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ONE CENTRE INTEGRALS IN SEMI-EMPIRICALS MOLECULAR ORBITAL THEORY

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1. INTRODUCTION

In recent times particular attention has been paid to the semi-empirical S.C.F.–L.C.A.O. approach to molecular orbital theory. This is due in particular to the successful work on the unsaturated hydrocarbons by Pariser and Parr[1, 2].

One of the characteristic aspects of the semi-empirical molecular orbital theory is the introduction of quantities estimated from the valence states of the atoms, in place of the one centre integrals. In such a way electronic correlation and effective electronegativity are taken into account.

Hitherto the semi-empirical theory had been applied mainly to the π-systems of aromatic compounds in which each atom participates with only one atomic orbital. The purpose of the present work is to generalise the criterions by which the one centre integrals are estimated so that the semi-empirical calculation can be applied to systems other than the unsaturated hydrocarbons.

2. SEMI-EMPIRICAL EVALUATION OF THE ONE CENTRE INTEGRALS

The valence state of an atom is characterised by the random distribution of the spins of the valency electrons.

The energy of an atom in its valence state can generally be represented by the following expression:

$$E = 2\sum_{k} \mathrm{H}_k + \sum_{r} \mathrm{H}_r + 2\sum_{k,l} (\mathrm{J}_{k,l} - \tfrac{1}{2}\mathrm{K}_{k,l}) + 2\sum_{k}\sum_{r} (\mathrm{J}_{k,r} - \tfrac{1}{2}\mathrm{K}_{k,r}) + \tfrac{1}{2} \sum_{r,s(\neq r)} (\mathrm{J}_{rs} - \tfrac{1}{2}\mathrm{K}_{rs}) \tag{1}$$

in which

$$\mathrm{H}_k = \int \phi_k^*(1)\mathrm{H}_{\mathrm{core}}(1)\phi_k(1)\, \mathrm{d}v_1$$

$$\mathrm{J}_{k,l} = \int \phi_k^*(1)\phi_l^*(2)\frac{1}{r_{12}}\phi_k(1)\phi_l(2) \cdot \mathrm{d}v_1\, \mathrm{d}v_2$$

$$\mathrm{K}_{k,l} = \int \phi_k^*(1)\phi_l^*(2)\frac{1}{r_{12}}\phi_l(1)\phi_k(2)\, \mathrm{d}v_1\, \mathrm{d}v_2$$

Coordin. Chem. Rev., 1 (1966) 13–17

ϕ_k, ϕ_l .... are doubly occupied atomic orbitals
ϕ_r, ϕ_s, ... are singly occupied atomic orbitals.

If one introduces for each atomic orbital ϕ_i, an occupation number n_i (= 0, 1 or 2, according to whether the orbital is empty, singly or doubly occupied respectively) then eqn. (1) can be re-written:

$$E = \sum_i \mathrm{H}_i n_i + \tfrac{1}{2} \sum_{i,\, j(\neq i)} g_{ij} n_i n_j + \tfrac{1}{2} \sum_i g_{ii} n_i (n_i - 1) \tag{2}$$

in which

$$g_{ij} = \mathrm{J}_{ij} - \tfrac{1}{2}\mathrm{K}_{ij}$$

and

$$g_{ii} = \mathrm{J}_{ii}$$

The integrals H_i, g_{ij}, and g_{ii} vary with the occupation number in much the same way as the Hartree-Fock self-consistent orbitals vary with the configuration.

Now in the molecular orbital calculations according to the S.C.F.–L.C.A.O. method, the integrals have values which correspond exactly with the occupation numbers of every atom in the molecule. In such situations the occupation numbers are rarely whole numbers.

In order to overcome this difficulty, one can postulate, as has been done by many authors[3,4], that the electronic energy of an atom in its valence state is a continuous function and may be differentiated with respect to the occupation numbers. Strictly speaking this assumption is not valid; nevertheless because each occupation number can only take three values ($n_i = 0$, 1 or 2), and the electronic energy takes a definite value for each state with a definite occupation number, it follows that such a postulate can be introduced.

