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Calculation of Transition Metal Compounds Using an Extension of the CNDO Formalism

I. Method of Calculation and Application to Mono-, Di- and Tetranuclear Compounds

Hans-Joachim Freund and Georg Hohlneicher

Lehrstuhl für Theoretische Chemie der Universität zu Köln, D-5000 Köln, Federal Republic of Germany

An extended CNDO formalism for the treatment of large transition metal cluster systems is presented. After a detailed discussion of parametrization it is applied to a family of compounds, namely to $Co(CO)_4^-$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, $Mn_2(CO)_{10}$.

The results can be interpreted in the light of simple electron counting rules and additionally allow detailed insight in bonding capabilities of large metal cluster systems.

Bridged and unbridged clusters are compared and the results are extrapolated to surface systems. In the case of $Co_4(CO)_{12}$ two possible stereoisomers of symmetry C_{3v} and T_d are discussed.

Key words: Transition metal compounds – Adsorbate systems – Extended CNDO

1. Introduction

During the last ten years many attempts have been made in order to gain deeper theoretical insight in chemical bonding and reactivity of those systems containing transition metal atoms [1], whereby the most frequently applied method probably is the Extended Hückel Method proposed by R. Hoffmann. One reason might have been the success of simple chemical reasoning (e.g. "18-Electron-Rule") in predicting the stability of transition metal compounds. Another, even more exciting aspect, seems to be the connection between surface chemistry, heterogeneous catalysis and organometallic chemistry [2]. This interrelation is based on the assumption of similar chemical bonding involved in transition metal compounds and surface adsorbates, which means to choose a localized description in both cases. In spite of all difficulties inherent in these considerations, nearly all theoretical ("numerical") approaches start from the so called cluster description, which is believed to take account of the main features of the problem [3].

The purpose of this paper is to study a family of transition metal compounds in the light of the addressed interrelation with the question in mind whether it is possible to transpose the results obtained with rather small well defined compound systems to adsorbate studies. One of the interesting problems in this context is to examine bonding capabilities and charge distributions in bridging and non-bridging ligands with respect to the experimental possibility of differentiating these sites on a surface.

Due to the fact that one has to deal with clusters of two to six metal atoms including ten and more ligands, an adequate *a priori* description is currently not obtainable with *ab initio* methods. As a consequence one is compelled to look for a semi-empirical treatment. In our opinion such a treatment should include electron repulsion explicitly and reach selfconsistency. So we have to go beyond the Extended Hückel scheme.

The simplest method meeting these requirements is an NDO-type formalism and especially the CNDO approximation, which has been applied so successfully to problems from organic chemistry such as study of electronic and geometric structure of molecules containing atoms of the first two rows of the periodic table [5].

Several authors have used the CNDO-formalism to describe molecules containing transition metals. The work of Baetzold [6], Clack *et al.* [7] and (especially in connection with surface chemistry) of Blyholder [8] should be mentioned. As all of these authors use different approximations for different parts of the Fock-operator, it is necessary to give a detailed, general discussion of possibilities to extend Pople's CNDO [4] formalism.

2. Method of Calculation

Starting from Roothaan's equations the matrix elements of the Fock-operator may be written in the ZDO-approximation:

$$\begin{aligned} F_{\mu\mu} &= H_{\mu\mu} - \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{z}\sum_{\sigma=1}^{z} P_{\sigma\sigma}\gamma_{\mu\sigma} \\ F_{\mu\nu} &= H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \end{aligned} \tag{1}$$

where Pople's nomenclature [4] has been used. The first sum in the diagonal element runs over atomic centers z and the second over basis functions $\phi_\mu, \phi_\nu, \phi_\sigma, \ldots$, centered on atom z. In Pople's formulation, one repulsion integral $\gamma_{\mu\nu}$ is chosen for each atom in order to achieve invariance with respect to rotation of the local coordinate system as well as to hybridization. The last requirement is not a necessary condition and thus implies an oversatisfaction of local invariance conditions, because it is only required to have one mean electron repulsion integral for each subset of the atomic basis set with constant quantum number l. This becomes obvious by considering that the unitary transformation of basis functions is defined by

$$t_m = \sum_{\mu} O_{m\mu}\phi_\mu. \tag{2}$$

Thus the transformed electron repulsion integral takes the form:

$$(t_m t_n \mid \phi_\lambda \phi_\lambda) = \sum_\mu O_{m\mu} O_{n\mu} (\phi_\mu \phi_\mu \mid \phi_\lambda \phi_\lambda). \tag{3}$$

If ϕ_μ belongs to an irreducible representation Γ_i of the spherical rotation group there exists by definition no unitary transformation which transforms ϕ_μ in such a way that it belongs to another irreducible representation Γ_j of the same group. Therefore, $(\phi_\mu \phi_\mu \mid \phi_\nu \phi_\nu)$ can be taken as constant for each quantum number l of the chosen atom:

$$\begin{gathered} \phi_\lambda \in \Gamma_i; \qquad \phi_k \in \Gamma_j; \qquad i \neq j, \lambda \neq k \\ A \coloneqq \left\{ \phi_s \mid \phi_s = \sum_\lambda O_{s\lambda} \phi_\lambda \right\} \curvearrowright \phi_\lambda \in A \wedge \phi_k \notin A. \end{gathered} \tag{4}$$

In introducing this symmetry argument, an important additional degree of freedom is gained. Some use has been made of this degree of freedom in earlier CNDO-type calculations of transition metal compounds by treating the d electrons separately but using a common sp set [6]. The limited success of these calculations is, in our opinion, connected with the latter approximation which seems to be especially crude for atoms having filled s orbitals but empty p orbitals in the ground state.

Consequently, the matrix elements of the Fock-operator have to be separated according to the splitting of the atomic basis set. If one considers only s, p and d orbitals, one finds three different diagonal and three non-diagonal terms. For the first transition metal row we restrict ourselves to 4s, 4p and 3d orbitals.

