

## A Semi-Empirical Unrestricted SCF MO Method for Valence Electron Systems

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The semi-empirical SCF MO method for valence electron systems previously proposed by the present authors was applied to various molecules of closed shell structure and successful results were obtained.<sup>1)</sup> Here, we will give the preliminary results obtained by extending the above method to some molecules of open-shell structure.

The unrestricted SCF equation for open shell molecule is<sup>2)</sup>

$$F^{\alpha}C_i^{\alpha} = \varepsilon_i^{\alpha}SC_i^{\alpha}; \quad F^{\beta}C_i^{\beta} = \varepsilon_i^{\beta}SC_i^{\beta}. \quad (1)$$

The matrix elements appearing in Eq. (1) are calculated by the method previously reported<sup>1)</sup> and the off-diagonal core Hamiltonian elements are calculated setting the Wolfsberg-Helmholtz parameter to be 1.1. The one-center exchange integrals are further taken into account.<sup>3)</sup>

The observed and calculated ionization potentials of allyl, vinyl, and nitrogen dioxide radicals are 8.16,<sup>4)</sup> 9.45<sup>4)</sup> and 12.3 eV,<sup>5)</sup> and 9.65, 10.99 and 13.01 eV, respectively.

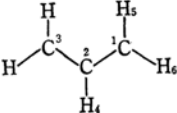
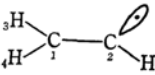
The SCF calculation for  $\pi$ -electron system<sup>6)</sup> gave  $\pi$ -spin densities ( $\rho$ ) of allyl radical of 0.609 and  $-0.185$  for the 1- and 2-carbons (in Table 1), respectively, and the ratio  $\rho_{11}/\rho_{22}$  was  $-3.29$ .<sup>7)</sup> In the present calculations, these values are;

$$\rho_{11} = 0.617, \quad \rho_{22} = -0.195, \quad \rho_{11}/\rho_{22} = -3.16.$$

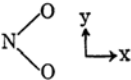
It is to be noticed that both calculations give negative spin density on the central carbon  $\pi$ -AO in agreement with experimental estimation.<sup>8)</sup>

Since the present treatment includes all valence electrons, it gives directly the spin densities on

TABLE 1. CALCULATED HYPERFINE COUPLING CONSTANTS AND SPIN DENSITIES

Radical	No.	$a_H$ , Calcd <sup>a)</sup>	$ a_H $ , Obsd <sup>b)</sup>
Allyl			
	4	5.64	4.06
	5	-13.56	$\left\{ \begin{array}{l} 13.93 \\ 14.83 \end{array} \right.$
	6	-14.02	
Vinyl			
	3	20.98	34.2
	4	40.74	68.5
	5	-11.18	15.7, 13.4

Radical	AO	$\rho$ , Calcd	$\rho$ , Obsd <sup>c)</sup>
	$s_N$	0.170	0.103
	$p_{xN}$	0.438	0.471
	$p_{yN}$	-0.008	—
	$p_{zN}$	0.036	0.054

a)  $a_H$  values are calculated by multiplying the calculated spin densities by 508G.

b) Reference 7.

c) M. C. R. Symons, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, Am. Chem. Soc., Washington, D. C. (1962), p 76.

various hydrogen atoms and valence AO's. The results are given in Table 1. Contrary to the results obtained by McLachlan<sup>9)</sup> with the extended Hückel method, the calculated  $a_H$  of the 5-hydrogen of vinyl radical is minus in sign. The assignments of the observed  $a_H$ 's of the terminal hydrogen atoms of allyl radical seem not to have been carried out, and the present work may assign the observed values of 13.93 and 14.83 G to the 5- and 6-hydrogens as seen in Table 1. However, assignments are not conclusive because the present calculation does not take into account the two center  $\sigma$ - $\pi$  type exchange integrals which are neglected by Mulliken approximation. The calculations which includes these integrals will be published in the near future.

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7) The value,  $\rho_{11}/\rho_{22}$ , estimated from observed hyperfine coupling constants ( $a_H$ 's) shown in Table 1, is  $-3.54$ ; R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

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