim. Acta 60 (1977) 730;
G. Calzaferri and H.R. Grüniger, Helv. Chim. Acta 62 (1979) 1112.
[4] K. Meier, R. Scheffold and G. Calzaferri, Helv. Chim. Acta 64 (1981) 2361.
[5] B. Sulzberger, Ph.D. Thesis, University of Bern (1983);
B. Sulzberger and G. Calzaferri, J. Photochem. 19 (1982) 321;
S. Leutwyler and E. Schumacher, Chimia 31 (1977) 475.
[6] W.M. Meier, Zeolite structures in molecular sieves (Soc. Chem. Ind., London, 1968).
[7] R.S. Mulliken, J. Chem. Phys. 46 (1949) 497.
[8] G. Calzaferri, Chem. Phys. Letters 87 (1982) 443.
[9] K. Fukui and H. Fujimoto, Bull. Chem. Soc. Japan 41 (1968) 1989; 42 (1969) 3399.
[10] C.J. Ballhausen and H.B. Gray, Inorg. Chem. 1 (1962) 111.
[11] L.C. Cusachs, J. Chem. Phys. 43 (1965) 157.
[12] M. Wolfsberg and L. Helmholz, J. Chem. Phys. 20 (1952) 837.
[13] J.H. Ammeter, H.B. Bürgi, J.C. Thibeault and R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 3686.
[14] K.F. Purcell and J.C. Kotz, Inorganic chemistry (Saunders, Philadelphia, 1977) ch. 9.
[15] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
[16] G. Calzaferri and R. Gleiter, J. Chem. Soc. Perkin II (1975) 559.
[17] P.D. Mollière and R. Hoffmann, J. Am. Chem. Soc. 97 (1975) 3680;
H.H. Dunken and R. Hoffmann, Z. Physik. Chem. NF 125 (1981) 207.
[18] H. Basch, A. Viste and H.B. Gray, Theoret. Chim. Acta 3 (1965) 458.
[19] H. Basch, A. Viste and H.B. Gray, J. Chem. Phys. 44 (1966) 10.
[20] J.W. Richardson, W.C. Niewpoort, R. Powell and W.F Edgell, J. Chem. Phys. 36 (1962) 1057.
[21] A. Anderson, J. Chem. Phys. 64 (1978) 1744.
[22] J. Texter, D.H. Strome, R.G. Hermann and K. Klier, J. Phys. Chem. 81 (1977) 333.