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### LNDO/S, a Semiempirical SCF-CI Method for the Calculation of Ionization Potentials and Electronic Transition Energies of Valence Electrons

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**Abstract:** A new semiempirical valence electron SCF-CI method for the calculation of ionization potentials and electronic transition energies is presented. The method is distinguished by explicit inclusion of electron correlation in a semiempirical frame on the base of large CI calculations. Simplifications in the SCF part of the method are achieved by use of the new LNDO (local neglect of differential overlap) approximation. The parameters for carbon and hydrogen atoms are derived. Vertical ionization potentials (VIPs) and electronic transition energies (ETEs) of a variety of hydrocarbons are calculated and compared to experimental data. The agreement obtained as measured by the average absolute errors (or standard deviations) is for 29 first VIPs 0.22/0.30 eV, for 84 VIPs below 15 eV 0.40/0.53 eV, for a total of 93 VIPs 0.47/0.64 eV, and for 54 ETEs 0.19/0.23 eV. These data indicate that the LNDO/S model works rather well for the lower VIPs and ETEs for a broad variety of C, H compounds.

#### I. Introduction

The prediction of electronic transition energies (ETEs) and vertical ionization potentials (VIPs) is an important field of quantum chemistry. For performing such work ab initio configuration interaction (CI) methods are available. Unfortunately, because of the high costs involved, such calculations are not expected to become routine for large molecules in the near future.

Therefore semiempirical valence electron procedures still present an important way out of this dilemma. Methods like CNDO/2, INDO/2,<sup>1</sup> or the various MINDO versions,<sup>2</sup> however, are not particularly appropriate for ETEs or VIPs. Rather successful with VIPs are the SPINDO<sup>3</sup> and MNDO<sup>4</sup> variants. However, the latter method has proved inadequate for ETE work.<sup>5</sup> The only method available so far to deal both with ETEs and VIPs is the CNDO/S procedure<sup>6</sup> and its modifications with respect to the parameters<sup>7-9</sup> or the model (INDO/S)<sup>10-13</sup> involved.

As usual the CNDO/S VIPs are based on Koopmans' theorem<sup>14</sup> and the ETEs on limited single excitation CI (SECI). However, several shortcomings remain. Triplet ETEs come out less accurate than singlet ETEs.<sup>12,15</sup> Singlet-triplet splittings of  $\sigma\pi^*$  and  $\pi\sigma^*$  ETEs are inaccessible. Although the first VIP is almost always predicted well, the higher VIPs may turn out less satisfactorily. Such shortcomings are often attributed to the usage of Koopmans' theorem. While such an argument is certainly valid for ab initio calculations, one should be careful with applying the same argument to semiempirical results. Thus it is our experience that good Koopmans' VIPs sometimes

worsen when CI is applied or that Koopmans' defects obtained in semiempirical and ab initio work may differ in sign (note, however, that large Koopmans' defects are always predicted reliably<sup>16,17</sup>). Large CI tends to stabilize CNDO/S excited states more than ground states leading to ETEs which are much too low. Even within the common SECI approximation the ETEs strongly depend on the number of configurations included. In particular larger SECI does not necessarily improve the results in contrast to the ab initio case. Finally, in the CNDO/S procedure the number of SECs is kept fixed for all molecules. Since the number of SECs increases with the square of the number of basis orbitals the latter approximation appears to be insufficient for larger molecules.

To overcome all these difficulties we have decided to develop a new semiempirical method for calculating ETEs and VIPs. As a main feature of the method the parameters involved are chosen with respect to large CI calculations. Thus electron correlation is explicitly taken account of and the method yields an approximation to the "true" eigenfunctions of the semiempirical model Hamiltonian involved. This is quite different from all other semiempirical procedures hitherto known. Designed and parameterized on a SCF or limited CI level only, the latter methods cannot be further improved (say by CI or larger CI) subsequently.

#### II. The Semiempirical Model

We start from the NDDO equations<sup>1</sup> (as obtained from the Roothaan-Hall equations<sup>19,20</sup> on applying the NDDO<sup>1</sup> ap-

proximation) written as

$$F c_i = \epsilon_i c_i \quad (1)$$

$$F_{\mu\nu}^{AA} = h_{\mu\nu}^{AA} + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \left[ (\mu\nu, \lambda\sigma) - \frac{1}{2} (\mu\lambda, \nu\sigma) \right] + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} (\mu\nu, \lambda\sigma) \text{ for } \mu, \nu \text{ both on atom A} \neq \text{B} \quad (2)$$

$$F_{\mu\nu}^{AB} = h_{\mu\nu}^{AB} - \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} (\mu\lambda, \nu\sigma) \text{ for } \mu \text{ on atom A and } \nu \text{ on atom B} \neq \text{A} \quad (3)$$

where  $F$  is the representation of the Fock operator  $F$  in the basis of atomic orbitals (AOs)  $\phi_{\mu}$  (with matrix elements  $F_{\mu\nu}$ ) and  $\epsilon_i$  and  $c_i$  the energies and vectors of coefficients of molecular orbitals (MOs).  $h_{\mu\nu}$  and  $P_{\lambda\sigma}$  denote matrix elements of the core Hamiltonian  $h$  and of the bond order matrix, respectively,<sup>1</sup> and  $(\mu\nu, \lambda\sigma)$  is a two-electron repulsion integral. The sums in eq 2 and 3 extend over all atomic orbitals on the respective centers A or B.

As AOs, we use a set of core-orthogonalized orbitals (COOs),  $\{\phi_{\mu}^{\text{COO}}\}$ , obtained by Schmidt orthogonalization of Slater-type orbitals (STOs) according to

$$\phi_{\mu}^{\text{COO,A}} = \sum_{\alpha} a_{\alpha\mu} \phi_{\alpha}^{\text{STO,A}} \text{ for } \phi_{\alpha}^{\text{STO}} \text{ on atom A} \quad (4)$$

where the  $a_{\alpha\mu}$  are the mixing coefficients and the sum extends over all STOs on atom A. As regards the atoms of the first period eq 4 is relevant only for 2s AOs. Henceforth in this paper, the  $\phi_{\mu}$  are understood to be the  $\phi_{\mu}^{\text{COO}}$ .

An important feature of the present semiempirical scheme is: All atomic two-center integrals (those in eq 1-3 and further ones needed in this paper) are calculated in local coordinate systems ( $x', y', z'$ ). Then they are transformed to the molecular system ( $x, y, z$ ) chosen. The local systems are defined as follows. Two arbitrarily chosen atoms A and B of the molecules are taken to define the  $z'$  axis of one of the local systems. A set of AOs on A,  $\{\phi_{\mu}^{\text{A}}\}$ , referred to the molecular system is then related to a corresponding set,  $\{\phi_{\mu}^{\text{A}}\}$ , in the local system by

$$\phi_{\mu}^{\text{A}} = \sum_{\alpha} b_{\alpha\mu} \phi_{\alpha}^{\text{A}} \quad (5)$$

with the expansion coefficients  $b_{\alpha\mu}$  and the sum extending over all AOs on A. Hence, once the local integrals (i.e., the primed ones in eq 6 and 7 are known, any corresponding one- ( $O_{\mu\nu}$ ) or two-electron integral  $[(\mu\nu, \lambda\sigma)]$  in the molecular system is then available from

$$O_{\mu\nu} = \sum_{\alpha} \sum_{\beta} b_{\alpha\mu} b_{\beta\nu} O'_{\alpha\beta} \quad (6)$$

or

$$(\mu\nu, \lambda\sigma) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} b_{\alpha\mu} b_{\beta\nu} b_{\gamma\lambda} b_{\delta\sigma} (\alpha\beta, \gamma\delta)' \quad (7)$$

where the sums are to be taken over all AOs on the respective atoms A and B.

This procedure offers the opportunity to apply semiempirical modifications to the aforementioned atomic integrals preserving rotational invariance provided that all degenerate AOs are treated in the same way. For an s, p basis set with the AOs s,  $p_x \equiv \pi$ ,  $p_y \equiv \bar{\pi}$ , and  $p_z \equiv \sigma$  this concerns the AOs  $\pi$  and  $\bar{\pi}$ . Under this condition any one-electron integral on the right-hand side of eq 6 can be multiplied with arbitrarily chosen factors or, correspondingly, any two-electron integrals of eq 7 can be neglected and rotational invariance is still preserved. The various sorts of integrals (primed ones in the local and unprimed ones in the molecular system) are obtained as follows.

