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SINDO/F THEORY, INDO-TYPE THEORY FREE OF MOLECULAR EMPIRICAL PARAMETERS VALID FOR TRANSITION METAL COMPOUNDS*

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A version of the INDO theory of electronic structure of molecules valid for transition metal compounds is developed. It is a semi-empirical approach with no empirical parameters chosen to fit any electronic property of molecules. The method is tested on the electronic absorption spectrum of O_2, N_2, CO, H_2O, acrolein, $TiCl_4$, VO_4^{3-}, CrO_4^{2-}, MnO_4^- and the photoelectron spectrum of $TiCl_4$. The character of molecular orbitals of oxyanions is compared with that obtained in recent ab initio calculations. The results confirm the utility of the method.

1. Introduction

Modern treatments of transition metal complexes and other large molecular systems are mostly based on the standard Roothaan formalism. Despite great progress in computational techniques, complete non-empirical SCF MO calculations are still time consuming and quite expensive. In the case of transition metal complexes the basic sets considered are relatively small. On the other hand, the results are here quite sensitive to the choice of the set. For all these reasons there is a continued interest in simple semi-empirical treatments.

In modern semi-empirical treatments the ZDO approximation is commonly introduced, on one of the following three basically different levels of sophistication: CNDO, INDO,

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NDDO [1]. Most of the integrals which remain in these theories are reduced to account for certain atomic properties. Therefore it is relatively easy to parametrize these integrals. A problem arises in the case of resonance integrals and core-core repulsion terms. Parameters which appear in the last two quantities are usually related to one or the other molecular property. The values of the appropriate parameters depend on the choice of molecular properties and their proper interpretation.

The situation is relatively simple in the case of the first and second row atoms, as long as one deals with only a few kinds of atoms and a large number of good experimental data. In the case of transition metal compounds one has a variety of atoms, with *s*, *p* and also *d* shells in general. Oxidation states differ, often significantly, from case to case, experimental data are scarce and frequently uncertain. As a result most of the methods elaborated hitherto appeared disappointing with results dependent heavily on the choice of empirical parameters. A review of presently known methods was given in Ref. [2] and the reader is referred to it for details; common interest seems to have invoked merely the CNDO/2 and INDO extension due to Clack, Hush and Yandle [3].

Our present interest is exclusively in treatments which try to avoid empirical parameters fitted from molecular properties, at least at the stage of the electronic structure calculation. Quite successful in this respect seem to be the methods based on Linderberg's formulae for resonance integrals [4–5]. Extensions to transition metal compounds have not yet been studied, however. In fact, according to Kracht and Nieuwpoort [6] there is no sound foundation for this approach in all-valence-electrons treatments.

Non-empirical treatments of transition metal compounds involving ZDO are far from being convincing as well (see Ref. [2]).

In this paper we are considering a new proposal of the INDO-type approach to molecules. It is based on the framework of the Scaled INDO theory, SINDO/2, explained in details in Ref. [2]. Version SINDO/F discussed in the present work is free of empirical parameters of molecular origin, when dealing with the problem of the electronic structure of the molecule; there is thus no subjectivity at this stage. There are, however, additional empirical parameters required when dealing with core-core repulsion.

2. *SINDO/F theory*

As in INDO the following types of integrals appear in this treatment:

U_{Al} — core integral: kinetic energy and core attraction energy of the electron occupying subshell l of atom A;

$(ab|cd)_A$ — one-centre electron-electron repulsion energy integral, with orbitals a, b, c, d referring to atom A;

g_{AB} (for $A \neq B$) — two-centre electron-electron repulsion energy integral for electrons on atoms A, B, independent of the orbital type;

$\beta_{Aa,Bb}$ (for $A \neq B$) — resonance integral;

V_{AB} — core-core repulsion energy of atoms A and B.

Core-core repulsion term is not needed for electronic structure calculations. The discussion of this term is postponed to the last section.

