Theoret. chim. Acta (Berl.) 18, 166—169 (1970)

A Semiempirical Method Based on Geminal Functions

II. Transition Moment and One-Electron Density with Geminal Basis Functions

A. NESZMELYI* and L. PAOLONI

Gruppo Chimica Teorica, C.N.R., Roma
Gruppo Chimica Teorica, Università, Palermo

Received March 10, 1970

An extention is reported of a previously proposed semiempirical approach based on geminal functions and formulas are given for the transition moments and the electronic population analysis.

The case of pyridine is considered as an example and used to predict the $n \to \pi^*$ or $\pi \to \pi^*$ character of its lower transition.

A semiempirical approach based on geminal functions has been recently [1] proposed for system containing π- and n-electrons and applied in two different levels of approximation to molecules containing separated pairs of π- and n-electrons.

An extension of the procedure appeared desirable in order to verify its applicability to heteroaromatic sytems including all the π- and n-electrons and to see to what extent it could be used to predict the value and the nature of their electronic transitions (both $\pi \to \pi^*$ and $n \to \pi^*$).

As a part of this work we report here some formulas for the transition moment and for the population analysis of electronic states when a geminal formulation is used for the molecular wave-function, and an example of their application to the simple case of pyridine.

The molecular, wave-function

$$\Psi(1, 2, \ldots, N) = \Phi_a \Phi_b \ldots \Phi_{N/2} \tag{1}$$

has been taken as the simple product of geminal functions $\Phi(1, 2)$ which are the correct linear combinations of molecular biorbitals – antisymmetrized products of MO's – as defined by Eqs. (9)–(12) of Ref. [1]. We here adopt a notation which is better suited to the present development by putting

$$\Phi_s(1, 2) = \sum_{t=1}^{NB} U_{ts} \phi_t(1, 2), \quad (s = 1, 2, \ldots, NG), \tag{2}$$

where NG is the total number of geminals and NB the total number of molecular biorbitals ϕ_t (expressed previously as λ_{ij} and τ_{ij} pair-singlet or pair-triplet

---

* Permanent Address: Central Research Institute for Chemistry, Budapest, 114, CP 17, Hungary.

functions [1]) defined by

$$\phi_t = N_{mn}[\chi_m(1)\,\chi_n(2) \pm \chi_m(2)\,\chi_n(1)]\,\eta(1,2)\,. \tag{3}$$

Here N_{mn} is the normalization factor, $\eta(1,2)$ the spin part of the biorbital and U_{ts} are the eigenvectors determined by the usual variational procedure[1]. The functions χ are molecular orbitals taken as linear combinations of atomic orbitals φ for each group of n- and π-electrons. Substituting these φ's into Eq. (3) and the result into Eq. (2) one obtains

$$\Phi_s(1,2) = \eta(1,2) \sum_k \sum_l C_{skl}\varphi_k(1)\,\varphi_l(2)\,, \tag{4}$$

where $C_{skl} = \pm C_{slk}$ (+ for singlet and − for triplet states).

The transition moment between molecular states differing by the geminals Φ_s and Φ_t takes the form

$$\boldsymbol{\mu}_{st} = \langle \Phi_s | \boldsymbol{r}_1 + \boldsymbol{r}_2 | \Phi_t \rangle = 2 \sum_{kk'} \sum_{ll'} C_{skl} C_{tk'l'} S_{ll'} S_{kk'} \boldsymbol{R}_{kk'}\,, \tag{5}$$

where the S_{ij} are the overlap integrals between the AO's and the $\boldsymbol{R}_{kk'}$ are the momentum integrals

$$\boldsymbol{R}_{kk'} = \langle \varphi_k | \boldsymbol{r} | \varphi_{k'} \rangle\,. \tag{6}$$

Eq. (5) gives also the π- and the n-electron density contribution to the dipole moment by putting $s=t$ and summing the contributions of the individual geminals for the molecular wave-function (1)

$$\boldsymbol{\mu}_{\mathrm{el}} = e \sum_s^{\mathrm{occ}} \boldsymbol{\mu}_{ss}\,, \tag{7}$$

where the summation runs over the $N/2$ geminals occupied in the state considered.

