Inorganica Chimica Acta, 11 (1974) L5 - L6

The One-Center Quantities for the Elements of the First and Second Transition Period in MO-CNDO Calculations

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(Received September 2, 1974)

In a previous paper[1] the one-center quantities for transition metal elements have been evaluated according to a procedure that proved useful to study the electronic structure of molecules or ions in the "zero differential overlap" ZDO scheme. However, the introduction of ZDO approximations makes the results depending upon the particular choice of the coordinate local systems of atoms and of the hybridization of the orbital basis set.

To overcome such peculiarities various improvements, starting from the CNDO scheme of Pople,[2] have been introduced.[3] They mainly consist of using a single two electron integral depending on the atom and not on the type of the orbital of the considered atom. However, dealing with transition metal complexes, many authors[4] pointed out that a unique coulomb integral cannot be used and that different integrals have to be introduced for different orbitals. Moreover, to preserve invariance to local axes rotation, such integrals have been evaluated on s-like orbitals, making use of single Slater radial wave functions whose exponents were assumed according to simple rules. In this way the integrals are often greater than those experimentally determined by atomic spectroscopy. Del Bene and Jaffé[5] showed that also in organic systems a substitution of the coulomb integrals with the corresponding semi-empirical quantities is necessary to obtain significant results about the calculated electronic spectra within the CNDO approach.

In the present paper the one-center quantities, namely the core integrals U_i and the coulomb integrals γ_{ij}, are both evaluated from the average energies of the electronic configurations belonging to three adjacent oxidation states of the atom. It is considered that every orbital of the usual valence set of transition metals, nd, $(n+1)s$, $(n+1)p$, has no angular dependence and may be represented by a single exponent Slater radial function. Such exponents, which determine the coulomb integral values, just constitute with the U_i the quantities which have been treated as parameters to fit the differences between the average energies. Because of the lack of some $d^{n-2}s^2$ and $d^{n-2}p^2$ configurations, the exponents for the $(n+1)s$ and $(n+1)p$ orbitals have been assumed to reproduce the g_{ss} and g_{pp} quantities of ref. 1.

The average energies of d^n, $d^{n-1}s$, $d^{n-1}p$ configurations for the oxidation states, 0, +1 and +2 have

TABLE I. One-Center Quantities for Transition Metals. U_i are in eV.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
U_s	−28.72	−37.90	−47.74	−58.25	−69.41	−81.24	−93.73	−106.88
U_p	−23.29	−30.48	−38.14	−46.26	−54.86	−63.93	−73.47	−83.48
U_d	−36.51	−51.30	−67.44	−84.93	−103.77	−123.96	−145.50	−168.39
ζ_s	1.15	1.20	1.25	1.30	1.35	1.40	1.45	1.50
ζ_p	1.00	1.03	1.06	1.09	1.12	1.15	1.18	1.21
ζ_d	1.65	1.75	1.85	1.95	2.05	2.15	2.25	2.35
	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
U_s	−28.33	−36.39	−45.07	−54.37	−64.30	−74.85	−86.02	−97.81
U_p	−22.37	−28.67	−35.66	−43.31	−51.64	−60.64	−70.32	−80.67
U_d	−31.74	−43.33	−56.34	−70.76	−86.61	−103.88	−122.56	−142.66
ζ_s	1.43	1.47	1.51	1.55	1.59	1.63	1.67	1.71
ζ_p	1.16	1.20	1.24	1.28	1.32	1.36	1.40	1.44
ζ_d	1.67	1.78	1.89	2.00	2.11	2.22	2.33	2.44

TABLE II. One-Center Quantities for Some Atoms Commonly Found in Ligands. U_i are in eV.

	C	N	O	F	Cl	Br
U_s	–53.74	–74.04	–100.84	–140.19	–102.87	–94.01
U_p	–42.59	–58.93	–76.62	–113.93	–80.50	–72.93
ζ_{ns}	1.19	1.29	1.56	1.76	2.34	2.72
ζ_{np}	1.03	1.13	1.18	1.57	1.48	1.72

been evaluated by means of the Slater–Condon parameters[6] for the sequence from Ti to Cu and from Zr to Ag and used to evaluate U_s, U_p, U_d and the exponents of the *d* orbitals.

As previously pointed out,[1] the restrictive condition that U_i and the exponents vary parabolically and linearly respectively with the atomic number has been imposed.

The calculated quantities are reported in Table I. In addition the one-center quantities for some of the most common atoms, which are found as ligands in transition metal complexes, are reported in Table II. In this latter case the oxidation states –1, 0 and +1 have been used following the same calculation procedure without any restriction.

These quantities are particularly suitable to perform molecular orbital calculations according to CNDO scheme. All the coulomb integrals can be theoretically evaluated with single Slater orbitals whose exponents are obtained from the elaboration of spectroscopic data. As far as the out diagonal core matrix elements are concerned, calculations on some transition metal complexes[7] showed that satisfactory results are obtained adopting the Mulliken formula.[8]

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