Apart from resonance integrals and core-core repulsion terms all the integrals depend in SINDO/F on the charge and electronic configuration of the appropriate atoms:

q_{Al} — population of valence shell l of atom A;

q_A — total population of the whole valence shell of atom A.

With this purpose in mind we define:

p_{Al} — the exponent in the Slater-type atomic orbitals (STO's) of subshell l of atom A, as following from the Burns rules [7];

p^+_{Al} — value of p_{Al} for $q_A = 0$.

(a) One-centre integrals

For the core integral U_{Al} it is assumed that

$$U_{Al} = U^0_{Al}\frac{p_{Al}(p_{Al}-2p^+_{Al})}{p^0_{Al}(p^0_{Al}-2p^+_{Al})}, \tag{1}$$

where the upper index 0 denotes a definite reference configuration of the atom in question. As a rule it is the ground state configuration of the neutral atom. The core integral for the reference configuration, U^0_{Al}, is a parameter to be defined later.

Dependence (1) is accurate in the case of hydrogen-like orbitals and the point charge model of the nuclear core. Slater-type orbitals yield, strictly speaking, a slightly more complex formula (2). We do not think that the point charge model is a satisfactory basis for estimating U_{Al} in an absolute sense; we do expect, however, that at least the changes in U_{Al} due to the variation of charge and configuration of atom A are reproduced satisfactorily by this model.

Electron-electron one-centre repulsion integrals, say for the reference configuration, can be always decomposed into two terms:

$$(ab|cd)^0_A = F_0(l_a l_c)^0_A \delta_{ab}\delta_{cd} + G(abcd)^0_A f^0_A, \tag{2}$$

where $F_0(l_a l_c)$ is one of the familiar Condon-Shortley parameters (here for the reference configuration of atom A), the remaining Condon-Shortley parameters being grouped together under $G(abcd)$. $G(abcd)^0_A$ is calculated theoretically with the use of approximate Hartree-Fock atomic orbitals. $F_0(l_a l_c)^0_A$ and f^0_A are empirical parameters. The purpose of f^0_A is to reduce the theoretical value of the most significant (for spectroscopy) Condon-Shortley parameter to its known spectroscopical value: $F_2(ll)$, with $l = 2$ for transition metals and $l = 1$ for main row elements.

The dependence of $(ab/cd)_A$ integrals on the charge and configuration of atom A is again that following from Slater-type orbitals:

$$(ab|cd)_A = (ab|cd)^0_A \frac{(ab|cd)_{A,\mathrm{STO}}}{(ab|cd)^0_{A,\mathrm{STO}}}. \tag{3}$$

To be strict this is the correction when dealing with orbitals of the same subshell. In the general case, in order to simplify numerical calculations, the ratio of $(ab|cd)_{A,\,\mathrm{STO}}$'s is replaced by a similar ratio of leading Condon-Shortley parameters, calculated with STO's.

Parameters of the type U^0_{Al}, $F_0(ll')^0_A$ are fitted from ionization potentials for several different oxidation states and several different configurations. Values of selected atomic empirical parameters to be used in SINDO/F have been listed in Ref. [2].

(b) Two-centre Coulomb integrals

There is always arbitrariness in the choice of two-centre Coulomb integrals g_{AB}. Certain popularity has been gained by the familiar Ohno approximation,

$$g_{AB} = e^2/(R^2_{AB}+a^2_{AB})^{1/2}, \tag{4}$$

where R_{AB} is the interatomic distance and

$$a_{AB} = \tfrac{1}{2}(a_A+a_B) \tag{5}$$

where a_A, a_B are empirical parameters; in SINDO/F they are estimated in an averaging process of the Condon-Shortley parameters $F_0(ll)_A$,

$$\frac{e^2}{a_A} = \frac{1}{q_A}\sum_l q_{Al}F_0(ll)_A. \tag{6}$$

Two-centre integrals g_{AB} depend thus on the charge and configuration of the atoms A and B.