Using this idea, one can work out the relative energies of the valence state, with respect to a given valence state, in a polynomial form:

$$E = E_0 + \sum_i a_i (n_i - n_i^0) + \tfrac{1}{2} \sum_{i,\, j} \mathrm{b}_{ij} (n_i - n_i^0)(n_j - n_j^0) + \ldots . \tag{3}$$

in which n_i^0 are the occupation numbers of the given reference state.

By considering only those valence states which do not differ much from the reference state, at least with respect to the oxidation number, (as we shall see later) the equation can be reduced to quadratic terms:

$$E = C + \sum_i \mathrm{H}_i^* n_i + \tfrac{1}{2} \sum_{i,\, j(\neq i)} g_{ij}^* n_i n_j + \tfrac{1}{2} \sum_i g_{ii}^* n_i (n_i - 1) \tag{4}$$

in which

$$C = E_0 - \sum_i a_i n_i^0 + \tfrac{1}{2} \sum_{i,\, j} \mathrm{b}_{ij} n_i^0 n_j^0$$

$$\mathrm{H}_i^* = a_i - \sum_j \mathrm{b}_{ij} n_j^0 - \mathrm{b}_{ii}(n_i^0 - \tfrac{1}{2})$$

$$g_{ij}^* = \mathrm{b}_{ij}$$

$$g_{ii}^* = \mathrm{b}_{ii}$$

Such an expression is analogous to equation (2), except in the constant C, there being a formal correspondence between the integrals H_i, g_{ij}, g_{ii} and the quantities H_i^*, g_{ij}^* and g_{ii}^*. Naturally these last quantities do not have an immediate physical significance and so much the less that attributed to the integrals.

Nevertheless we shall see that such quantities, which are called *semi-empirical integrals*, have several advantageous properties. Above all they are constants independent of the occupation numbers.

When these are introduced into the equations for the vertical ionisation potentials and electron affinities, one obtains the experimental values for these quantities:

$$\begin{aligned} E(n_r=1)-E(n_r=0) &= \mathrm{H}_r^* + \sum_{i\neq r} n_i g_{ir}^* = -\mathrm{I}_{r_{\mathrm{exp.}}} \\ E(n_r=2)-E(n_r=1) &= \mathrm{H}_r^* + \sum_{i=r} n_i g_{ir}^* + g_{rr}^* = -\mathrm{A}_{r_{\mathrm{exp.}}} \end{aligned} \tag{5}$$

from which it follows that they also give correctly the electronegativity according to Mulliken's definition[5]:

$$\chi_r = \tfrac{1}{2}(\mathrm{I}_{r_{\mathrm{exp.}}} + \mathrm{A}_{r_{\mathrm{exp.}}}) = \tfrac{1}{2}[E(n_r=0)-E(n_r=2)] \tag{6}$$

Finally such semi-empirical integrals reproduce the criteria of Pariser and Parr[1,2]:

$$\begin{aligned} \int \phi_r^*(1)\phi_r^*(2)\frac{1}{r_{12}}\phi_r(1)\phi_r(2)\,\mathrm{d}v_1\,\mathrm{d}v_2 &= \mathrm{I}_{r_{\mathrm{exp.}}} - \mathrm{A}_{r_{\mathrm{exp.}}} = g_{rr}^* \\ \int \phi_r^*(1)[T(1)+V_r(1)]\phi_r(1)\,\mathrm{d}v_1 &= -\mathrm{I}_{r_{\mathrm{exp.}}} = \mathrm{H}_r^* + \sum_{i=r} g_{ir}^* n_i \end{aligned} \tag{7}$$

The last expression (7) is similar to that of Goeppert-Mayer and Sklar[6], in which T represents the kinetic energy and V_r the potential energy of the nucleus and all the electrons.

