A Semi-empirical Approach to the Self-consistent Molecular Orbitals

By Hideo KON

(Received August 12, 1954)

The semi-empirical ASMO method proposed recently by Pariser and Parr[1] presents a way to calculate the transition energy of a variety of π-electron systems without much labor in conformity with experimental results that is rarely to be found in this kind of calculations. One of the essential points of the method is to alter the values of Coulomb repulsion integrals over atomic orbitals by computing $(pp|pp)$ through the empirical ionization potential and electron affinity values of the atom p and by computing $(pp|qq)$ as the electrostatic interaction between the uniformly charged spheres.

It is of some interest to reflect this reasonable revision of integral values on the form of molecular orbitals. One way might be to resort to the iterative procedure of Roothaan[2], by incorporating Pariser and Parr's semi-empirical scheme into the former. In the present letter, the above mentioned idea is applied to the simple oxygen containing molecules (formaldehyde and glyoxal) as to which no account was given in Pariser and Parr's article.

The best set of coefficients (c_{ip}) in a molecular orbital (ϕ_i) expressed as a linear combination of atomic orbitals (χ_p),

$$\phi_i=\sum_p c_{ip}\chi_p,$$

is obtained by the iterative solution of a set of homogeneous equations derived by Roothaan, with the overlap integrals S_{pq} being replaced by δ_{pq},

$$\sum_q c_{ip}(L_{pq}-\delta_{pq}\epsilon_i)=0,$$

δ_{pq} being Kronecker's delta. (As to the definitions of L_{pq} and ϵ_i, see ref. 2.) In computing the matrix elements L_{pq}, the simplifications by Pariser and Parr such as; 1) zero differential overlap, 2) neglect of non neighbor resonance integrals are taken in. In addition to this, following assumptions are made: 1) The Coulomb integral α_p can be approximated as the valence state ionization potential (W_{2p}) of the free atom, less the sum only of the Coulomb repulsion integrals $(pp|qq)$. This neglect of Coulomb penetration integrals is found to reduce the labor without having a significant influence on the numerical results. 2) The resonance integral β_{pq} is proportional for a type of bond (C=C, C=N, or C=O, etc.) to the inverse sixth power of the bond length, the proportionality constants being selected so as to reproduce, as closely as possible, the observed N→V, transition of a particular molecule in the final result by the iterative process. In the case of formaldehyde, -2.95 ev is found suitable for β_{co} (1.20 Å), and the same value is used for predicting glyoxal $N \rightarrow V_1$ transition. The geometricals and numberings for formaldehyde and glyoxal are shown in Fig. 1, together with the computed π-electron densities.

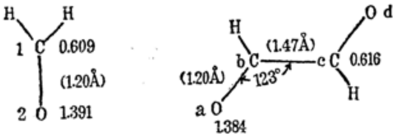

Fig. 1.

The calculated transition energies (E) and self-consistent molecular orbitals are given in the following, where V_1 and T_1 designate the lowest excited singlet and triplet state, respectively.

Formaldehyde,

$E(N\rightarrow V_1)=8.09$ ev, observed, 7.95 ev,3)

$E(N\rightarrow T_1)=4.75$ ev, — —

$$\phi_1=0.5519\ \chi_1+0.8339\ \chi_2,$$

$$\phi_2=0.8339\ \chi_1-0.5519\ \chi_2.$$

Glyoxal,

$E(N\rightarrow V_1)=7.47$ ev, estimated, 7.51 ev*),

$E(N\rightarrow T_1)=5.09$ ev, — —

$$\phi_1=0.5541\ (\chi_a+\chi_d)+0.4393\ (\chi_b+\chi_c),$$

$$\phi_2=0.6205\ (\chi_a-\chi_d)+0.3390\ (\chi_b-\chi_c),$$

$$\phi_3=0.4393\ (\chi_a+\chi_d)-0.5541\ (\chi_b+\chi_c),$$

$$\phi_4=0.3390\ (\chi_a-\chi_d)-0.6205\ (\chi_b-\chi_c).$$

*) Estimated roughly from the 57,000 cm^{-1} band of diacetyl, assuming that the two -CH$_3$ groups cause the bathochromic shift of the same magnitude as the difference between the 60,600 cm^{-1} band of acetone and the corresponding band of formaldehyde.

Detailed discussion of these results will be published soon, with the result of calculations for several other molecules which are now in progress.

The author is grateful to Professor H. Tominaga for his kind guidance through the course of this calculation.

---

1) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
2) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1333 (1950).
3) A. D. Walsh, *Proc. Roy. Soc.* (London), **185A**, 176 (1946).

Department of Chemistry, Faculty of Science, Tôhoku University