With this atomic basis set the elements of the Fock-operator are given by:

$$\begin{aligned} F_{ss} &= H_{ss} - \tfrac{1}{2} P_{ss} \gamma_{ss} + P_{AA}(S) \gamma_{ss}^{AA} + P_{AA}(P) \gamma_{sp}^{AA} + P_{AA}(D) \gamma_{sd}^{AA} \\ &\quad + \sum_{B \neq A} [P_{BB}(S) \gamma_{ss}^{AB} + P_{BB}(P) \gamma_{sp}^{AB} + P_{BB}(D) \gamma_{sd}^{AB}] \\ F_{pp} &= H_{pp} - \tfrac{1}{2} P_{pp} \gamma_{pp} + P_{AA}(S) \gamma_{ps}^{AA} + P_{AA}(P) \gamma_{pp}^{AA} + P_{AA}(D) \gamma_{pd}^{AA} \\ &\quad + \sum_{B \neq A} [P_{BB}(S) \gamma_{ps}^{AB} + P_{BB}(P) \gamma_{pp}^{AB} + P_{BB}(D) \gamma_{pd}^{AB}] \\ F_{dd} &= H_{dd} - \tfrac{1}{2} P_{dd} \gamma_{dd} + P_{AA}(S) \gamma_{sd}^{AA} + P_{AA}(P) \gamma_{dp}^{AA} + P_{AA}(D) \gamma_{dd}^{AA} \\ &\quad + \sum_{B \neq A} [P_{BB}(S) \gamma_{ds}^{AB} + P_{BB}(P) \gamma_{dp}^{AB} + P_{BB}(D) \gamma_{dd}^{AB}] \end{aligned} \tag{5a}$$

$$\begin{aligned} F_{sp} &= H_{sp} - \tfrac{1}{2} P_{sp} \gamma_{sp} \\ F_{sd} &= H_{sd} - \tfrac{1}{2} P_{sd} \gamma_{sd} \\ F_{pd} &= H_{pd} - \tfrac{1}{2} P_{pd} \gamma_{pd} \end{aligned} \tag{5b}$$

$$\text{e.g. } P_{BB}(D) = \sum_{\sigma=1}^{u_\alpha^B} P_{\sigma\sigma}, \quad (\mu_\alpha^B \text{ number of } d\text{-function on } B).$$

Addition of f functions leads to four diagonal and six nondiagonal elements. The corresponding formulae are compiled in Appendix A.

The atomic terms $H_{\mu\mu}$ and $H_{\mu\nu}$ are approximated by Pople's expression:

$$\begin{aligned} H_{\mu\mu} &= U_{\mu\mu} - \sum_{B \neq A} V_{AB} \\ H_{\mu\nu} &= \beta^0_{\mu\nu} S_{\mu\nu} \end{aligned} \tag{6}$$

with:

$$\begin{aligned} U_{\mu\mu} &= (\mu| -\tfrac{1}{2}\nabla^2 - V_A |\mu) \\ V_{AB} &= (\mu| r_{AB}^{-1} |\mu). \end{aligned} \tag{7}$$

While Baetzold [7] splits the atomic basis set into a *d* and a combined *sp* set, we additionally separate *s* and *p* electrons and consequently have to consider different resonance parameters β^0_s, β^0_p and β^0_d.

The $U_{\mu\mu}$ and V_{AB} terms need some further discussion in connection with transition metal elements. Both quantities depend on the electron configuration ($s^i p^j d^k$) on the atoms.

For first row elements the V_{AB} term is approximated by $Z_B \gamma_{AB}$. In the case of basis set separation, V_{AB} depends on the type of orbital on *A* and the electron configuration on *B*. As an example the interaction of an *s* electron on a transition metal atom center is described by:

$$V_{AB}(S) = i\gamma^{AB}_{ss} + j\gamma^{AB}_{sp} + k\gamma^{AB}_{sd}\,[1]. \tag{8}$$

Following Pople's treatment the average energies of configurations $E_{av}(s^i p^j d^k)$ are calculated for neutral atom- and ion-states which define orbital ionization energies and orbital affinities. The arithmetic mean leads to $U_{\mu\mu}$ as a sum of a Mulliken electronegativity factor and one-center-repulsion-integrals.

An important question, not discussed in detail in the cited papers, is, which configuration one has to choose for evaluation of $U_{\mu\mu}$.

The ground state electron configuration which is spectroscopically determined, corresponds to the absolute lowest multiplet of this configuration.

With the exception of Cr and Cu,

Cr $4s3d^5$ Cu $4s3d^{10}$

it is $4s^2 3d^{n-2}$, if *n* is the number of valence electrons of a third row transition element.

Within the CNDO method, however, we are considering average energies in calculating $U_{\mu\mu}$ and thus have to determine whether E_{av} depends on atomic number. This is done in Fig. 1, where E_{av}'s for five different configurations are compiled [10].

From Fig. 1 we learn that in going from manganese to iron the lowest average energy switches from $s^2 d^{n-2}$ to $s^1 d^{n-1}$. Thus another $U_{\mu\mu}$ has to be used for the elements Sc to Mn than that for Fe to Cu.

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[1] Clack *et al.* [7] left out the V_{AB} term in H_{AB}. This seems to be a rather inadequate approximation since this term is the leading one in core Hamiltonian calculation.

The effect may be demonstrated for the d electron case:

$$\begin{aligned} s^2d^{n-2} \quad & U_{dd} = -\tfrac{1}{2}(I_d + A_d) - 2\gamma_{3d4s} - Z_A\gamma_{3d3d} + \tfrac{5}{2}\gamma_{3d3d} \\ s^1d^{n-1} \quad & U_{dd} = -\tfrac{1}{2}(I_d + A_d) - \gamma_{3d4s} - Z_A\gamma_{3d3d} + \tfrac{3}{2}\gamma_{3d3d}. \end{aligned} \tag{9}$$

From Eq. (9) it is evident that U_{dd} strongly depends on the relative magnitude of γ_{dd} and γ_{sd} so that the orbital exponents have to be determined very carefully.