Ohno's formula is one of several interpolation formulae for intermediate interatomic distances. Another possibility, not explored hitherto, is to use the theoretical formula for the repulsion of two electrons for this purpose. The simplest formula is that for repulsion of two $1s$ electrons of the same element:

$$g_{AB} = \frac{e^2}{R_{AB}}\{1-e^{-2t}(1+\tfrac{11}{8}\,t+\tfrac{3}{4}\,t^2+\tfrac{1}{6}\,t^3)\}, \tag{7}$$

where

$$t = x_{AB}R_{AB}/a_0, \tag{8}$$

$$x_{AB} = (8a_0)/(5a_{AB}). \tag{9}$$

It is interesting to note that more complex formulae, for example for the repulsion of two equivalent $2s$ electrons, yield results very close to one another when used for the purpose of interpolation. In order to partly consider the effect of higher principal quantum numbers we have somewhat arbitrarily changed the coefficient $\frac{1}{6}$ in Eq. (7) to $\frac{1}{19}$. Formula (7) with this minor change defines what we call the STO-type approximation of g_{AB}.

In what follows both approximations of g_{AB} will be considered.

(c) Two-centre resonance integral

In SINDO/F an entirely new approach to the old problem of resonance integrals is suggested. Suppose we are going to estimate $\beta_{Aa,Bb}$, the resonance integral referring to the orbitals f_{Aa} and f_{Bb}. We define this integral in terms of locally orthogonalized orbitals $\bar{f}_{Aa}$ and $\bar{f}_{Bb}$,

$$\left.\begin{aligned}\bar{f}_{Aa} &= xf_{Aa}-yf_{Bb}\\ \bar{f}_{Bb} &= xf_{Bb}-yf_{Aa}\end{aligned}\right\}, \tag{10}$$

where x, y ensure orthogonality and normalization of the new orbitals. Introducing the point charge model for atomic cores:

$$\beta_{Aa,Bb} = \int \bar{f}_{Aa}[T + eQ^{\text{eff}}_{Aa}/r_A + eQ^{\text{eff}}_{Bb}/r_B]\bar{f}_{Bb}dV \tag{11}$$

where T is the kinetic energy operator, r_A is the distance of the electron from the nucleus A, Q^{eff}_{Aa} is the effective charge of atom A seen by an electron occupying the orbital f_{Aa} and the meaning of remaining symbols follows by analogy. The effective charge Q^{eff}_{Aa} is defined by the appropriate one-centre integral:

$$U^0_{Aa} = \int f_{Aa}[T + eQ^{\text{eff}}_{Aa}/r_A]f_{Aa}dV. \tag{12}$$

Since U^0_{Aa} is already known Eq. (12) may be considered as definition of the effective charge.

Definition of resonance integrals in terms of orthogonalized orbitals and with the use of the point charge model is not entirely new. As a rule, however, orthogonalization of the whole basis is considered. Our goal was a definition of a resonance integral of a local property, independent of orbitals other than f_{Aa} and f_{Bb}.

However, with this definition of resonance integrals the theory would not be invariant towards rotations of the coordinate system. In order to guarantee invariance we substitute $\bar{f}_{Aa}$ and $\bar{f}_{Bb}$ in Eq. (11) in accordance with Eq. (10), develop x, y in a series over overlap integrals $S_{Aa,Bb}$ and neglect in Eq. (11) all terms non-linear with respect to $S_{Aa,Bb}$.

In this way we arrive at the final formula for $\beta_{Aa,Bb}$:

$$\beta_{Aa,Bb} = U_{Aa,Bb} - \tfrac{1}{2} S_{Aa,Bb}(U^0_{Aa} + U^0_{Bb} + u_{Aa,Bb}), \tag{13}$$

where

$$U_{Aa,Bb} = \int f_{Aa}(T + eQ^{\text{eff}}_{Aa}/r_A + eQ^{\text{eff}}_{Bb}/r_B)f_{Bb}dV,$$

$$u_{Aa,Bb} = eQ^{\text{eff}}_{Aa}\int f_{Bb}\frac{1}{r_A}f_{Bb}dV + eQ^{\text{eff}}_{Bb}\int f_{Aa}\frac{1}{r_B}f_{Aa}dV.$$

One can hardly compare the values of resonance integrals obtained by different methods. Nevertheless they should be of comparable magnitude and of the same sign. For p-type orbitals and an O_2 molecule the comparison is as follows:

Method	π-type	σ-type
CNDO/2 [1]	−4.49 eV	+ 9.52 eV
CNDO/S [8]	−3.82 eV	+13.82 eV
SINDO/F	−2.72 eV	+13.16 eV

Several satisfactory results have been obtained with this new approximation.

