An Improved Semi-Empirical SCF MO Method for Valence Electron Systems

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Although the semi-empirical SCF MO method or valence electron systems previously presented by the present authors has given almost completely satisfactory results, there remains some room for improvement.[1] For this purpose, the one-center exchange integrals which were neglected in our previous treatment are here taken into account, and a modified formula for the off-diagonal core integrals is adopted.

With reference to the values estimated by Hinze and Jaffé,[2] the one-center exchange integrals are evaluated by the formulas:

$$(\mathrm{sp}|\mathrm{sp}) = 0.045 Z_{\mathrm{A}} (\mathrm{ss}|\mathrm{pp})$$

$$(\mathrm{pp}'|\mathrm{pp}') = 0.011 Z_{\mathrm{A}} (\mathrm{pp}|\mathrm{p}'\mathrm{p}') \qquad (1)$$

where s and p denote the valence s and p atomic orbitals (AO) and where Z_{A} is the number of the valence electrons of the A atom.

Extending the Ohno approximation,[3] we represent the off-diagonal core integrals, H_{rs}, between the rth AO of the A atom and the sth AO of the B atom as follows:

$$H_{rs} = (S_{rs}/2)\{-(Z_{\mathrm{A}} + Z_{\mathrm{B}})C/R_{\mathrm{AB}} - (\mathrm{B}|rr) - (\mathrm{A}|ss) + (H_{rr} + H_{ss})\} \qquad (2)$$

where C is a constant and is put at 1.0 in this treatment; the other notations have already been given in Ref. 1.

With those improved approximations, we then made calculations on some familiar compounds. In Table 1, some calculated transition energies are collected, together with the observed values. The results imply that considerable improvements is achieved. As to the ionization potentials, the present results are closer to the observed values than the previous ones by *ca.* 1.0 eV. In addition, regarding butadienes, the trans-form is more stable than the cis-form by 0.30 eV, which is in accordance with the experiments.

TABLE 1. THE CALCULATED TRANSITION ENERGIES OF SOME COMPOUNDS

Compound	Transition	Calcd.		Obs.	
		Singlet	Triplet	Singlet	Triplet
C_2H_4	π-π^*	8.08	4.62	7.6[a]	4.6[a]
H_2CO	n-π^*	4.37	3.40	4.2[b]	3.0[b]
	π-π^*	8.06	4.09	8.0[b]	4.2[b]
NO_2^-	n-π^*	1.43	0.34	3.50[c]	—
	π-π^*	5.59	2.56	5.95[c]	—
trans-Butadiene	2-3[*1]	6.38	4.18	6.0[a]	(3.92)[d]
	1-3	7.37	5.51	7.2[a]	(4.61)
cis-Butadiene	2-3	6.03	4.11	(5.91)	(3.96)
	1-3	7.48	5.44	(8.29)	(4.62)
Pyridine	n-3	4.33	3.73	4.59[e]	4.09[e]

[*1] The number 1 and 2 refer to the lowest and highest occupied π orbitals, and 3 to the lowest vacant π orbital.
[a] See R. G. Parr, "Quantum Theory of Molecular Electronic Structure," Benjamin, N. Y. (1963).
[b] See J. M. M. Parks and R. G. Parr, *J. Chem. Phys.*, **32**, 1657 (1960).
[c] See K. L. McEwen, *ibid.*, **34**, 547 (1961).
[d] The number in parenthesis refers to the values calculated by Pariser and Parr (*J. Chem. Phys.*, **21**, 767 (1953)).
[e] L. Goodman, *J. Mol. Spectr.*, **6**, 109 (1961).

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1) T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 535 (1967); T. Yonezawa, H. Nakatsuji and H. Kato, *ibid.*, **39**, 2788 (1966).

2) J. Hinze and H. H. Jaffé, *J. Chem. Phys.*, **38**, 1834 (1963).

3) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).