Formulae for other cases are given in Appendix B.

3. Parametrization

There are nine free parameters for each atom to be determined:

1) three electronegativity factors $1/2(I_\mu + A_\mu)$; $\mu = s, p, d$,
2) three resonance parameters β_μ^0
3) three Slater exponents ξ_μ.

The ionization potentials can be obtained from atomic data [9] and electron affinities by isoelectronic extrapolation, vertical and horizontal analysis as has been done by several authors [4, 7, 11, 12, 13]. Values derived in these ways seem to be reliable within 0.5 eV.

ξ exponents and β parameters were chosen in such a way that atomic charges and orbital splittings fit those data best calculated by *ab initio* or pseudopotential methods on small transition metal compounds such as $Ni(CO)_4$, $Cr(CO)_6$ and $Fe(CO)_5$ [16–18]. Data for other third-row elements were then evaluated by linear interpolation. Table 1 summarizes parameters for Ni, Co and Mn. It appears that ξ exponents obtained by this procedure are considerably smaller than those given

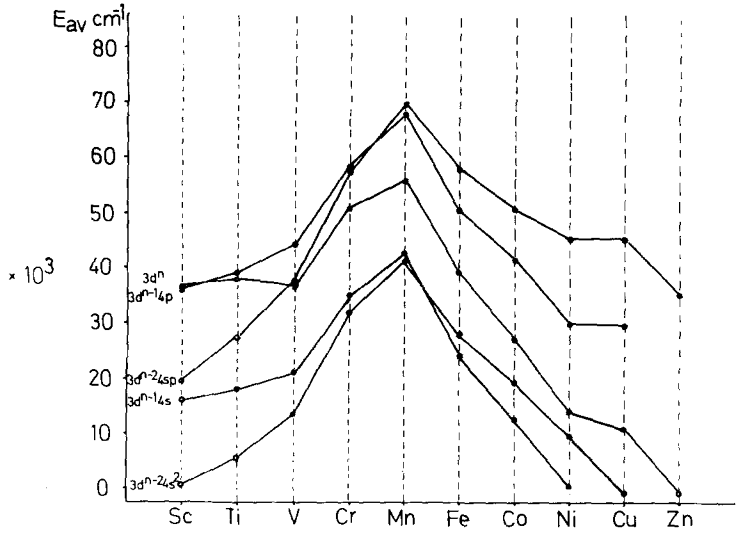


Fig. 1. Average energies of configuration with respect to the ground state multiplet of the atom after [10]

Table 1. CNDO parameters for Mn, Co and Ni (in eV)

	$-\frac{1}{2}(I_\mu + A_\mu)$			$-\beta^0_\mu$			ξ_μ		
Element	4*s*	3*d*	4*p*	4*s*	4*p*	3*d*	4*s*	4*p*	3*d*
Mn	3.98	5.16	0.98	4	4	8	1.325	0.388	1.499
Co	4.17	5.84	0.85	5	5	10	1.45	0.44	1.93
Ni	4.31	6.20	1.05	5	5	10	1.53	0.45	2.18

by Clementi and Raimondi [14]. This result can be supported by the same argument which is used in connection with first-row elements: the one-center repulsion integral is approximately given by the difference in orbital ionization potential and orbital electron affinity [15]. With given $I_\mu + A_\mu$ one can calculate ξ exponents by applying the analytical expression for one-center integrals with Slater radial functions.

A typical result for orbital sequence gained with these data is presented for $Ni(CO)_4$ and compared to two *ab initio* calculations and a pseudopotential results in Table 2. The overall agreement is satisfactory especially if one compares the orbital energies of the upper three states. All other energies are too small, but nevertheless in correct sequence. The deviation of the energy values must be attributed to ligand parametrization. We have taken CNDO/2 parameters [4] to describe carbon and oxygen and this leads to enlarged Koopmans ionization energies compared to *ab initio* results and to experiment [19] (see Figs. 3–6).

To demonstrate the usefulness of these results we analyse the density matrix with respect to σ and π donor and acceptor abilities. In Table 3 the atomic orbital population of $Ni(CO)_4$ and CO are compiled and Table 4 contains the decomposed populations according to σ and π. For CO this procedure is self-evident; with regard to $Ni(CO)_4$ it has been done by projecting the orbital population to the threefold axis of complexation.

Table 2. Comparison of occupied orbital energy levels for $Ni(CO)_4$ (in a.u.)

"Veillard" *ab initio* [16]		Pseudo-potential [17]		"Hillier" *ab initio* [18]		This work	
5 t_2	−1.575	5 t_2	−1.533	5 t_2	−1.530	5 t_2	−1.6890
6 a_1	−1.574	6 a_1	−1.531	6 a_1	−1.530	6 a_1	−1.6754
7 a_1	−0.855	7 a_1	−0.859	7 a_1	−0.809	7 a_1	−1.1224
6 t_2	−0.830	6 t_2	−0.857	6 t_2	−0.793	6 t_2	−0.9217
8 a_1	−0.720	1 *e*	−0.687	8 a_1	−0.693	8 a_1	−0.8284
7 t_2	−0.697	7 t_2	−0.687	1 *e*	−0.665	1 *e*	−0.8201
1 *e*	−0.697	8 t_2	−0.682	7 t_2	−0.662	7 t_2	−0.8145
1 t_1	−0.687	1 t_1	−0.675	1 t_1	−0.653	1 t_1	−0.7803
8 t_2	−0.679	8 a_1	−0.671	8 t_2	−0.644	8 t_2	−0.6889
2 *e*	−0.496	2 *e*	−0.479	2 *e*	−0.471	2 *e*	−0.4186
9 t_2	−0.429	9 t_2	−0.391	9 t_2	−0.395	9 t_2	−0.3295