We recall that in SINDO/F all integrals referring to the reference configuration are calculated with the use of approximate Hartree-Fock orbitals; the charge and configuration effect, on the other hand, is always estimated with the use of Slater-type orbitals with Burns's rules.

3. *Electronic absorption spectrum*

Correct interpretation of the electronic absorption spectrum of molecules is certainly a crucial test of a theory. For this reason we have calculated the vertical excitation energies for a set of molecules. The calculations were performed on the ΔE_{SCF} level, carrying out SCF calculations separately for the ground state and the various excited states. The configuration interaction, basically required, would require a different set of atomic empirical parameters, optimized on exactly the same level.

The results of these calculations are compared with experiment in Table I. To some extent they depend on the interpolation formula used for g_{AB}. Except for acroleine the STO approximation is slightly better. The best overall agreement is obtained when applying a weighted formula, as stated in Table I. Standard deviation for this case is 0.15 eV; deviations are usually smaller than half of an eV, but in a few cases are as large as 1 eV. If we recall that not a single parameter is used to fit the spectrum the agreement with experiment may be rated as good. The experimental results in Table I do not always refer to vertical excitations; possible differences can hardly change the conclusion, however.

Agreement with experiment obtained in other semi-empirical treatments is certainly not better, even if limited to main-row elements and with extra empirical parameters. The first two transitions in formaldehyde [31–33] are a good example. In eV's:

CNDO/2 with virtual orbitals	5.02;	9.61
CNDO/2 CI with single replacements	4.61;	9.43
CNDO/2 CI with single and double replacements	5.45;	9.83
CNDO/S with virtual orbitals	3.50;	8.92
CNDO/S CI with single replacements	3.44;	8.89
CNDO/S CI with single and double replacements	3.57;	8.10
RCNDO CI with single replacements	3.25;	5.75
Experiment	3.51;	7.08

Some problems appeared in the case of oxyanions namely there is a large scattering of observed bond lengths in these systems, 1.57–1.85 Å for VO_4^{3-}, 1.60–1.65 Å for CrO_4^{2-} and 1.59–1.63 Å for MnO_4^-. On the other hand, calculated transition energies depend (at least according to SINDO/F) quite strongly on the bond lengths (Fig. 1). The calculated transitions in Table I refer to weighted mean bond lengths as found by Kálmán [34]: 1.705 Å for VO_4^{3-}, 1.651 Å for CrO_4^{2-} and 1.629 Å for MnO_4^-.

Except (partly) for oxyanions the assignments given in Table I are in agreement with those of other authors. Therefore let us discuss the spectrum of MnO_4^- in more detail.

A review of suggested assignments of bands of MnO_4^- was given by Brown et al. [35]. The assignment by these authors was $t_1 \to e$ for the band at 2.27 eV, $t_2 \to e$ for 3.47 eV and $t_1 \to t_2$ for 3.99 eV, all transitions of type ${}^1A_1 \to {}^1T_2$; symmetry forbidden transitions like ${}^1A_1 \to {}^1T_1$ have been ignored. The same assignment was given by Gubanov et al. [36] on the basis of transition state $X\alpha$ calculations and by Ziegler et al. [37] on the basis of the HFS Discrete Variational Method. Term splitting was neglected in these two treatments. According to our calculations the same orbital excitation follows for the first two

TABLE I

Electronic transitions according to experiment and SINDO/F theory on the ΔE_{SCF} level (in eV)