**The One-Electron Integrals.** The one-center core integrals  $h_{\mu\nu}^{AA}$  are approximated<sup>21</sup> as

$$h_{\mu\nu}^{AA} = U_{\mu\nu} - \sum_{\text{B} \neq \text{A}} Z_{\text{B}} (s_{\text{B}} s_{\text{B}, \mu \text{A} \nu \text{A}}) \quad (8)$$

where  $U_{\mu\nu}$  represents the "atomic" part of the core energy and the sum the contributions from all other atoms.  $U_{\mu\nu}$  disappears for  $\mu \neq \nu$ . The remaining quantities  $U_{ss}$  and  $U_{pp}$  are treated as parameters.  $Z_{\text{B}}$  is the core charge on atom B. The two-center repulsion integrals  $(s_{\text{B}} s_{\text{B}, \mu \text{A} \nu \text{A}})$  will be discussed later in this section.

The two-center core integrals  $h_{\alpha\beta}^{\text{AB}}$  are calculated from

$$h_{\alpha\beta}^{\text{AB}} = \frac{1}{2} (\beta_{\text{A}} \kappa_{\alpha} + \beta_{\text{B}} \kappa_{\beta}) S'_{\alpha\beta} \quad (9)$$

where the  $\beta$ 's and  $\kappa$ 's are again adjustable parameters. Equation 9 corresponds to a generalization of the  $\kappa$ -parameter scheme of the CNDO/S method where all  $\kappa$ 's are set equal to one except for  $\kappa_{\pi} = \kappa_{\bar{\pi}}$ . In the present method we ascribe different values to  $\kappa_{\sigma}$  and  $\kappa_{\pi} = \kappa_{\bar{\pi}}$  (again treated as parameters) while  $\kappa_s$  is kept fixed (with  $\kappa_s = 1$ ). For the C, H interaction, however, a better fit to experiment was achieved when using the average  $\frac{1}{3}(\kappa_{\sigma} + 2\kappa_{\pi})$  for  $\kappa_{\sigma}$ .

The one-center overlap integrals  $S$  needed in the core orthogonalization process (cf. eq 4) are easily obtained from

$$S_{n_1 n_2} = A / \xi \quad (10)$$

with

$$A = m! / [(2n_1)! (2n_2)!]^{1/2} \quad (11)$$

$$\xi = [^{1/2}(\xi_1 + \xi_2)^{m+1}] / [\xi_1^{2n_1+1} + \xi_2^{2n_2+1}]^{1/2} \quad (12)$$

$$m = n_1 + n_2 \quad (13)$$

where  $n_1, n_2$  and  $\xi_1, \xi_2$  are the quantum number and exponents of the STOs involved.

The one-center s, p dipole integrals over STOs needed for calculating the dipole moments and oscillator strengths are accessible from

$$\langle n_1 s | r_i | n_2 p_i \rangle = A / (2\sqrt{3}\xi), \quad i = x, y, z \quad (14)$$

with

$$m = n_1 + n_2 + 1 \quad (15)$$

All inner shell exponents of eq 10-15 are taken from atomic calculations.<sup>22</sup> The valence shell exponents are treated as parameters.

**Two-Electron Integrals.** One-center two-electron integrals are available as sums over Slater-Condon parameters (SCPs).<sup>23</sup> For an s, p valence basis set and the INDO method the reader is referred to ref 1. We treat the SCs  $F_{ss}^0$  and  $F_{pp}^0$  as parameters. In order to reduce the number of independent parameters the remaining SCs  $F_{sp}^0, F_{pp}^2$ , and  $G_{sp}^1$  are calculated from the theoretical STO relations 17-20 using the exponents available from eq 16.

$$F_{\mu\mu}^0 = 93\xi_{\mu}/256, \quad \mu = s, p \quad (16)$$

$$F_{sp}^0 = (\xi_s/256)\{128 - (a^3/b^7)(5 + 10c + 12c^2 + 8c^3)\} \quad (17)$$

$$F_{pp}^2 = 45\xi_p/256 \quad (18)$$

$$G_{sp}^1 = 185a^4\xi_p/(768b^9) \quad (19)$$

with  $a = \xi_p/\xi_s, b = (1+a)/2$ , and  $c = b/a$  (20)

As will be shown later the SCs obtained in this way are in reasonable agreement with those determined from fitting them to atomic spectral data.<sup>1,24</sup> The procedure chosen involves two

minor inconsistencies with respect to preceding assumptions. At first, for simplicity, we use STO instead of COO relations and, secondly, exponents in eq 16–20 that differ from those used in eq 9–15. The first approximation leads, for first-row elements, to small deviations only, and the second inconsistency is usual with other semiempirical procedures such as MINDO or MNDO.

For calculating the two-center two-electron integrals we introduce an approximation intermediate between CNDO and INDO on the one hand and NDDO on the other. The basic idea is contained in the application of the ZDO approximation in the local instead of the molecular coordinate system. We refer to this approximation as local neglect of differential overlap (LNDO). In this approximation all integrals except the Coulomb ones are set equal to zero. Moreover, different values for different types of Coulomb integrals may be used. This possibility enables us to preserve a strong feature of the PPP  $\pi$ -electron methods,<sup>25</sup> namely, to choose particular  $\pi$ -electron Coulomb integrals. It was these integrals (among other particular  $\pi$ -electron parameters) that ensured a good fit of the PPP calculated to experimental results. Rotational invariance requires that all integrals involving the  $\pi$  and  $\bar{\pi}$  AOs, i.e.,  $(\pi_A\pi_A, \pi_B\pi_B)'$ ,  $(\pi_A\pi_A, \bar{\pi}_B\bar{\pi}_B)'$ ,  $(\bar{\pi}_A\bar{\pi}_A, \pi_B\pi_B)'$ , and  $(\bar{\pi}_A\bar{\pi}_A, \bar{\pi}_B\bar{\pi}_B)'$ , must have ascribed the same value. We use the average and, for simplicity, refer to it as  $(\pi_A\pi_A, \pi_B\pi_B)'$ . It should be noted, however, that the deviation of the average from any of the four individual values is very small, even for STOs. The transformation of the remaining six independent integrals,  $(s_A s_A, s_B s_B)'$ ,  $(s_A s_A, \sigma_B \sigma_B)'$ ,  $(s_A s_A, \pi_B \pi_B)'$ ,  $(\sigma_A \sigma_A, \sigma_B \sigma_B)'$ ,  $(\sigma_A \sigma_A, \pi_B \pi_B)'$ , and  $(\pi_A \pi_A, \pi_B \pi_B)'$ , according to eq 7 generates up to 49 integrals of the more general (i.e., not only Coulomb integrals) type  $(\mu\nu, \lambda\sigma)$ . The number is reduced to 25 or 16 if the pair of atoms A and B is located on a plane or an axis of the molecular coordinate system. Thus the number of integrals in LNDO is smaller by a factor of 2–3 than in NDDO. In spite of this reduction being unimportant for the SCF calculations it is of crucial importance in the time-consuming transformation of the atomic to molecular integrals.

The six independent integrals of local Coulomb type mentioned above are calculated using a combined approach of the uniformly charged sphere model (UCSM)<sup>18,25</sup> extended from  $\pi$  to  $\sigma, \pi$  systems and models similar to those of Mataga–Nishimoto<sup>26</sup> and Klopman–Ohno.<sup>27</sup> For sufficiently large distances  $R$  between atoms A and B the integrals are obtainable from uniformly charged spheres with radii  $r_{\sigma_A}, r_{\pi_A}, \dots$  as illustrated in Figure 1. In order to avoid the difficulties with smaller interatomic distances we use the UCSM formulas but write for the distances  $r$  between the centers of the respective spheres functions  $\rho_{\alpha\beta}(r)$  of these distances. Thus we have

$$(s_A s_A, s_B s_B)' = 1/\rho_{s_A s_B}(r) \quad (21)$$

$$(s_A s_A, \sigma_B \sigma_B)' = 1/2\{1/\rho_{s_A \sigma_B}(|R + r_{\sigma_B}|) + 1/\rho_{s_A \sigma_B}(|R - r_{\sigma_B}|)\} \quad (22)$$

$$(s_A s_A, \pi_B \pi_B)' = 1/\rho_{s_A \pi_B}([R^2 + r_{\pi_B}^2]^{1/2}) \quad (23)$$

$$(\sigma_A \sigma_A, \sigma_B \sigma_B)' = 1/4\{1/\rho_{\sigma_A \sigma_B}(|R + r_{\sigma_A} + r_{\sigma_B}|) + 1/\rho_{\sigma_A \sigma_B}(|R + r_{\sigma_A} - r_{\sigma_B}|) + 1/\rho_{\sigma_A \sigma_B}(|R - r_{\sigma_A} + r_{\sigma_B}|) + 1/\rho_{\sigma_A \sigma_B}(|R - r_{\sigma_A} - r_{\sigma_B}|)\} \quad (24)$$

$$(\sigma_A \sigma_A, \pi_B \pi_B)' = 1/2\{1/\rho_{\sigma_A \pi_B}([(R - r_{\sigma_A})^2 + r_{\pi_B}^2]^{1/2}) + 1/\rho_{\sigma_A \pi_B}([(R + r_{\sigma_A})^2 + r_{\pi_B}^2]^{1/2})\} \quad (25)$$

$$(\pi_A \pi_A, \pi_B \pi_B)' = 1/2\{1/\rho_{\pi_A \pi_B}([R^2 + (r_{\pi_A} - r_{\pi_B})^2]^{1/2}) + 1/\rho_{\pi_A \pi_B}([R^2 + (r_{\pi_A} + r_{\pi_B})^2]^{1/2})\} \quad (26)$$

with

$$\rho_{\alpha\beta}(r) = r + [1/2(I_\alpha \exp(K_\alpha r) + I_\beta \exp(K_\beta r))]^{-1} \quad (27)$$