Table 3. Atomic orbital populations for $Ni(CO)_4$ in comparison to free CO

Ni-atom	$4s$ 0.4841	
	$4p_x$ 0.1030	
	$4p_y$ 0.1030	$4p_{tot}$: 0.3090
	$4p_z$ 0.1030	
	$3d_{z^2}$ 1.7839	
	$3d_{xy}$ 1.7839	$3d(e)_{tot}$: 3.5678
	$3d_{x^2-y^2}$ 1.8131	
	$3d_{xz}$ 1.8131	$3d(t_2)_{tot}$: 5.4393
	$3d_{yz}$ 1.8131	
Density:	$9.8006\ e^-$	Charge: $+0.1794\ e^-$

	CO in $Ni(CO)_4$		CO free	
	C	O	C	O
$2s$	1.5771	1.6955	1.6907	1.7013
$2p_x$	0.9188	1.4757	1.0847	1.5234
$2p_y$	0.6652	1.4584	0.5886	1.4114
$2p_z$	0.7920	1.4671	0.5886	1.4114
Density	3.9532	6.0967	3.9526	6.0474
Charge	+0.047	−0.097	+0.047	−0.047

It is shown in Table 3 and Table 4 that CO via its free electron pair on carbon is a strong σ donor but simultaneously an even better π acceptor which brings about a small positive charge on the Ni atom. The population of Ni in the compound has changed relative to the $4s^1 3d^9$ reference state. The compound population is $4s^{0.5} 3d^{9.0} 4p^{0.3}$, which indicates the importance of $4p$ orbitals for π backbonding in $Ni(CO)_4$. The charge distribution of the CO unity is considerably different from the one in the CO molecule. This is of course due to the discussed countermovement of σ and π bonding effects. The stronger π acceptor ability leads to a larger negativation of oxygen in comparison to carbon, which keeps its charge as in free CO.

As it has been pointed out, the CNDO formalism in this extended form seems to be a well suited tool in the study of transition metal compounds.

Table 4. Decomposition of populations according to local symmetry in $Ni(CO)_4$

	CO	$Ni(CO)_4$	CO	$Ni(CO)_4$	$\Delta(\rho_{CO} - \rho_{Ni(CO)_4})$	
	σ		π		σ	π
C	2.7754	2.4114	1.1772	1.5418	−0.3640	+0.3646
O	3.2247	3.1691	2.8228	2.9285	−0.0556	+0.1075

Thus we may afford to use this type of calculation in the study of polynuclear transition metal compounds in order to analyse orbital populations and charge distributions.

4. Applications to Mono- and Polynuclear Metal Compounds

We have chosen a series of cobaltcarbonyls and the dimanganese-decacarbonyl to compare bridged and unbridged structures (see Fig. 2). In Figs. 3–6 the eigenvalue schemes are plotted for the shown (Fig. 2) structures together with the individual ligand fields which have been calculated separately using the same parameters as in the complex calculation.

4.1. Co(CO)$_4^-$

The eigenvalue structure of this molecule resembles very much the one of Ni(CO)$_4$, but the orbital energies are considerably larger for equivalent states as it is to be expected for an anion. At the same time the splitting of the highest occupied MOs t_2 and e is larger due to the blown-up d functions on Co^{-1}.

A population analysis leads to the following electron density distribution:

$$\mathrm{Co}: 9.2754\ \mathrm{e}^-; \qquad \mathrm{C}: 3.9825\ \mathrm{e}^-; \qquad \mathrm{O}: 6.1987\ \mathrm{e}^-$$

with a $4s^{0.5}4p^{0.8}3d^{8.0}$ configuration on the cobalt atom. Decomposition with respect to, and π symmetry for, the CO unity brings about similar results as in the case of Ni (see Table 5).

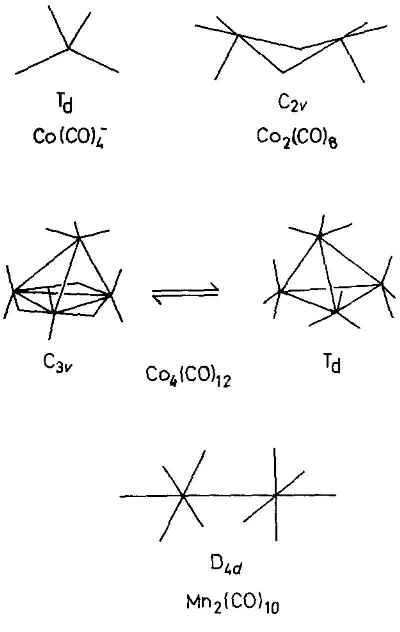


Fig. 2. Structures of the studied carbonyls. The X-ray study is cited in [27, 28]

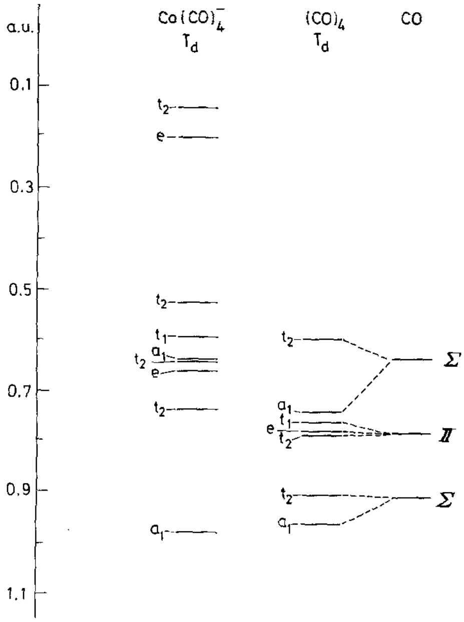


Fig. 3. Calculated eigenvalue spectrum of occupied levels for $Co(CO)_4^-$

The σ donor properties are about the same for CO coordination on Co and Ni, but as the Co atom is in a formal anionic oxidation state more electron density is π backdonated. By this mechanism the CO unity gains a little bit more negative charge.