Molecule, Ground state	Assignment of the excited state	For:			Experiment
		γ_{Ohno}	γ_{STO}	γ_{wtd}*	
$O_2(^3\Sigma_g^-)$	$^1\Delta_g$	0.83	0.83	0.83	0.98 [9]
	$^1\Sigma_g^+$	1.67	1.67	1.67	1.63
	$(\pi \rightarrow \pi^*)$ $^3\Sigma_u^+$	3.22	3.76	3.58	4.43
	$(\pi \rightarrow \pi^*)$ $^3\Sigma_u^-$	7.63	7.09	7.27	6.12
$N_2(^1\Sigma_g^+)$	$(\sigma \rightarrow \pi^*)$ $^1\Pi_g$	7.37	7.30	7.32	7.95 [9]
	$(\pi \rightarrow \pi^*)$ $^1\Delta_u$	7.38	7.89	7.72	8.93
	$^1\Sigma_u^-$	10.70	10.70	10.70	11.65
	$^1\Sigma_u^+$	12.88	13.39	13.22	—
$CO(^1\Sigma)$	$(\pi \rightarrow \pi^*)$ $^3\Pi$	4.42	4.06	4.18	6.01 [9]
	$^1\Pi$	7.13	6.94	7.00	8.01
$H_2O(^1A_1)$	$(n \rightarrow \sigma^*)$ $^3B_1$	6.87	8.20	7.76	7.0–7.2 [10]
	$^1B_1$	7.00	8.33	7.89	7.4–7.5
CH_2CHCHO $(^1A')$	$(n \rightarrow \pi^*)$ $^1A''$	4.66	1.79	2.75	3.71 [11]
	$(\pi \rightarrow \pi^*)$ $^1A'$	6.47	4.35	5.06	6.41
$TiCl_4(^1A_1)$	$(t_1 \rightarrow 2e)$ $^1T_1$	4.14	3.67	3.83	4.00 [12]
	$^1T_2$	4.59	4.29	4.39	4.43
	$(3t_2 \rightarrow 2e)$ $^1T_1$	6.56	6.50	6.52	5.39
	$^1T_2$	6.78	6.74	6.75	7.07
$VO_4^{3-}(^1A_1)$	$(t_1 \rightarrow 2e)$ $^1T_1$	2.66	4.98	4.21	3.8(tail) [15]
	$^1T_2$	3.03	5.27	4.52	4.5–4.6 [14]
	$(4t_2 \rightarrow 2e)$ $^1T_1$	3.93	6.20	5.44	?
	$^1T_2$	4.24	6.45	5.71	5.60 [13]
$CrO_4^{2-}(^1A_1)$	$(t_1 \rightarrow 2e)$ $^1T_1$	1.51	3.29	2.70	3.0 [16]
	$^1T_2$	2.05	3.73	3.17	3.25–3.56 [16, 17]
	$(4t_2 \rightarrow 2e)$ $^1T_1$	3.17	4.86	4.30	?
	$^1T_2$	3.64	5.24	4.71	4.59–4.65 [16, 17]
$MnO_4^-(^1A_1)$	$(t_1 \rightarrow 2e)$ $^1T_1$	0.14	1.46	1.02	1.8 [18]
	$^1T_2$	0.99	2.12	1.74	2.27
	$(4t_2 \rightarrow 2e)$ $^1T_1$	2.29	3.52	3.11	3.47
	$^1T_2$	3.03	4.12	3.76	3.99
Standard deviation		0.21	0.18	0.15	— —

* $\gamma_{wtd} = \frac{1}{3}\gamma_{Ohno} + \frac{2}{3}\gamma_{STO}$

bands except that the (weak) band at 3.47 eV is now associated with a forbidden transition to $^1T_1$, and not $^1T_2$. Assignment of the band at 3.99 eV is now very different: $(4t_2 \rightarrow 2e)\ ^1T_2$.