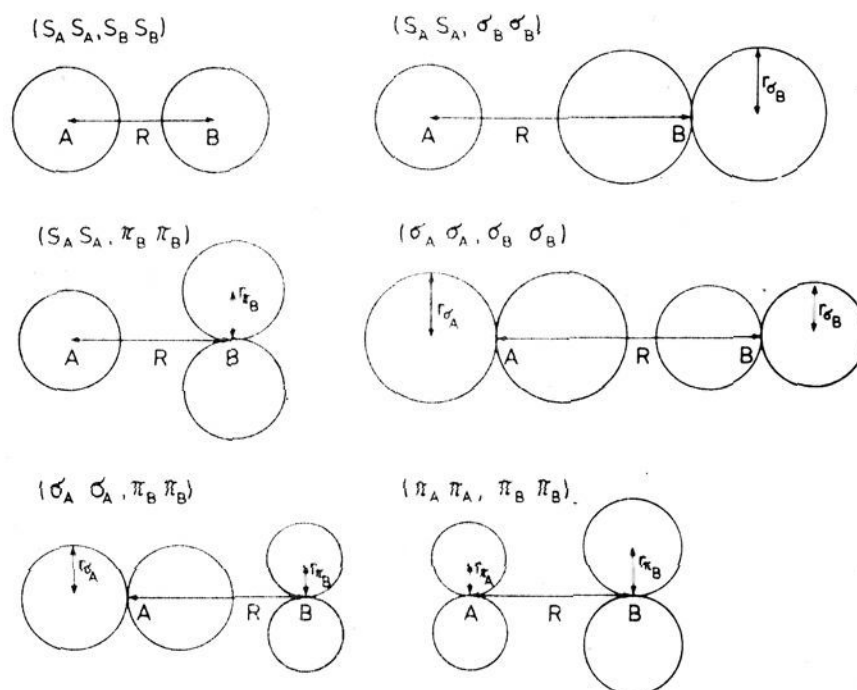


Figure 1. Types of two-center two-electron repulsion integrals used and represented here in the UCSM.

Equation 27 in the form of  $1/\rho_{\alpha\beta}(r)$  is known as the Klondike formula.<sup>28</sup> The  $K$ 's and  $I$ 's are parameters. Equation 27 yields  $\rho_{\alpha\beta}(r) \rightarrow r$  for  $r \rightarrow \infty$  (note that  $K \geq 0$ ). For  $K_\alpha = K_\beta = 0$  the Klondike formula becomes identical with the Mataga–Nishimoto expression.<sup>26,28</sup> For large values of the  $K$ 's eq 27 behaves like the Klopman–Ohno<sup>27</sup> or theoretical expressions. Thus the Klondike formula appears to be the most flexible semiempirical integral approximation. In our present approach, we use one  $K_s$  value for all s AOs of an element and one  $K_p$  value for its p AOs. We treat the  $K_s$ 's and  $K_p$ 's and additionally the  $r_\sigma$ 's and  $r_\pi$ 's as parameters. The  $I$  parameters then must be chosen in such a way that eq 21–26 yield the proper one-center integrals  $(ss,ss)$ ,  $(ss,pp)$ , and  $(pp,pp)$  for  $R \rightarrow 0$  in an homonuclear case. To this aim we use

$$I_s(s,s) = (ss,ss) \quad (28)$$

$$I_\alpha(s,\alpha) = 2/\{[(ss,pp)^{-1} - r_\alpha] \{ \exp(K_s r_\alpha) ((ss,ss)/(pp,pp)) + \exp(K_p r_\alpha) \} \} \quad (29)$$

$$I_s(s,\alpha) = I_\alpha(s,\alpha) ((ss,ss)/(pp,pp)) \quad (30)$$

$$I_\alpha(\alpha,\alpha) = 2(pp,pp) - \{2r_\alpha + [I_\alpha(\alpha,\alpha) \exp(2K_p r_\alpha)]^{-1}\}^{-1} \quad (31)$$

$$I_\alpha(\sigma,\pi) = \{ \exp(K_p r_{\sigma\pi}) [(pp,pp)^{-1} - r_{\sigma\pi}] \}^{-1} \quad (32)$$

with

$$r_{\sigma\pi} = (r_\sigma^2 + r_\pi^2)^{1/2} \quad (33)$$

In eq 29 and 30  $\alpha$  stands for a p AO (i.e.,  $\sigma, \pi$ , or  $\bar{\pi}$ ) and the  $I$ 's in eq 28–33 are additionally specified by the type of interacting AOs (added in parentheses) involved. Equation 29 has to be solved iteratively with  $I_\alpha(\alpha,\alpha) = (pp,pp)$  as the starting value. For hydrogen, eq 30 cannot be applied. Instead we make use of

$$I_s(s,\alpha) = \exp(-K_s r_\alpha) \{ 2/(A^{-1} - r_\alpha) - I_\alpha(s,\alpha) \exp(K_p r_\alpha) \} \quad (34)$$

with

$$A = 1/2\{(ss,ss) + (pp,pp)\} \quad (35)$$

and  $I_\alpha(s,\alpha)$  as given by eq 29.

### III. Outline of the CI Method Used

In this paper only a brief outline of the CI method applied is given. For further details and VIP ab initio results the reader is referred elsewhere.<sup>29</sup>

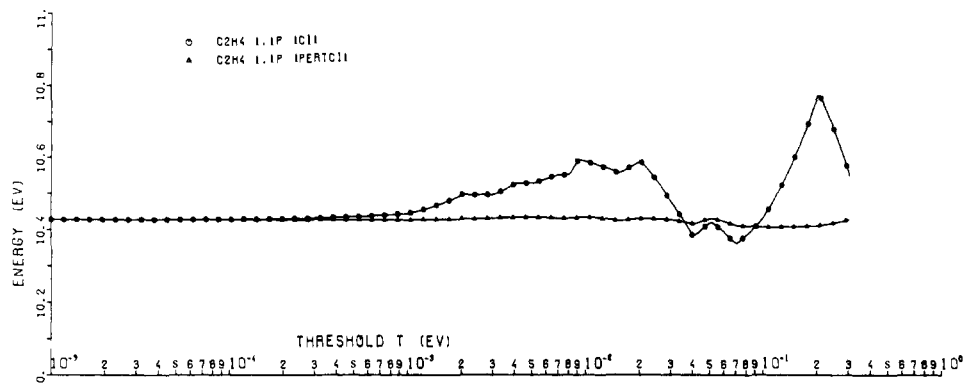


Figure 2. CI and PERTCI first VIP of ethylene vs. thresholds  $T$ .

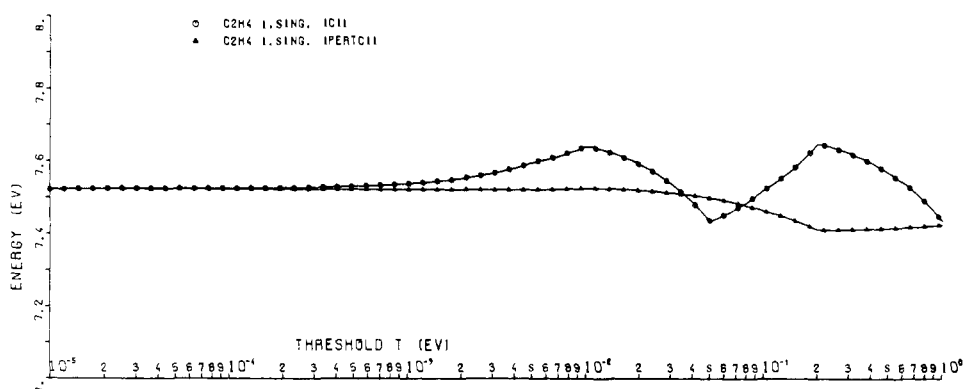


Figure 3. CI and PERTCI first singlet ETE of ethylene vs. thresholds  $T$ .