4.2. $Co_2(CO)_8$ *and* $Mn_2(CO)_{10}$

The dinuclear carbonyls of cobalt and manganese differ essentially in structure. While in $Co_2(CO)_8$ two Co atoms are linked by two bridging CO groups there are only terminal ligands in $Mn_2(CO)_{10}$ and the manganese atoms are coupled by a metal-metal bond.

First we consider the simpler case of $Mn_2(CO)_{10}$. Dividing the orbital set (Fig. 4) into two subsets, from −0.6 a.u. to −1.1 a.u. which are mainly ligand orbitals, and another one from −0.6 a.u. to HOMO, the second group consists of four states: e_1, e_2, e_3 and a_1. The three e states are relevant for π backbonding from d orbitals of the metal to π ligand orbitals. The character of the metal-metal interaction in these orbitals is of π type, but it has bonding, antibonding and nonbonding features. Thus we think that π interaction does not contribute to metal-metal bonding in unbridged CO clusters in contrast to halogenide clusters of the lighter transition elements where it has been experimentally supported to exist.

Table 5. Decompositions of populations according to local symmetry in $Co(CO)_4^-$

	σ	π
C	2.4003	1.5821
O	3.1778	3.0209

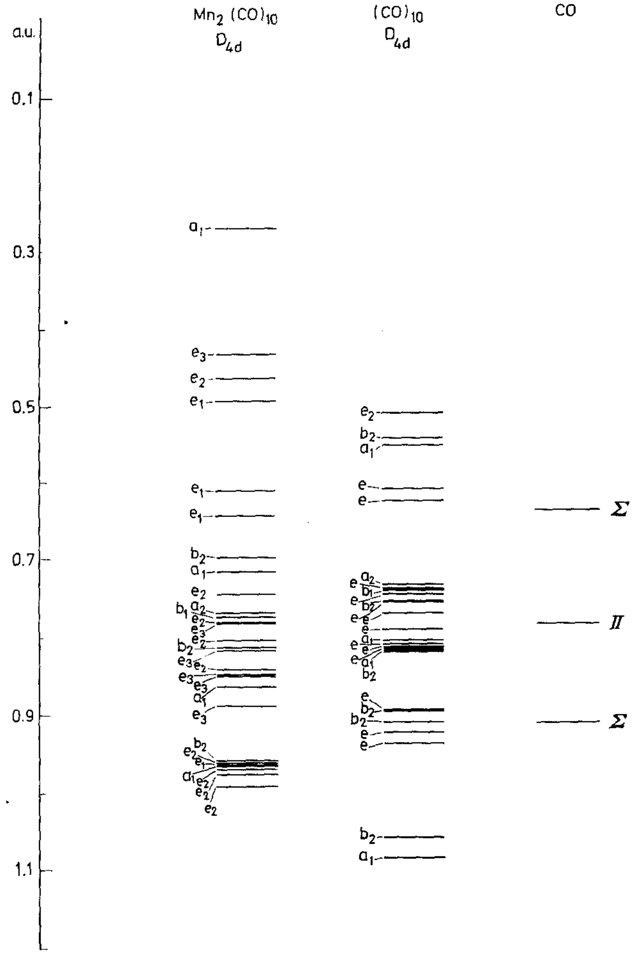


Fig. 4. Calculated eigenvalue spectrum of occupied levels for $Mn_2(CO)_{10}$

The metal–metal σ bond is formed by occupation of the a_1 state. This orbital is strongly σ bonding with respect to metal–metal interaction but it is antibonding as to those metal to ligand interactions which are in line with the metal–metal bond. In our opinion this is a reason for the a_1 state to be higher in energy than the e states.

The electron counting rule is simply explained using the orbital scheme:

Six electrons from each metal fill the e states, being responsible for metal to ligand bond formation, and there has to be one extra electron on each metal to establish a σ metal to metal bond by occupying the a_1 state. Therefore those metal to metal bonded dinuclear clusters with this geometry should be stable where seven electrons per atom are available.

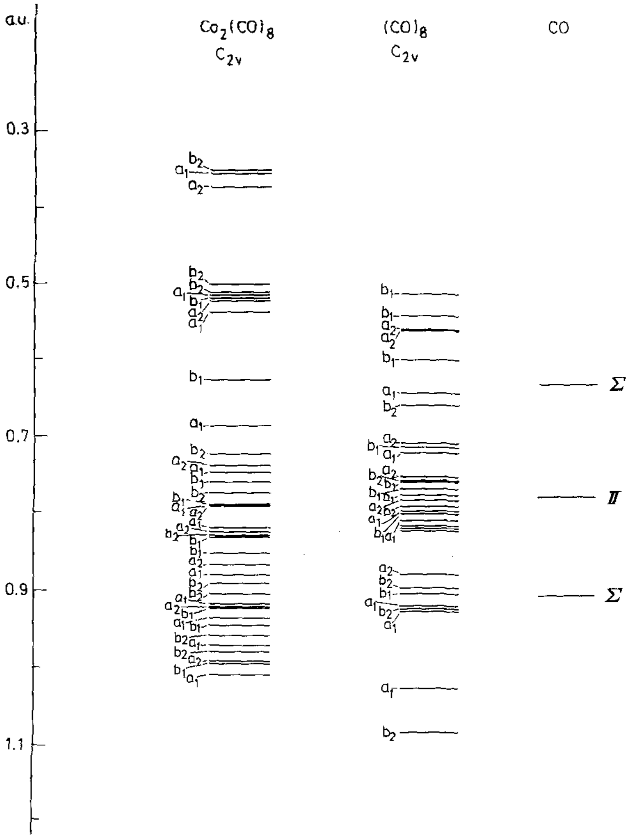


Fig. 5. Calculated eigenvalue spectrum of occupied levels for $Co_2(CO)_8$

For instance [27]:

$Re_2(CO)_{10}$; $Tc_2(CO)_{10}$; $ReMn(CO)_{10}$
$Cr_2(CO)_{10}^{2-}$; $Mo_2(CO)_{10}^{2-}$; $W_2(CO)_{10}^{2-}$.