Still a different assignment was given by Hillier and Saunders [24] on the basis o approximate SCF CI ab initio calculations. Our assignment agrees with theirs in the case of the first forbidden band at 1.8 eV, $(t_1 \rightarrow e)^1T_1$ and in the case of the fourth band at 3.99 eV, $(t_2 \rightarrow e)^1T_2$. The transition $(t_1 \rightarrow e)^1T_2$ is assigned by us to the band at 2.27 eV and by those authors to that at 3.47 eV.

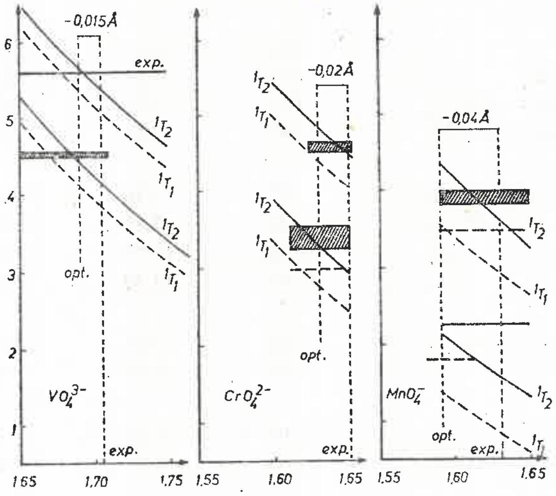

Fig. 1

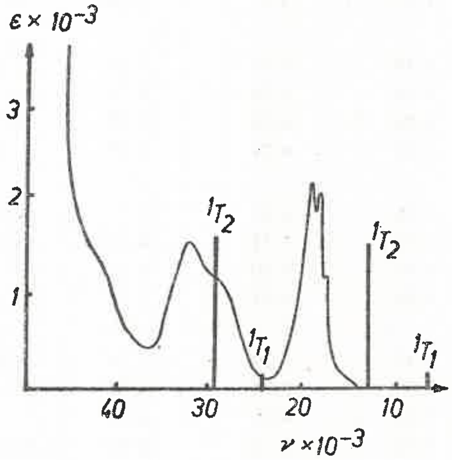

Fig. 2

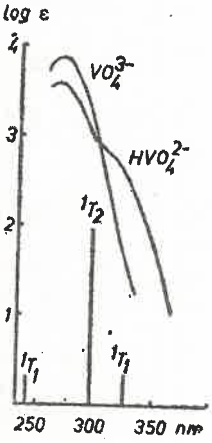

Fig. 3

On the other hand, our assignment of the first three bands is in a complete agreement with that of Viste and Gray [38] and Fenske and Sweaney [39]. It is also consistent with the observed intensities (Fig. 2). It is particularly evident when considering the interpretation of the spectrum of the related anion, VO_4^{3-} (Fig. 3). Protonation leading to HVO_4^{2-} perturbs the symmetry, the enhancing thus the excitation ${}^1A_1 \rightarrow {}^1T_1$ which has hitherto been forbidden.

In Figs. 2 and 3 symmetry allowed transitions are drawn one order of magnitude higher than the symmetry forbidden ones. Otherwise the scale is arbitrary.

It has been said for years that the first electronic transition in oxyanions is a ligand to metal charge transfer band. Some doubt has been raised by Ziegler et al. [37]. According to those authors the concept of charge transfer is a misnomer, at least for these systems. Our calculations confirm the previous view: we have found a $L \rightarrow M$ charge transfer of 0.45 e. A similar conclusion follows from the best available SCF CI ab initio calculations [24].

4. *Photoelectron spectrum*

Within the framework of the SINDO/F theory the Koopmans theorem yields ionization energies which are much too high. This should have been expected as just in SINDO/F the orbitals are far from being kept frozen due to the charge and configuration effect. Reasonable accuracy is obtained on the ΔE_{SCF} level, when considering relaxation effects in the ionized states. For this reason we do not attribute much significance to the concept of the orbital level in transition metal compounds as do many other authors. We recall that also according to recent ab initio calculations for transition metal compounds there seems to be no obvious relation between the ordering of orbitals and the real ground state electronic configuration of the system [40], [44].