According to this method the space spanned by all configurations to be generated from a given set of MOs is partitioned in four subspaces: (1) the space of main configurations (MCs),  $\{|M\rangle\}$ ,<sup>30</sup> (2) the space of selected configurations (SCs),  $\{|S\rangle\}$ ; (3) the space of remaining configurations (RCs),  $\{|R\rangle\}$ ; and (4) the space of neglected configurations (NCs),  $\{|N\rangle\}$ . The MCs comprise the most important configurations. The diagonalization of the corresponding matrix yields a set of eigenvectors  $\{|M_v\rangle\}$  referred to as selection vectors (SVs). All configurations differing from the MCs by higher than double excitations are neglected (i.e., the NCs). From all other configurations  $\{|C\rangle\}$  the SCs are selected on two criteria: (1) the threshold criterion

$$|\langle M_v | H | C \rangle|^2 / |E_{M_v} - E_C| \geq T \quad (36)$$

(2) the energy gap criterion

$$0 < (E_{M_v} - E_C) < G \quad (37)$$

where the  $E$ 's are the configurational energies,  $T$  and  $G$  the threshold and gap parameters. Criterion 1 ensures the selection of the most efficient configurations and criterion 2 avoids difficulties with the subsequent perturbation procedure. Degenerate configurations are selected if at least one of them meets eq 36 or 37. Equations 36 and 37 may be applied to one or more SVs. The type of selection applied is characterized in shorthand as  $mMsS$ , where  $m$  and  $s$  are the respective numbers of MCs and SVs chosen in the selection procedure. The RCs are supposed to influence the state energies only owing to their huge number so that their effects may be estimated by Brillouin-Wigner (BW) perturbation theory.

From the sets of MCs and SCs a CI matrix is built up. Its diagonalization yields the zeroth-order approximation  $\{|\Phi^{(0)}\rangle\}$  and  $E_{\Phi^{(0)}}$  to the true state  $|\Phi\rangle$  with energy  $E_{\Phi}$  that is desired. The unperturbed Hamiltonian  $H_0$  is defined to include all diagonal elements, all interactions between the SCs, and all in-

teractions between degenerate RCs. Hence the eigenfunctions of  $H_0$  comprise the zeroth-order vectors  $\{|\Phi^{(0)}\rangle\}$ , all nondegenerate RCs, and the proper linear combinations of the degenerate RCs. The eigenfunction of  $H_0$  built up from the RCs are denoted as  $\{|R^{(0)}\rangle\}$ . The perturbation operator  $H'$  couples all SCs with all RCs and the RCs with themselves. Thus, by second-order BW perturbation theory, we have

$$E_{\Phi}^{(2)} = E_{\Phi}^{(0)} + \sum_{R^{(0)}} |\langle \Phi^{(0)} | H' | R^{(0)} \rangle|^2 / (E_{\Phi}^{(2)} - E_R^{(0)}) \quad (38)$$

Equation 38 must be solved iteratively. Only a few interactions are sufficient to calculate  $E_{\Phi}^{(2)}$  to an accuracy of  $10^{-8}$  au.

The ETEs and VIPs are obtained as the difference in energy between the various excited and ion states and the ground state with all states calculated by the perturbational CI method described above using the ground state SCF MOs. All single and double excitations with respect to the MCs are considered. Spin and symmetry adapted configurations are used throughout. The gap parameter  $G$  was set equal to 0.5 au (i.e., 13.605 eV) and kept fixed in all calculations. The threshold parameter  $T$  was varied in the range of 0.001–0.008 eV. Under these conditions the convergence of the CI results was even better than in the ab initio case.<sup>29</sup> This is a consequence of the reduced values of the repulsion integrals in semiempirical methods. As Figures 2 and 3 show the deviations of the perturbational CI results (PERTCI) from the full CI results are less than 0.005 eV for  $T < 0.01$  eV for ethylene.<sup>31</sup>

#### IV. Optimization of Parameters

The C and H parameters were optimized on the ETEs and VIPs of hydrogen, methane, ethane, ethylene, acetylene, butadiene, cyclopropane, cyclopropene, cyclopentadiene, and benzene. Vapor data of vertical transitions are used throughout. The optimization was performed by a modified least-squares procedure.<sup>32</sup> The modifications include (1) a damping

**Table I.** Optimized Parameters in LNDO/S

parameter	optimized value
For C Atoms	
$\beta_C$	-19.967 08 eV
$\kappa_\sigma$	0.942 98
$\kappa_\pi$	0.771 00
$U_{ss}$	-48.587 92 eV
$U_{pp}$	-38.348 37 eV
$F_{ss}^0$	10.825 17 eV
$F_{pp}^0$	10.176 00 eV
$\xi_s$	1.8568
$\xi_p$	1.8568
$K_s$	0.407 63
$K_p$	0.338 85
$r_\sigma$	0.563 007 6 Å
$r_\pi$	0.338 410 0 Å
For H Atoms	
$\beta_H$	-8.005 97 eV
$U_{ss}$	-13.654 00 eV <sup>a</sup>
$F_{ss}^0$	13.102 00 eV <sup>a</sup>
$\xi_s$	1.3648
$K_s$	0 <sup>b</sup>

<sup>a</sup> Optimization stopped at cycle 17. <sup>b</sup> Tended to negative values in all test calculations and was excluded from the optimization process in the final cycles.

option in order to prevent overdue parameter changes and (2) introduction of secondary conditions in order to maintain the parameters in physically reasonable ranges. On the whole 20 optimization cycles were performed on varying numbers of parameters. The final number of parameters was 18. They are listed in Table I. Table II presents the various SCPs. Some experiences with the optimization process appears to be worth noting. So the restriction of  $\kappa_\sigma = \kappa_\pi$  was tested and rejected. The distinction between  $r_\sigma$  and  $r_\pi$  was found to be significant, maybe to compensate for the neglect of the  $(\alpha\beta, \gamma\delta)$  integrals in the local system. The orbital exponents  $\xi_s^c$ ,  $\xi_p^c$ , and  $\xi_s^H$  proved to be crucial to obtain good ETEs and, at the same time, good VIPs.

The values of parameters of the present LNDO/S (i.e., local neglect of differential overlap/for spectroscopy) method are similar to those of other semiempirical procedures. However, LNDO/S uses rather high two-center core integrals (e.g., for  $R = 1.397$  Å,  $-2.67$  eV; MNDO,  $-1.53$  eV) which are necessary to produce ETEs of correct magnitude. To predict good (and not too high) VIPs the one-center core integrals had to be increased. The LNDO/S repulsion integrals emerge slightly larger than the Klopman-Ohno and much larger than the Mataga-Nishimoto ones (e.g., for  $(ss,ss)$  at  $R = 1.397$  Å,  $7.78$  eV; Klopman-Ohno,  $7.46$  eV; Mataga-Nishimoto,  $5.28$  eV). This tendency to larger repulsion integrals stems from the explicit incorporation of electron correlation into LNDO/S.

An extension of LNDO/S to other elements appears to be both desirable and manageable. In that case the number of independent parameters could be drastically reduced by using  $\xi_s = \xi_p$ , by scaling  $r_\sigma$ ,  $r_\pi$ , and the Klondike parameters on the orbital exponents and SCPs, respectively, and finally by utilizing SCPs from spectral data. Then only six parameters per element,  $\beta$ ,  $U_{ss}$ ,  $U_{pp}$ ,  $\xi$ ,  $\kappa_\pi$ , and  $\kappa_\sigma$ , remain to be determined.