The pair-density function of a molecular state may be defined as

$$\varrho(1,2) = \sum_s^{\mathrm{occ}} \Phi_s^2 = \sum_s^{\mathrm{occ}} \left\{ \sum_{kk'} \left[\sum_{ll'} C_{skl} C_{sk'l'} \varphi_l(2)\,\varphi_{l'}(2) \right] \varphi_k(1)\,\varphi_{k'}(1) \right\}. \tag{8}$$

Starting with this expression and introducing the matrix

$$P_{kk'} = 2 \sum_s^{\mathrm{occ}} p_{skk'} \tag{9}$$

where

$$p_{skk'} = \sum_{ll'} C_{skl} C_{sk'l'} \langle \varphi_l(2) | \varphi_{l'}(2) \rangle \tag{10}$$

the one-electron density takes the form

$$\varrho = \int \varrho(1,2)\,\mathrm{d}v_2 + \int \varrho(1,2)\,\mathrm{d}v_1 = \sum_{kk'} P_{kk'} \varphi_k \varphi_{k'}\,. \tag{11}$$

From Eqs. (9) and (10) it is possible to get the partitioning of the electronic population into different groups according to the nature of the atomic orbitals.

---

[1] The index t corresponds to a given combination of two orbital indices m, n.

Table. *Biorbital population analysis of lower states of pyridine*

State	Energy eV	Population (π,π)	(n,π)	(n,n)	Change in (π,π)
0	0.	3.76	3.05	1.19	—
1	2.7	4.20	2.46	1.34	+0.44
2	3.1	4.46	2.35	1.19	+0.70
3	3.3	4.13	2.53	1.34	+0.37
4	3.8	4.46	2.35	1.19	+0.70
5	4.1	2.46	4.35	1.19	−1.30
6	5.3	4.38	2.34	1.28	+0.62
7	5.7	4.64	2.24	1.12	+0.88
8	6.0	4.32	2.41	1.27	+0.56
9	6.5	4.64	2.24	1.12	+0.88

Having started with atomic orbitals of the type n and π there are three groups of atomic biorbitals, (n, n), (n, π) and (π, π), and therefore three fractions of the electronic population in each molecular state.

This subdivision of the electronic population may be illustrated in the case of pyridine. Assuming eight electrons and seven atomic orbitals (six $2p\pi$- and one n-orbital) we characterize the ground state and the excited states by product functions of the type (1) containing four geminal factors, each filled with two electrons.

The simplest Hückel MO's were taken as the basis set, and the molecular biorbitals formed with all the 28 possible $\chi_m \chi_n$ products. The one-electron integrals, scaled to $\alpha_C = 0$, were evaluated by taking $\beta_{CC} = -2.60$ eV, giving -1.56 for $\alpha_{N\pi}$ and -3.12 eV for α_{Nn}. The two-electron integrals were calculated for an hexagonal frame with side 1.394 Å using Slater AO's and Roothaan's formulas, as done before [1].

The electronic population analysis for the ground state and for the excited states is given in the Table together with the population change in the (π, π) biorbitals with respect to the ground state. There are four states with energies between 2.7 and 3.8 eV above the ground state and showing a similar population shift from (n, π) to (π, π) biorbitals. These energy levels could give origin to the low energy side of the observed absorption band, usually assigned to $n \rightarrow \pi^*$ transitions [2]. The next calculated excited state at 4.1 eV shows instead a decrease in the electronic population of the (π, π) biorbitals, and might be responsible for the main portion of the observed band, commonly assigned to $\pi \rightarrow \pi^*$ transitions [2]. Other excited states are predicted between 5.3 and 6.5 eV, with their population shifted from (n, π) to (π, π) biorbitals.

It is not surprising that, when the approximations made are considered, the calculated transition energies are about 1 eV smaller than the experimental values [2]. An optimization of the procedure is being attempted by a systematic examination of our approximations applied to the series of the aromatic azines. The results will be reported later and compared with those available in the literature [3].

This work was carried out with the financial support of the Consiglio Nazionale delle Ricerche (C.N.R.), Roma.

References

1. Ciampi, A., Paoloni, L.: Theoret. chim. Acta (Berl.) **12**, 229 (1968).
2. Murrell, J. N.: The theory of the electronic spectra of organic molecules, p. 176. London: Methuen 1963.
3. Bessis, G., Espagnet, P., Bratoz, S.: Int. J. quant. Chemistry **3**, 205 (1969), and literature therein.

Professor L. Paoloni
Gruppo Chimica Teorica
Università
Via Archirafi, 20
I-90123 Palermo, Italy