In Table II we compare the calculated photoelectron spectrum of gaseous $TiCl_4$ with experiment and with results of other methods. Numerical agreement with experiment is good and comparable to that of $X\alpha$. Assignment of the first two bands is identical in all treatments. There is no evidence as to which assignment is correct in the case of the remaining two bands. It is worthwhile to mention that the Koopmans theorem yields within the framework of SINDO/F exactly the same order of ionization energies as that following from the transition state $X\alpha$ method. Relaxation effects cause the change of this ordering. For this reason our assignment may be more adequate.

TABLE II

Photoelectron spectrum of gaseous $TiCl_4$ (in eV)

Experiment [19]	CNDO2-GTO [20]	INDO [21[	$X\alpha$ [22]	SINDO/F (γ_{Ohno})
11.78	14.39(t_1)	13.69(t_1)	12.2(t_1)	10.60(t_1)
12.79	15.32(t_2)	15.89(t_2)	12.7(t_2)	12.91(t_2)
13.23	15.86(t_2)	17.00(e)	13.0(e)	13.01(a_1)
		17.03(a_1)		
13.97	16.54(1e)	19.42(t_2)	13.8(t_2)	13.91(e)
	16.82(a_1)		14.1(a_1)	17.53(t_2)

TABLE III

Contribution of atomic subshells to valence shell molecular orbitals of MnO_4^- (in %)

MO: subshells	$X\alpha$	Ab initio			Non-emp. CNDO [26]	Semi-emp. CNDO [27]	SINDO/F	
		HF AO [29]	d: 2ζ [24]	single-ζ [25]			γ_{Ohno}	γ_{STO}
$1t_1$: $2p$O	–	100	100	100	100	100	100	100
$6a_1$: $4s$Mn; $2p$O	–	8; 88	1; 95	5; 89	55; 13	7; 93	6; 78	5; 80
$6t_2$: $4p$Mn; $2p$O	–	7; 88	3; 93	9; 81	16; 72	2; 98	5; 90	4; 91
$1e$: $3d$Mn; $2p$O	38; 30	29; 71	44; 56	22; 78	48; 52	54; 46	21; 79	17; 83
$5t_2$: $3d$Mn; $2p$O	43; 33	53; 40	51; 40	44; 44	23; 37	75; 25	25; 66	22; 69
$4t_2$: $3d$Mn; $2s$O	–	7; 88	9; 86	5; 90	14; 76	–	8; 75	7; 76
$5a_1$: $4s$Mn; $2s$O	–	8; 92	7; 90	9; 88	35; 63	–	24; 70	22; 72
q(Mn)	+0.64	+0.99	+0.93	+1.29	−3.00	+0.17	+2.52	+3.02
q(O)	−0.41	−0.50	−0.48	−0.57	+0.50	−0.29	−0.88	−1.01

However, reproduction of the observed photoelectron spectra was not always as quantitative as in the case of $TiCl_4$: for small molecules (CO, N_2, H_2O) the theory predicted ionization potentials too low by a few eV's. The qualitative assignment, however, was correct also in these cases.

5. *Nature of valence shell molecular orbitals*

In Tables III and IV we give the contribution of atomic subshells to valence shell molecular orbitals of MnO_4^-, CrO_4^{2-} and VO_4^{3-}. The nature of the bonding is closely related to this characteristics. It follows from the tables that the contributions obtained by SINDO/F compare most favourably just to the best ab initio results available. Non-empirical CNDO results are definitely worse.

TABLE IV

Contribution of atomic subshells to molecular orbitals of CrO_4^{2-} and VO_4^{3-} (in %)