## V. Results and Discussion

The LNDO/S VIPs and ETEs of 29 hydrocarbons are listed in Table III along with the experimental data. In the first column the name of the molecule, its point group, the designation of states (group theoretical and for ETEs whenever possible also the Mulliken<sup>40</sup> or Platt<sup>97</sup> notations) and the type of MO(s) involved in the MC(s) of the states are specified. The second column contains the Koopmans' theorem (KT) VIPs

**Table II.** Optimized and Derived<sup>a</sup> Slater-Condon Parameters and Reference Values for C Atoms (eV)

parameter	LNDO/S <sup>a</sup>	Oleari <sup>b</sup>	Pople <sup>c</sup>	Hinze <sup>f</sup>
$F_{ss}^0$	10.825 17	12.23	10.778 <sup>d,e</sup>	12.10 <sup>d</sup>
$F_{sp}^0$	10.485 49 <sup>a</sup>	11.47		
$F_{pp}^0$	10.176 00	10.253 33	10.196 <sup>d,e</sup>	10.93 <sup>d</sup>
$G_{sp}^1$	6.929 55	7.29	7.284 33	6.897 63
$F_{pp}^2$	4.923 87	5.166 66	4.726 92	4.509 77

<sup>a</sup> Calculated from  $F_{ss}^0$ ,  $F_{pp}^0$  values using eq 16-20. <sup>b</sup> Reference 24a. <sup>c</sup>  $G_{sp}^1$ ,  $F_{pp}^2$  from ref 1 (INDO/2). <sup>d</sup>  $F_{\mu\mu}^0$  values ( $\mu = s, p$ ) obtained from the relation  $I_\mu - A_\mu$  with data given in ref 1. <sup>e</sup> In INDO/2  $F_{ss}^0 = F_{pp}^0 = 16.062$  93 eV obtained for STOs with  $\xi = 1.625$  is used. <sup>f</sup> Reference 24b.

and the virtual orbital (VO) ETEs. These are often in reasonable agreement with the PERTCI and experimental results of the third and fourth columns, although the stabilization of the individual states involved amounts to several electron volts. The PERTCI column further contains the  $T$  value (on the same line as the name of the molecule). The same value was applied to all states listed. The observed VIPs and ETEs refer to vertical transition and, whenever possible, vapor phase data were taken. In the last column of references, the first reference shown (on the same line as the name of the molecule) refers to the geometrical data used (where available microwave and electron diffraction vapor phase data). In some cases where the location of vertical ETEs is uncertain (e.g., for acetylene) or where no valence ETEs have been observed (e.g., for methane) only VIPs are given.

All CI calculations are based on the 12 highest occupied MOs and the 12 lowest VOs. For most states (particularly for all ion states) consideration of one MC was sufficient. For some singlet or triplet states, however, up to four MCs had to be taken. Thus the number of SCs was in the range of 30-150 while the total number of configurations reached up to several thousands.

For singlet ETEs approximate oscillator strengths  $f$  have been calculated. The calculations make use of the usual dipole approximation,<sup>98</sup> the excited state vectors  $|\Phi^{(0)}\rangle$ , and the ground-state SCF determinant. It is to be expected that the errors in  $f$  made in this way are unimportant as compared to the uncertainties of the experimental counterparts. Nonetheless, the present calculations are still an improvement over those performed in the SECI approximation.

Considering the data of Table III and limiting ourselves to those transitions that have been unambiguously assigned this table comprises 29 first VIPs, 84 VIPs below 15 eV (experimental), a total of 93 VIPs, and 58 ETEs. The agreement between calculations and experiment (as measured by the average absolute errors or standard deviations) obtained for each of these groups is

29 first VIPs	0.22/0.30 eV
84 VIPs below 15 eV	0.40/0.53 eV
93 VIPs	0.47/0.64 eV
54 ETEs	0.19/0.23 eV

These data indicate that the LNDO/S model works rather well for the lower VIPs and ETEs for a broad variety of C, H compounds. Higher VIPs are less accurately predicted. However, in no case is a wrong sequence of states (as evaluated from the experimental assignments) predicted. As in the ab initio case the KT VIPs are generally much too large. They must be corrected by CI. Nonetheless, the sequence of states remains almost always unaffected by CI. Exceptions are encountered with higher VIPs as, e.g., with azulene where the right sequence of ionizations ( $\pi, \pi, \pi, \pi, \sigma$ ) is only obtained after CI. Moreover, CI leads to more realistic gaps between the various ion states. In some cases (propene, norbornadiene, and

Table III. LND0/S and Observed VIPs and ETEs (Intensities<sup>a</sup>)<sup>kk</sup>

molecule, point group, designation of ion or excited states	KT/VO	PERTCI	obsd <sup>b</sup>	ref
hydrogen, $D_{\infty h}$				33
$2\Sigma_g^+$ ( $\sigma$ )	15.91		15.88*	34
methane, $T_d$		$T = 0.002$		35
$2T_2$ ( $\sigma$ )	14.98	14.69	14.4*	36
$2A_1$ ( $\sigma$ )	28.07	27.24	22.91	37
methylene ( $1A_1$ ), $C_{2v}$		full C1		38
$2A_1$ ( $\sigma$ )	10.86	10.82	10.40 (10.1)	35
ethane, $D_{3d}$		$T = 0.005$		33
$2E_g$ ( $\sigma$ )	13.25	12.79	12.4*	39
$2A_{1g}$ ( $\sigma$ )	14.41	13.96	13.5	
$2E_u$ ( $\sigma$ )	16.86	16.37	15.0	
ethylene, $D_{2h}$		$T = 0.003$		33
$2B_{1u}$ ( $\pi$ )	10.55	10.44	10.51*	34
$2B_{1g}$ ( $\sigma$ )	12.99	12.73	12.80*	
$2A_g$ ( $\sigma$ )	15.47	15.20	14.66*	
$2B_{2u}$ ( $\sigma$ )	17.88	17.32	15.87	
$1B_{2g}$ ( $\pi\sigma^*$ )	7.68	7.73 (0)		
$1B_{1u}$ , V, ( $\pi\pi^*$ )	7.73	7.82 (0.463)	7.65 (0.34)*	40
$1B_{1g}$ ( $\sigma\pi^*$ ) <sup>aa</sup>	8.84	8.85 (0)	9.03	41
$3B_{1u}$ , T, ( $\pi\pi^*$ )	4.35	4.59 (0)	4.4*	42
acetylene, $D_{\infty h}$		$T = 0.002$		33
$2\Pi_u$ ( $\pi$ )	11.39	11.40	11.40*	34
$2\Sigma_g^+$ ( $\sigma$ )	16.78	16.80	16.72*	
$2\Sigma_u^+$ ( $\sigma$ )	21.23	20.34	18.75	
propene (cis gauche), $C_s$		$T = 0.005$		43
$2A''$ ( $\pi$ )	10.06	9.76	9.9	44
$2A'$ ( $\sigma$ )	12.66	12.53	12.3	
$2A'$ ( $\sigma$ )	13.92	13.49	13.2	
$2A''$ ( $\pi$ )	15.80	15.28		
$2A'$ ( $\sigma$ )	16.01	15.53	14.5	
$1A''$ ( $\pi\sigma^*$ )	7.35	7.30 (0.002)		
$1A'$ , V, ( $\pi\pi^*$ )	7.43	7.33 (0.523)	7.19 (0.32)	45
$1A''$ ( $\pi\sigma(\text{CH}_3)^*$ ) <sup>n.bb</sup>	8.69	8.41 (0.032)	8.55 (strong)	46
$3A'$ , T, ( $\pi\pi^*$ )	4.44	4.50 (0)		
cis-2-butene, $C_{2v}$		$T = 0.007$		43, 47 <sup>d</sup>
$2B_1$ ( $\pi$ )	9.73	9.34	9.32	48
$2B_2$ ( $\sigma$ )	12.84	12.35	11.52	
$2A_1$ ( $\sigma$ )	13.28	13.28	12.52	
$1A_2$ ( $\pi\sigma^*$ )	6.97	6.95		
$1B_2$ , V, ( $\pi\pi^*$ )	7.13	7.00 (0.575)	7.13 (0.59)	45
$3B_2$ , T, ( $\pi\pi^*$ )	4.41	4.40 (0)	4.2	42
trans-2-butene, $C_{2h}$		$T = 0.007$		43, 47 <sup>d</sup>
$2A_u$ ( $\pi$ )	9.68	9.32	9.28	49
$2A_g$ ( $\sigma$ )	12.93	12.44	11.9	
$2A_g$ ( $\sigma$ )	13.69	13.58	12.7	
$1B_g$ ( $\pi\sigma^*$ )	6.93	6.89 (0)		
$1B_u$ , V, ( $\pi\pi^*$ )	7.13	6.99 (0.579)	7.08 (0.32)	45
$3B_u$ , T, ( $\pi\pi^*$ )	4.42	4.40 (0)	4.42	42
isobutene, $C_{2v}$		$T = 0.008$	01 50	
$2B_1$ ( $\pi$ )	9.83	9.43	9.44	48
$2B_2$ ( $\sigma$ )	13.04	12.57	11.59	
$2A_1$ ( $\sigma$ )	13.72	13.25	13.21	
$1A_1$ , V, ( $\pi\pi^*$ )	7.27	7.07 (0.550)	6.74 (0.39)	45
$1B_1$ ( $\pi\sigma^*$ )	7.15	7.12 (0.007)		
$3B_1$ , T, ( $\pi\pi^*$ )	4.51	4.52 (0)		
tetramethylethylene, $D_{2h}$		$T = 0.008$		50 <sup>d</sup>
$2B_{3u}$ ( $\pi$ )	9.41	8.96	8.41	48
$2B_{3g}$ ( $\sigma$ )	12.93	12.45	10.83	
$2A_g$ ( $\sigma$ )	13.57	13.12	12.75	
$1B_{2g}$ ( $\pi\sigma^*$ )	6.54	6.48 (0)		
$1B_{1u}$ , V, ( $\pi\pi^*$ )	6.68	6.50 (0.720)	6.63 (0.45)	45
$3B_{1u}$ , T, ( $\pi\pi^*$ )	4.27	4.32 (0)		
trans-butadiene, $C_{2h}$		$T = 0.007$		33
$2B_g$ ( $\pi$ )	9.21	9.00	9.03*	51
$2A_u$ ( $\pi$ )	12.26	11.81	11.46*	
$2A_g$ ( $\sigma$ )	12.40	12.00	12.20*	
$1B_u$ , V, ( $\pi\pi^*$ )	6.35	6.17 (0.878)	5.93 (0.53)*	52, 53
$1A_u$ ( $\pi\sigma^*$ )	6.68	6.49 (0.0007)		53
$1B_g$ ( $\pi\sigma^*$ )	7.57	7.21 (0)		
$1A_g$ , V, ( $\pi\pi^*$ )	7.98	7.23 (0) <sup>e</sup>	7.28	