The second case considered here in detail is $Co_2(CO)_8$. Again we may separate two regions in the eigenvalue scheme and we restrict ourselves to the discussion of the nine upmost orbitals because the other part of the eigenvalue spectrum has predominantly ligand orbital character. Comparing the structure of the upper group with the $Mn_2(CO)_{10}$ case, striking similarities are found. There are six states at lower and three orbitals at higher energy. Those orbitals belonging to the first group again have partly metal to metal bonding, antibonding and nonbonding features, so that in total there is no large contribution to metal–metal bonding. They establish the metal to ligand π backbonding.

Turning to the a_1 orbital of the second group, it is found that this orbital is responsible for a strong direct metal to metal interaction with a dominating portion of $4p$ character. The last observation underlines the importance of $4p$ orbitals, not only in metal to ligand but also in metal to metal interaction. Similar to the manganese cluster the a_1 state is antibonding to the quasi-trans in-line ligands. The same is true for the a_2 and b_2 orbitals, but they are metal to metal antibonding as well. They are responsible for coupling the metal electrons by the bridging ligands. Thus, by occupying these orbitals, the metal to metal carbonyl bridge is strongly stabilized.

A comparative population analysis for both clusters shows a small positive charge on manganese and cobalt with the following configurations:

Mn $+0.16\,e^-$ $4s^{0.54}4p^{0.33}3d^{6.0}$

Co $+0.13\,e^-$ $4s^{0.54}4p^{0.53}3d^{7.9}$

As far as the CO unities are concerned, the polarization mentioned in connection with $Co(CO)_4^-$ is reproduced. The charge densities on carbon and oxygen are compiled in Table 6. There are approximately no differences in C and O populations as far as distinct ligand positions are concerned in $Mn_2(CO)_{10}$. A different situation is met in $Co_2(CO)_8$. The charge on the ligand atoms varies within 0.1 e^-, but the polarization is nearly the same in all ligand types. Bridging ligand positions gain more electron density than terminal positions as well on carbon as on oxygen.

4.3. $Co_4(CO)_{12}$

The next largest neutral cobaltcarbonyl cluster compound in this series is $Co_4(CO)_{12}$, which was thought [28] to exist in two isomeric forms: one structure may be looked at as a bridged equilateral triangle coordinated with an apical $Co(CO)_3$ group building a molecule of C_{3v} symmetry; the other structure is a regular tetrahedron carrying only terminal CO ligands. If one chooses the ligand field to be of I_h symmetry, one form is transformed into the other by rotating the tetrahedron around the threefold axis.

In Fig. 7 a correlation diagram for both isomers is presented. Only the upmost occupied and a few unoccupied levels are shown. The 36 electrons of Co_4 fill three t_2, one t_1, two e, and two a_1 orbitals. Thus the electron rule is satisfied. Splitting of

Table 6. Electron charge densities on C and O in $Co_2(CO)_8$ and $Mn_2(CO)_{10}$

$Mn_2(CO)_{10}$		Axial	Equatorial	
	C	3.8453	3.8964	
	O	6.1658	6.1407	
$Co_2(CO)_8$		Bridge	Terminal quasi trans	Terminal
	C	4.0359	3.8955	3.9035
	O	6.2285	6.0788	6.0434

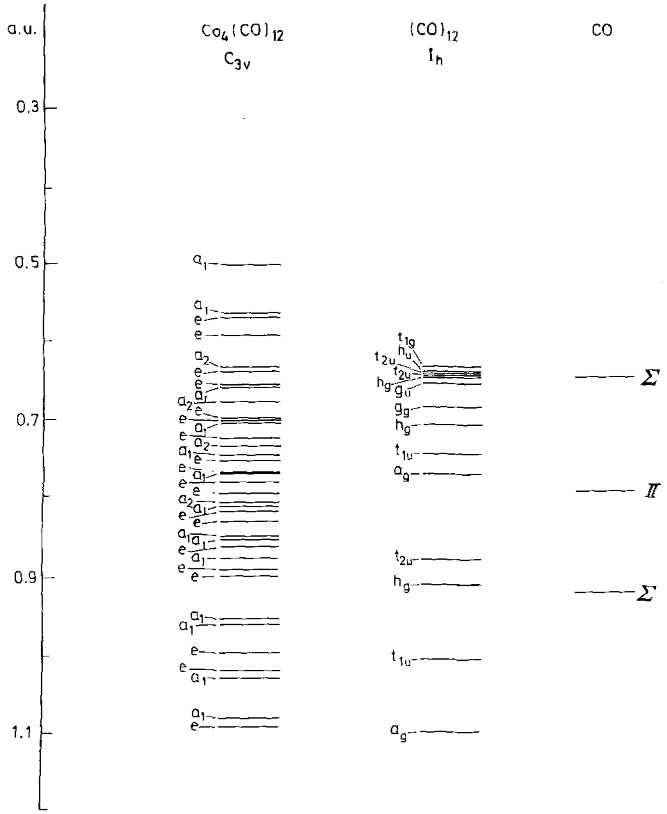


Fig. 6. Calculated eigenvalue spectrum of occupied levels for $Co_4(CO)_{12}$

the *t* representation in T_d into a_1, a_2 and *e* states in C_{3v} is clearly observed but the energy separation is rather small and consequently the overall structure is conserved.

Table 7 collects the population analysis data for the C_{3v} form. The Co atoms are all positive, but the apical one is by 0.18 e^- more positive than the basal Co atoms. The missing density is partly donated to the directly coordinated ligands but also to the basal fragment where it is distributed on the ligands. Again the bridged positions are more negative than the terminals but the differences in charge density are not as large as in the case of the dinuclear cluster.