MO: subshells	An initio d: double-ζ [28]	Ab initio single-ζ [25, 28]	Non-emp. CNDO [26, 30]	SINDO/F γ_{Ohno}	SINDO/F γ_{STO}
CrO_4^{2-}:					
$1t_1$: $2p$O	100	100	100	100	100
$6t_2$: $2p$O; $4p$Cr; $2s$O; $3d$Cr	92; 5; 2; 1	78; 12; 4; 5	80; 0; 7; 13	92; 4; 4; 0	94; 3; 3; 0
$6a_1$: $2p$O; $2s$O; $4s$Cr	96; 3; 1	87; 5; 7	8; 46; 47	84; 11; 5	86; 10; 4
$1e$: $2p$O; $3d$Cr	61; 39	80; 20	72; 28	85; 15	88; 12
$5t_2$: $2p$O; $3d$Cr; $4p$Cr	52; 40; 5	54; 32; 14	36; 18; 45	73; 19; 0	77; 17; 0
q(Cr); q(O)	+0.58; −0.64	+0.63; −0.66	—	+2.28; −1.07	+2.77; −1.19
VO_4^{3-}:					
$1t_1$: $2p$O	100	100	100	100	100
$6t_2$: $2p$O; $4p$V; $3d$V	88; 11; 1	75; 11; 12	90; 1; 7	94; 3; 0	95; 2; 0
$6a_1$: $2p$O; $4s$V; $2s$O	92; 5; 2	70; 24; 6	7; 44; 50	91; 3; 6	92; 3; 5
$1e$: $2p$O; $3d$V	65; 35	91; 9	75; 25	90; 10	92; 8
$5t_2$: $2p$O; $3d$V; $4p$V	63; 32; 4	60; 19; 21	36; 12; 53	79; 15; 0	82; 13; 0
q(V); q(O)	−0.08; −0.73	−0.29; −0.68	—	+1.97; −1.24	+2.37; −1.34

As regards the net charges of atoms they are now usually distinctly larger in absolute value than in other treatments. This is not what one would perhaps expect. However, the charge of atoms in molecules is a very subjective concept depending much on the definition and the basical set used. Indeed, the charge of manganese is varying in other methods from −3.0 e to +1.29 e. Charge of atoms is merely a comparative quantity within the same theoretical framework. In this sense the results are comparable. According to ab initio calculations the charge of the metal decreases in the order Mn (+0.93e), Cr (+0.58e), V (−0.08 e). In the case of SINDO/F the order is the same: Mn (+2.52e), Cr (+2.28 e), V (+1.97 e); in a sense SINDO/F theory is much closer to the crystal field theory than are the other methods.

One might claim that highly uneven charge distributions are unphysical leading to an overestimation of dipole moments. If deorthogonalization is carried through as in CNDO/2D [41] this is not the case. A good example is CO. With the charge distribution (in atomic units) $C^{+0.57}$ $O^{-0.57}$ one finds that $d = -2.18$ D. If we deorthogonalize the orbitals and then calculate the dipole moment exactly we find that $d = +0.60$ D. The experimental value is $d = +0.11$ D. In fact, deorthogonalization causes substantial changes in estimated dipole moments also in the case of CNDO/2 [41]:

	CNDO/2	CNDO/2D	Experiment
pyrrole	−2.00 D	+1.00 D	+2.20 D

Admittedly, the problem of charge distributions and dipole moments requires a more extensive study before drawing final conclusions.

6. *Conclusions and comments*

It has been shown that SINDO/F is a reliable basis for electronic structure calculations of molecules. There are two main features which make SINDO/F basically different from other related treatments: 1° a new simple way of evaluation of resonance integrals with no additional parameters and 2° charge and configuration scaling not only of two-electron repulsion integrals (a procedure occasionally performed also by other authors), but also of one-centre core integrals U_{Aa}.

The method has found application also to other problems. It was applied to the problem of the oxidation of acroleine to acrylic acid in a homogeneous catalysis as well as heterogeneous catalysis on cobalt oxides [42]. Another study was concerned with the relative stability and reactivity of complexes of the general formula $[Fe(CN)_5L]^{q-}$, where $L = CN^-$, N_2, N_3, NH_3, N_2H_4, NH_2OH, NO and N_2O [43]. Results of these two studies fully confirm the adequacy of this approach also to problems related to the total energy of the system. These two studies required a supplemental discussion of the core-core repulsion energy V_{AB}. This energy has been estimated in exactly the same way as in MINDO [43].

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