Table III (continued)

molecule, point group, designation of ion or excited states	KT/VO	PERTCI	obsd <sup>b</sup>	ref
<sup>3</sup> B <sub>u</sub> , T, ( $\pi\pi^*$ )	4.06	3.67 (0)	3.22	
<sup>3</sup> A <sub>g</sub> , T, ( $\pi\pi^*$ )	6.35	5.16 (0) <sup>e</sup>	4.91	
cyclopropane, D <sub>3h</sub>		T = 0.005		54
<sup>2</sup> E', ( $\sigma$ )	11.50	11.10	10.53*	55
<sup>2</sup> E'', ( $\pi$ )	13.86	13.42	13.24*	
<sup>2</sup> A <sub>2</sub> , ( $\sigma$ )	16.87	16.32	15.7	
<sup>2</sup> A <sub>1</sub> , ( $\sigma$ )	19.25	18.67	16.5	
<sup>1</sup> A <sub>2</sub> , ( $\sigma\sigma^*$ ) <sup>cc</sup>	9.25	9.14 (0) <sup>e</sup>	8.67*	55
<sup>1</sup> A <sub>1</sub> , ( $\sigma\sigma^*$ ) <sup>cc</sup>		9.23 ( $2 \times 10^{-5}$ ) <sup>e</sup>		
<sup>1</sup> E', ( $\sigma\sigma^*$ ) <sup>cc</sup>	9.38	9.38 ( $9 \times 10^{-4}$ ) <sup>e</sup>		
<sup>1</sup> E', ( $\sigma\sigma^*$ ) <sup>n,cc</sup>	10.27	10.16 (0.092)	10.17	
cyclopropene, C <sub>2v</sub>		T = 0.005		56
<sup>2</sup> B <sub>1</sub> , ( $\pi$ )	9.69	9.49	9.86*	57
<sup>2</sup> B <sub>2</sub> , ( $\sigma$ )	11.20	10.89	10.89*	
<sup>2</sup> A <sub>1</sub> , ( $\sigma$ )	13.13	12.82	12.7	
<sup>2</sup> B <sub>1</sub> , ( $\pi$ )	16.51	16.05	15.09	
<sup>1</sup> A <sub>2</sub> , ( $\pi\sigma^*$ ) <sup>n,dd</sup>	6.45	6.38 (0)	6.45 ( $\epsilon \approx 1000$ ) <sup>c</sup>	58
<sup>1</sup> B <sub>2</sub> , V, ( $\pi\pi^*$ )	7.15	6.99 (0.232)	7.19 ( $\epsilon \approx 3000$ ) <sup>*</sup>	
<sup>1</sup> B <sub>1</sub> , ( $\pi\sigma^*$ )	7.16	7.06 ( $1 \times 10^{-6}$ )		
<sup>1</sup> B <sub>1</sub> , ( $\sigma\pi^*$ )	7.18	7.26 (0.005)		
<sup>1</sup> A <sub>1</sub> , ( $\sigma\sigma^*$ ) <sup>ee</sup>	8.82	8.52 (0.119)	8.06 (strong)	
<sup>3</sup> B <sub>2</sub> , T, ( $\pi\pi^*$ )	4.54	4.57 (0)	4.16	59
cyclobutene, C <sub>2v</sub>		T = 0.005		60
<sup>2</sup> B <sub>1</sub> , ( $\pi$ )	9.83	9.49	9.43	61
<sup>2</sup> B <sub>2</sub> , ( $\sigma$ )	12.24	11.83	11.3	
<sup>1</sup> A <sub>2</sub> , ( $\pi\sigma^*$ )	6.51	6.50 (0)		
<sup>1</sup> B <sub>2</sub> , V, ( $\pi\pi^*$ )	7.02	7.12 (0.360)	7.03 (0.28)	45
<sup>3</sup> B <sub>2</sub> , T, ( $\pi\pi^*$ )	4.16	4.27 (0)	4.23	59
cyclopentene, C <sub>s</sub>		T = 0.007		62
<sup>2</sup> A', ( $\pi$ )	9.92	9.50	9.18	61
<sup>2</sup> A'', ( $\sigma$ )	13.44	12.78	11.7	
<sup>1</sup> A'', ( $\pi\sigma^*$ )	6.73	6.46 (0.002) <sup>e</sup>		
<sup>1</sup> A'', V, ( $\pi\pi^*$ )	6.90	6.94 (0.483) <sup>e</sup>	7.06 (0.32)	45
<sup>3</sup> A'', T, ( $\pi\pi^*$ )	4.81	4.31 (0) <sup>e</sup>	4.15	59
cyclohexene, C <sub>2</sub>		T = 0.007		63
<sup>2</sup> B, ( $\pi$ )	10.11	9.70	9.12	64
<sup>2</sup> B, ( $\sigma$ )	12.54	11.92	10.66	
<sup>2</sup> A, ( $\sigma$ )	12.92	12.32	11.27	
<sup>1</sup> A, ( $\pi\sigma^*$ )	6.97	6.64 ( $2 \times 10^{-4}$ ) <sup>e</sup>		
<sup>1</sup> B, V, ( $\pi\pi^*$ )	7.09	6.95 (0.544)	6.81 (0.38)	45
<sup>3</sup> B, T, ( $\pi\pi^*$ )	4.43	4.33 (0)	4.24	59 <sup>f</sup>
benzvalene, C <sub>2v</sub>		T = 0.007		65
<sup>2</sup> B <sub>1</sub> , ( $\pi$ )	9.14	8.81	8.54	66
<sup>2</sup> A <sub>1</sub> , ( $\sigma$ )	10.28	9.74	9.60	
<sup>2</sup> A <sub>2</sub> , ( $\pi$ )	11.45	10.97	10.69	
<sup>2</sup> B <sub>2</sub> , ( $\sigma$ )	13.37	12.85	12.3	
<sup>2</sup> B <sub>1</sub> , ( $\pi$ )	14.03	13.43	12.7	
<sup>2</sup> B <sub>2</sub> , ( $\sigma$ )	14.09	13.59	13.0	
<sup>2</sup> A <sub>1</sub> , ( $\sigma$ )	14.48	13.94	13.2	
<sup>1</sup> A <sub>2</sub> , ( $\pi\sigma^*$ ) <sup>n,ff</sup>	5.85	5.69 (0)		
<sup>1</sup> B <sub>1</sub> , ( $\pi\sigma^*$ ) <sup>n,ff</sup>	6.16	5.83 (0.015)	5.71 (0.069) <sup>c</sup>	67
<sup>1</sup> B <sub>2</sub> , V, ( $\pi\pi^*$ ) <sup>ff</sup>	6.32	6.12 (0.182)		
cyclobutadiene, D <sub>2h</sub>		T = 0.005		68, 5 <sup>f</sup>
geom I; II				69
<sup>2</sup> B <sub>1g</sub> , ( $\pi$ )	8.19; 7.66	8.03; 7.51	(8.50 <sup>g</sup> )	
<sup>2</sup> B <sub>1u</sub> , ( $\sigma$ )	11.46; 12.02	11.28; 11.83		
<sup>2</sup> B <sub>2u</sub> , ( $\pi$ )	13.17; 13.15	12.86; 12.90		
<sup>1</sup> B <sub>2g</sub> , V, ( $\pi\pi^*$ )	3.48; 2.50	3.75 (0); 2.83 (0)	4.12 ( $\epsilon$ 100) <sup>c</sup>	70, 71
<sup>1</sup> B <sub>3g</sub> , ( $\pi\sigma^*$ )	4.34; 3.89	4.30 (0); 4.00 (0)		
<sup>1</sup> A <sub>g</sub> , Z, ( $\pi\pi\pi^*\pi^*$ )	5.80; 3.85	5.79 (0); 4.08 (0) <sup>e</sup>		
<sup>1</sup> B <sub>2u</sub> , ( $\pi\sigma^*$ )	5.93; 5.61	5.85 (0.049); 5.56 (0.47)		
<sup>1</sup> B <sub>1g</sub> , ( $\pi\sigma^*$ )	6.79; 6.22	6.48 (0); 6.00 (0)		
<sup>1</sup> B <sub>1u</sub> , V, ( $\pi\pi^*$ )	6.98; 6.49	6.61 (0.206); 6.22 (0.207)		
<sup>3</sup> B <sub>2g</sub> , T, ( $\pi\pi^*$ )	2.33; 1.35	2.41 (0); 1.50 (0)		
cyclobutadiene, D <sub>4h</sub> <sup>h</sup>		T = 0.005		5 <sup>f</sup>
<sup>2</sup> E <sub>g</sub> , ( $\pi$ )	6.68	6.93		
<sup>2</sup> E <sub>u</sub> , ( $\sigma$ )	12.90	12.89		
<sup>2</sup> A <sub>2u</sub> , ( $\pi$ )	12.93	12.96		
<sup>3</sup> E <sub>g</sub> , ( $\pi\sigma^*$ )	2.93	2.91 ( $\sigma$ )		
<sup>3</sup> E <sub>u</sub> , ( $\pi\pi^*$ )	3.64	3.45 ( $\sigma$ )		