For $Co_4(CO)_{12}$ in T_d symmetry all densities achieve a value which is nearly the arithmetic mean of the different positions in the C_{3v} structure.

5. Conclusion

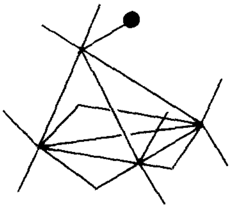
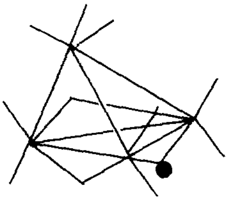
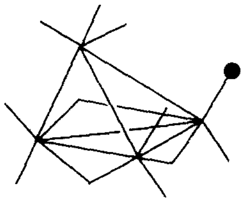
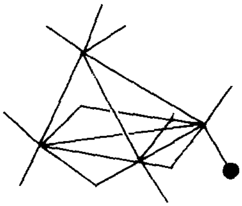
The presented CNDO formalism has been shown to be an adequate tool to treat transition metal compounds, when the atomic basis set is split and the corresponding parametrization is carried through rigorously.

Table 7. Population analysis for $Co_4(CO)_{12}$ in C_{3v}-symmetry

Co-atoms

apical:		basal:	
$4s$	0.6097	$4s$	0.7232
$4p_x$	0.1623	$4p_x$	0.1534
$4p_y$	0.1623	$4p_y$	0.1456
$4p_z$	0.1383	$4p_z$	0.1643
$3d_{z^2}$	1.7451	$3d_{z^2}$	1.3055
$3d_{xz}$	1.6254	$3d_{xz}$	1.5427
$3d_{yz}$	1.6254	$3d_{yz}$	1.4362
$3d_{x^2-y^2}$	1.3395	$3d_{x^2-y^2}$	1.7109
$3d_{xy}$	1.3362	$3d_{xy}$	1.7467
Density:	8.7445 e$^-$	Density:	8.9289 e$^-$
Charge:	+0.2555 e$^-$	Charge:	+0.0711 e$^-$
Configuration:	$4s^{0.6}4p^{0.5}3d^{7.7}$	Configuration:	$4s^{0.7}4p^{0.5}3d^{7.7}$

CO-ligands

		C	tot	O	tot
	$2s$	1.5217	3.8790	1.8397	6.1246
	$2p_x$	0.6681		1.6956	
	$2p_y$	0.8345		1.5770	
	$2p_z$	0.8547		1.0122	
	$2s$	1.6962	3.9544	1.8289	6.1158
	$2p_x$	0.6255		1.5482	
	$2p_y$	0.9269		1.1816	
	$2p_z$	0.7059		1.5571	
	$2s$	1.4453	3.8805	1.8404	6.1866
	$2p_x$	1.0813		1.7947	
	$2p_y$	0.5836		1.7692	
	$2p_z$	0.7703		1.7823	
	$2s$	1.4635	3.8529	1.8406	6.1617
	$2p_x$	0.7463		1.2327	
	$2p_y$	0.5522		1.7483	
	$2p_z$	1.0908		1.3403	

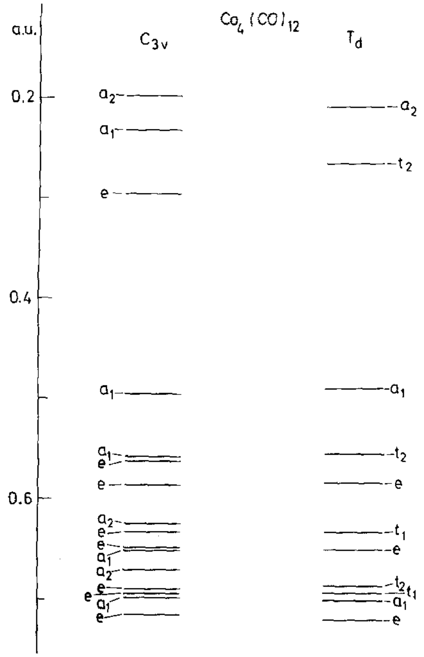


Fig. 7. Correlation diagram for the transformation of $Co_4(CO)_{12}$ from C_{3v} to T_d symmetry

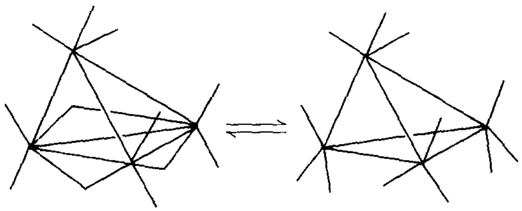
Especially one has to ensure adequate handling of core-Hamiltonian elements.

The eigenvalue spectra allow an interpretation in terms of simple electron counting rules and the wavefunction can be analysed to shed some light on bonding capabilities of large metal cluster systems, especially in connection with differences in populations on bridging and nonbridging ligands.

The better π acceptor ability of the CO ligand leads to a slightly enlarged negative charge on the ligand and a positive charge on the metal. As a function of the position of coordination, different situations are found.

The bridging ligand gains more electron density than the terminal one and the negative charge on oxygen is always larger in comparison to carbon, where the density is only slightly altered relative to free CO. The largest effects are observed with bridged dinuclear clusters. These differences between bridging and nonbridging ligands, however, shrink when going from dinuclear to tetranuclear clusters.

In the case of the transformation:



the discussed tendency becomes quite obvious. In switching from T_d to C_{3v} the eigenvalue spectrum is altered only with respect to a rather small symmetry splitting. The overall structure remains nearly unchanged. The metal and ligand densities in the T_d form are approximately the arithmetic mean of the C_{3v} case.

If one extrapolates these lines of thoughts to the study of adsorbates one would expect the differences of a molecule sitting in a bridged or unbridged adsorption site to be rather small.

A good experimental property with which to correlate calculated densities are core level shifts measured by X-ray photoelectron spectroscopy [24]. In the light of the considerations presented here, it seems rather doubtful whether one will be able to distinguish bridged and unbridged sites from each other by this method because of the limited resolution. This statement is in good agreement with experimental studies of transition metal cluster compounds using UPS and XPS spectroscopy [25, 26].