3. DISCUSSION AND CONCLUSIONS

As an illustrative example of eqn. (4), we choose the carbon atom and take as the reference valence state $V_2(s^2, p_x, p_y)$. In such a case the semi-empirical integrals take the following values (in eV):

$$\begin{array}{ll} \mathrm{C} = -24.47 & g_{ss}^* = 12.234 \\ \mathrm{H}_s^* = -52.136 & g_{sp_x}^* = g_{sp_y}^* = g_{sp_z}^* = 10.264 \\ \mathrm{H}_{p_x}^* = \mathrm{H}_{p_y}^* = \mathrm{H}_{p_z}^* = -40.876 & g_{p_xp_x}^* = g_{p_yp_y}^* = g_{p_zp_z}^* = 11.084 \\ & g_{p_xp_y}^* = g_{p_xp_z}^* = g_{p_yp_z}^* = 9.534 \end{array} \tag{8}$$

The electronic energies of the valence states of C^-, C^0, C^+ and C^{2+} are reported in Table I column B. The electronic energies calculated as the sum of the ionisation

TABLE I

VALENCE STATE ENERGIES (IN eV)*

	Ground State	*Volence State*	*Promotion energy*[7]	*Valence state energy*	
			P	*A*	*B*
C^-	$^4S(s^2p^3)$	$V_3(s^2, p_x, p_y, p_z)$	0.73	−148.95	−148.95
	$E_f = -149.68$	$V_1(s^2, p_x^2, p_y)$	1.71	−147.97	−147.40
		$V_3(s, p_x^2, p_y, p_z)$	9.38	−140.30	−140.30
C^0	$^3P(s^2p^2)$	$V_2(s^2, p_x, p_y)$	0.31	−147.67	−147.67
		$V_1(s^2, p_x^2)$	1.68	−146.30	−146.12
	$E_f = -147.98$	$V_4(s, p_x, p_y, p_z)$	8.14	−139.84	−139.84
		$V_2(s, p_x^2, p_y)$	9.69	−138.29	−138.29
C^+	$^2P(s^2p)$	$V_1(s^2, p_x)$	0	−136.716	−136.856
		$V_3(s, p_x, p_y)$	8.42	−128.295	−128.296
	$E_f = -136.716$	$V_1(s, p_x^2)$	10.34	−126.376	−126.746
		$V_3(p_x, p_y, p_z)$	18.22	−118.496	−118.496
C^{2+}	$^1S_0(s^2)$	$V_0(s^2)$	0	−112.340	−116.508
	$E_f = -112.340$	$V_2(s, p_x)$	8.04	−104.300	−107.218
		$V_2(p_x, p_y)$	17.32	−95.02	−96.688

* The energies of the ground state E_f are estimated as the sum of successive ionisation potentials $E_f = -\sum_i I_i$. The energies of the valence states in column A, are obtained from the relationship $E_v = E_f + P$.

potentials (starting from the ground state to the configuration $(1s)^2$, whose energy is not included) and of the promotion energy to the valence state are given in column A. The two sets are in good agreement for the valence states of C^-, C^0 and C^+, the difference being very small; in the case of C^{2+}, the difference between the two columns increases, the increase being in the same sense for all the states. It is therefore evident that the simplification of equation (3) to a quadratic form prevents the data given above (8) from correctly predicting the energies of the valence states of C^{2+}.

In general for elements of the first and second period, equation (4) gives, with a good degree of accuracy, all the valence states of three adjacent oxidation numbers, provided that the reference state belongs to the intermediate oxidation number.

Recently Klopman[8] has proposed the following formula for the calculation of valence state energies:

$$E = \sum_i B_x^I + \tfrac{1}{2}\sum_{ij} A_x^+ \delta_{ij} + \tfrac{1}{2}\sum_{ij} A_x^-(1-\delta_{ij}) \qquad (9)$$

in which B_x^I, A_x^+ and A_x^- are constants.

i and *ij* represent each electron and each pair of electrons respectively,

δ_{ij} is the Kronecker delta; δ_{ij} takes the values 1 or 0 according to whether the electrons i and j have parallel or anti-parallel spins.

This formula is in many ways similar to equation (4); for example it reproduces with reasonable accuracy the energies for three adjacent oxidation states. The fundamental difference is that this formula does not give the total electronic energy understood as the sum of the successive ionisation potentials (from the ground state of the atom or ion) and the promotion energies to the valence state. In conclusion, because the semi-empirical integrals provide a good description of the atom, and because they contain especially the criteria adopted with success by Pariser and Parr, we propose that they can be advantageously introduced into calculations of the semi-empirical molecular orbital theory.

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