Table III (continued)

molecule, point group, designation of ion or excited states	KT/VO	PERTCI	obsd <sup>b</sup>	ref
cyclopentadiene, C <sub>2v</sub>				
		<i>T</i> = 0.008		72
<sup>2</sup> A <sub>1</sub> (π)	8.87	8.55	8.57*	73
<sup>2</sup> B <sub>1</sub> (π)	11.45	11.00	10.72*	
<sup>1</sup> B <sub>2</sub> , V, (ππ*)	5.06	5.06 (0.139)	5.33 (0.07)*	74, 75
<sup>1</sup> A <sub>2</sub> , (πσ*)	5.86	5.73 (0)		
<sup>1</sup> B <sub>1</sub> , (πσ*)	6.05	5.85 (0.001)		
<sup>1</sup> A <sub>1</sub> , V, (ππ*)	7.53	6.45 (0.004)	6.25*	
<sup>1</sup> A <sub>1</sub> , V, (ππ*)	8.08	7.91 (0.777) <sup>i</sup>	8.06 (strong)	45
<sup>3</sup> B <sub>2</sub> , T, (ππ*)	3.47	3.25 (0)	3.1	76
1,3-cyclohexadiene, C <sub>2</sub>				
		<i>T</i> = 0.008		77
<sup>2</sup> A <sub>1</sub> (π)	8.76	8.40	8.25	61
<sup>2</sup> A <sub>1</sub> (π)	10.96	10.39	10.75	
<sup>1</sup> B, V, (ππ*)	5.26	5.08 (0.140) <sup>e</sup>	5.00 (0.135)	75, 78
<sup>1</sup> B, (πσ*)	5.64	5.55 (0.150) <sup>e</sup>		
<sup>1</sup> B, (πσ*)	6.47	6.24 (0.002)		
<sup>1</sup> A <sub>1</sub> , (πσ*)	7.08	6.44 (0.007) <sup>j</sup>		
<sup>1</sup> A, V, (ππ*)	7.24	6.74 (0.038) <sup>j</sup>		
<sup>1</sup> A, V, (ππ*)	8.20	7.81 (0.240) <sup>i,j</sup>	8.06 (strong)	45
<sup>3</sup> B, T, (ππ*)	3.90	3.41 (0)	2.9	76
1,4-cyclohexadiene, D <sub>2h</sub>				
		<i>T</i> = 0.007		77 <sup>k</sup>
<sup>2</sup> B <sub>2u</sub> , (π)	9.56	9.22	8.80	64
<sup>2</sup> B <sub>3g</sub> , (π)	10.43	10.09	9.80	
<sup>2</sup> B <sub>2g</sub> , (σ)	12.51	11.97	11.00	
<sup>2</sup> A <sub>g</sub> , (σ)	13.00	12.48	11.97	
<sup>1</sup> B <sub>1g</sub> , (πσ*)	6.61	6.38 (0)		
<sup>1</sup> B <sub>2g</sub> , V, (ππ*)	6.90	6.68 (0) <sup>e</sup>		
<sup>1</sup> B <sub>3u</sub> , V, (ππ*)	7.20	6.80 (0.630)		
<sup>1</sup> B <sub>2g</sub> , V, (ππ*)	7.40	7.40 (0) <sup>e</sup>	7.93 (very strong, broad) <sup>c</sup>	45
<sup>1</sup> B <sub>3u</sub> , V, (ππ*)	8.11	7.79 (0.213)		5 <sup>l</sup>
Dewar benzene, C <sub>2v</sub>				
		<i>T</i> = 0.007		78
<sup>2</sup> B <sub>2</sub> , (π)	9.62	9.30	9.40	
<sup>2</sup> A <sub>1</sub> , (π)	9.71	9.38	9.70	
<sup>2</sup> A <sub>1</sub> , (σ)	11.64	11.22	10.95	
<sup>2</sup> A <sub>2</sub> , (σ)	12.15	11.67	11.5	
<sup>2</sup> B <sub>1</sub> , (σ)	13.16	12.62	12.2	
<sup>1</sup> A <sub>2</sub> , (πσ*)	5.95	5.76 (0) <sup>j</sup>		
<sup>1</sup> B <sub>1</sub> , (ππ*/πσ*) <sup>n,gg</sup>	6.25	5.87 (0.053) <sup>j</sup>		
<sup>1</sup> A <sub>2</sub> , V, (ππ*) <sup>gg</sup>	6.24	6.02 (0) <sup>j</sup>	6.05 (0.023) <sup>c</sup>	79
<sup>1</sup> B <sub>1</sub> , (ππ*/πσ*) <sup>n,gg</sup>	6.29	6.16 (0.149) <sup>j</sup>		
<sup>1</sup> A <sub>2</sub> , V, (ππ*)	6.66	6.71 (0) <sup>j</sup>		
<sup>1</sup> B <sub>1</sub> , V, (ππ*) <sup>n,gg</sup>	7.18	7.02 (0.181) <sup>j</sup>	6.70 (0.04)	
norbornadiene, C <sub>2v</sub>				
		<i>T</i> = 0.008		80
<sup>2</sup> B <sub>1</sub> , (π)	9.65	9.31	8.69	100
<sup>2</sup> A <sub>1</sub> , (π)	10.13	9.76	9.55	
<sup>2</sup> B <sub>2</sub> , (σ)	13.11	12.54		
<sup>2</sup> A <sub>2</sub> , (π)	13.09	12.56	11.26	
<sup>2</sup> B <sub>1</sub> , (σ)	13.94	13.40		
<sup>2</sup> A <sub>1</sub> , (σ)	13.98	13.43	12.51–12.75	
<sup>2</sup> B <sub>2</sub> , (σ)	14.60	14.02		
<sup>2</sup> A <sub>1</sub> , (σ)	15.32	14.69	14.24	
<sup>1</sup> A <sub>2</sub> , (πσ*)	5.55	5.38 (0)		
<sup>1</sup> B <sub>2</sub> , (πσ*)	6.31	5.97 (0.002) <sup>e</sup>		
<sup>1</sup> A <sub>2</sub> , V, (ππ*)	6.37	6.19 (0)	(5.8, 6.2) <sup>c</sup>	45, 81
<sup>1</sup> B <sub>1</sub> , (πσ*)	6.47	6.24 (0.008)		
<sup>1</sup> A <sub>1</sub> , (πσ*)	7.06	6.78 (0.019)		
<sup>1</sup> B <sub>2</sub> , V, (ππ*)	6.88	6.84 (0.451) <sup>e</sup>	6.82 (ε ≈ 60 000)	
dimethylenecyclobutene, C <sub>2v</sub>				
		<i>T</i> = 0.007		82
<sup>2</sup> B <sub>1</sub> , (π)	8.97	8.64	8.80	83
<sup>2</sup> A <sub>2</sub> , (π)	9.71	9.29	9.44	
<sup>2</sup> A <sub>1</sub> , (σ)	12.20	11.75	11.5	
<sup>2</sup> B <sub>2</sub> , (σ)	12.69	12.22	12.3	
<sup>1</sup> B <sub>2</sub> , V, (ππ*) <sup>n,ii</sup>	5.55	5.16 (0.310) <sup>e</sup>	5.16 (log ε 4.2)	84
<sup>1</sup> A <sub>2</sub> , (πσ*)	6.31	5.26 (0)		
<sup>1</sup> A <sub>1</sub> , V, (ππ*) <sup>n,ii</sup>	6.37	5.43 (2 × 10 <sup>-4</sup> ) <sup>e</sup>	5.83 (log ε 4.8)	
<sup>1</sup> B <sub>1</sub> , (πσ*)	6.47	6.08 (0.001)		
<sup>1</sup> A <sub>1</sub> , V, (ππ*) <sup>n,ii</sup>	6.61	6.41 (0.498) <sup>e</sup>		
<sup>1</sup> B <sub>2</sub> , V, (ππ*) <sup>n,ii</sup>	6.88	6.50 (0.397) <sup>e</sup>	6.05 (log ε 5.0)	