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Appendix A

Diagonal and nondiagonal matrix elements of the Fock operator if *f*-basis functions are included.

$$F_{ss} = H_{ss} - \tfrac{1}{2}P_{ss}\gamma_{ss} + P_{AA}(S)\gamma_{ss}^{AA} + P_{AA}(P)\gamma_{ps}^{AA} + P_{AA}(D)\gamma_{sd}^{AA} + P_{AA}(F)\gamma_{sf}^{AA} + \sum_{B \neq A} [P_{BB}(S)\gamma_{ss}^{AB} + P_{BB}(P)\gamma_{sp}^{AB} + P_{BB}(D)\gamma_{sd}^{AB} + P_{BB}(F)\gamma_{sf}^{AB}]$$

$$F_{pp} = H_{pp} - \tfrac{1}{2}P_{pp}\gamma_{pp} + P_{AA}(S)\gamma_{sp}^{AA} + P_{AA}(P)\gamma_{pp}^{AA} + P_{AA}(D)\gamma_{pd}^{AA} + P_{AA}(F)\gamma_{pf}^{AA} + \sum_{B \neq A} [P_{BB}(S)\gamma_{ps}^{AB} + P_{BB}(P)\gamma_{pp}^{AB} + P_{BB}(D)\gamma_{pd}^{AB} + P_{BB}(F)\gamma_{pf}^{AB}]$$

$$F_{dd} = H_{dd} - \tfrac{1}{2}P_{dd}\gamma_{dd} + P_{AA}(S)\gamma_{sd}^{AA} + P_{AA}(P)\gamma_{pd}^{AA} + P_{AA}(D)\gamma_{dd}^{AA} + P_{AA}(F)\gamma_{df}^{AA} + \sum_{B \neq A} [P_{BB}(S)\gamma_{ds}^{AB} + P_{BB}(P)\gamma_{dp}^{AB} + P_{BB}(D)\gamma_{dd}^{AB} + P_{BB}(F)\gamma_{df}^{AB}]$$

$$F_{ff} = H_{ff} - \tfrac{1}{2}P_{ff}\gamma_{ff} + P_{AA}(S)\gamma_{fs}^{AA} + P_{AA}(P)\gamma_{fp}^{AA} + P_{AA}(D)\gamma_{fd}^{AA} + P_{AA}(F)\gamma_{ff}^{AA} + \sum_{B \neq A} [P_{BB}(S)\gamma_{fs}^{AB} + P_{BB}(P)\gamma_{fp}^{AB} + P_{BB}(D)\gamma_{fd}^{AB} + P_{BB}(F)\gamma_{ff}^{AB}]$$

$$F_{sp} = H_{sp} - \tfrac{1}{2}P_{sp}\gamma_{sp}$$

$$F_{sd} = H_{sd} - \tfrac{1}{2}P_{sd}\gamma_{sd}$$

$$F_{sf} = H_{sf} - \tfrac{1}{2}P_{sf}\gamma_{sf}$$

$$F_{pd} = H_{pd} - \tfrac{1}{2}P_{pd}\gamma_{pd}$$

$$F_{pf} = H_{pf} - 2P_{pf}\gamma_{pf}$$

$$F_{df} = H_{df} - \tfrac{1}{2}P_{df}\gamma_{df}$$

e.g. $P_{BB}(s) = \sum_{k=1}^{\mu_a{}^B} P_{kk}$, ($\mu_a$ = number of *s*-function on *B*).

Appendix B

$U_{\mu\mu}$-terms for different atomic configurations and basis sets.

1) Basis set: $s^i p^j d^k$, valence-electron configuration: $s^2 d^{n-2}$.

$$U_{ss} = -\tfrac{1}{2}(I_s + A_s) - Z_A\gamma_{ds} + \tfrac{3}{2}\gamma_{ds} - \gamma_{ss}$$

$$U_{pp} = -\tfrac{1}{2}(I_p + A_p) - Z_A\gamma_{dp} + \tfrac{5}{2}\gamma_{dp} - 2\gamma_{sp}$$

$$U_{dd} = -\tfrac{1}{2}(I_d + A_d) - Z_A\gamma_{dd} + \tfrac{5}{2}\gamma_{dd} - 2\gamma_{ds}$$

2) Basis set: $s^i p^j d^k$, valence-electron configuration: sd^{n-1}.

$$U_{ss} = -2(I_s + A_s) - Z_A\gamma_{ds} + \gamma_{ds} - \tfrac{1}{2}\gamma_{ss}$$

$$U_{pp} = -\tfrac{1}{2}(I_p + A_p) - Z_A\gamma_{dp} + \tfrac{3}{2}\gamma_{pd} - \gamma_{sp}$$

$$U_{dd} = -2(I_d + A_d) - Z_A\gamma_{dd} + \tfrac{3}{2}\gamma_{dd} - \gamma_{ds}$$

3) Basis set: $s^i p^j d^k f^l$, valence-electron configuration: $s^2 f^{n-2}$.

$$U_{ss} = -\tfrac{1}{2}(I_s + A_s) - Z_A\gamma_{fs} + \tfrac{3}{2}\gamma_{fs} - \gamma_{ss}$$

$$U_{pp} = -\tfrac{1}{2}(I_p + A_p) - Z_A\gamma_{fp} + \tfrac{5}{2}\gamma_{fp} - 2\gamma_{sp}$$

$$U_{dd} = -\tfrac{1}{2}(I_d + A_d) - Z_A\gamma_{fd} + \tfrac{5}{2}\gamma_{fd} - 2\gamma_{sd}$$

$$U_{ff} = -\tfrac{1}{2}(I_f + A_f) - Z_A\gamma_{ff} + \tfrac{5}{2}\gamma_{ff} - 2\gamma_{fs}.$$

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