Table III (continued)

molecule, point group, designation of ion or excited states	KT/VO	PERTCI	obsd <sup>b</sup>	ref
fulvene, C <sub>2v</sub>		T = 0.008		85
<sup>2</sup> A <sub>2</sub> , (π)	8.86	8.46	8.55	83
<sup>2</sup> B <sub>1</sub> , (π)	9.58	9.27	9.54	
<sup>2</sup> B <sub>2</sub> , (σ)	12.84	12.36	12.1	
<sup>2</sup> A <sub>1</sub> , (σ)	13.62	13.10		
<sup>2</sup> B <sub>1</sub> , (π)	13.98	13.12	12.8	
<sup>2</sup> A <sub>1</sub> , (σ)	14.34	13.80		
<sup>2</sup> B <sub>2</sub> , (σ)	14.68	14.12	13.6	
<sup>1</sup> B <sub>2</sub> , V, (ππ*)	3.93	3.67 (0.027) <sup>e</sup>	3.44 (0.004)	86, 87
<sup>1</sup> A <sub>1</sub> , V, (ππ*)	5.88	5.35 (0.389) <sup>e</sup>	5.28 (0.34)	
<sup>1</sup> B <sub>1</sub> , (πσ*)	5.79	5.60 (0.001)		
<sup>1</sup> A <sub>2</sub> , (πσ*)	6.25	5.65 (0)		
<sup>1</sup> B <sub>1</sub> , (πσ*) <sup>n,ii</sup>	6.46	6.31 (0.003)	6.14 <sup>c</sup>	
<sup>1</sup> A <sub>1</sub> , V, (ππ*)	7.33	6.95 (0.365) <sup>e</sup>		
<sup>1</sup> B <sub>2</sub> , V, (ππ*)	7.68	6.98 (0.98) <sup>e</sup>	7.01	
benzene, D <sub>6h</sub>		T = 0.008		33
<sup>2</sup> E <sub>1g</sub> , (π)	9.52	9.22	9.24*	34
<sup>2</sup> E <sub>2g</sub> , (σ)	12.79	12.31	11.7*	
<sup>2</sup> A <sub>2u</sub> , (π)	14.01	12.99	12.2*	
<sup>1</sup> B <sub>2u</sub> , <sup>1</sup> L <sub>b</sub> , (ππ*)	6.46	4.86 (0) <sup>e</sup>	4.93 (0.002)*	88, 89
<sup>1</sup> B <sub>1u</sub> , <sup>1</sup> L <sub>a</sub> , (ππ*)	6.62	5.89 (0.0003) <sup>e</sup>	6.21 (0.094)*	
<sup>1</sup> E <sub>2u</sub> , (πσ*)	6.31	6.10 (0)		88, 90
<sup>1</sup> E <sub>1u</sub> , <sup>1</sup> B, (ππ*)	6.46/6.62	6.98 (0.852) <sup>e</sup>	6.96 (0.88)*	
<sup>3</sup> B <sub>1u</sub> , <sup>3</sup> L <sub>a</sub> , (ππ*)	4.57	4.09 (0) <sup>e</sup>	3.95*	91
<sup>3</sup> E <sub>1u</sub> , <sup>3</sup> B, (ππ*)	4.57/5.08	4.80 (0) <sup>e</sup>	4.75*	
<sup>3</sup> B <sub>2u</sub> , <sup>3</sup> L <sub>b</sub> , (ππ*)	5.08	5.75 (0) <sup>e</sup>	5.60*	
toluene, C <sub>s</sub>		T = 0.008		33
<sup>2</sup> A'', (π)	9.28	8.91	9.0	92
<sup>2</sup> A'', (π)	9.57	9.21	9.3	
<sup>2</sup> A', (σ)	12.70	12.16	11.4	
<sup>1</sup> A', <sup>1</sup> L <sub>b</sub> , (ππ*)	6.36	4.78 (0.002) <sup>m</sup>	4.72 (ε 260)	93
<sup>1</sup> A', <sup>1</sup> L <sub>a</sub> , (ππ*)	6.38	5.76 (0.020) <sup>m</sup>	5.93 (0.12)	45, 93
<sup>1</sup> A', <sup>1</sup> B <sub>b</sub> , (ππ*)	6.56	6.84 (0.858) <sup>i,m</sup>	6.57 (1.09)	
<sup>1</sup> A', <sup>1</sup> B <sub>a</sub> , (ππ*)	6.76	6.87 (0.745) <sup>m</sup>		
azulene, C <sub>2v</sub>		T = 0.008		94
<sup>2</sup> A <sub>2</sub> , (π)	7.44	7.23	7.43	95
<sup>2</sup> B <sub>1</sub> , (π)	8.59	8.42	8.50	
<sup>2</sup> A <sub>2</sub> , (π)	11.45	10.70	10.07	
<sup>2</sup> B <sub>1</sub> , (π)	12.67	11.77	10.85	
<sup>2</sup> A <sub>1</sub> , (σ)	12.45	11.98	11.0	
<sup>1</sup> B <sub>2</sub> , <sup>1</sup> L <sub>b</sub> , (ππ*)	2.88	2.13 (0.009) <sup>e</sup>	2.13 (0.009)	93, 96
<sup>1</sup> A <sub>1</sub> , <sup>1</sup> L <sub>a</sub> , (ππ*)	4.42	3.50 (0.067) <sup>e</sup>	3.63 (0.08)	
<sup>1</sup> B <sub>1</sub> , (πσ*)	4.63	4.39 (0)		
<sup>1</sup> B <sub>2</sub> , <sup>1</sup> B <sub>b</sub> , (ππ*)	5.15	4.50 (0.179) <sup>e</sup>	4.50 (1.10)	
<sup>1</sup> A <sub>1</sub> , <sup>1</sup> B <sub>a</sub> , (ππ*)	4.98	4.99 (1.226) <sup>e</sup>	5.22 (0.38)	

<sup>a</sup> Oscillator strengths if not otherwise stated. <sup>b</sup> Estimated values are given in parentheses. <sup>c</sup> Transition not included in the statistics because of ambiguity of assignment. <sup>d</sup> Molecular geometries estimated also from reference compounds. <sup>e</sup> Type of selection: 2M2S. <sup>f</sup> Geometry I from STO-3G calculations (Å): 1.313/1.569 for the short/long C-C bonds. Geometry II from CNDO/S calculations (Å): 1.349/1.515. Square geometry (Å) 1.435/1.435 from CNDO/S calculations (STO-3G: 1.431/1.431). <sup>g</sup> Derived from measurements on cyclobutadiene iron tricarbonyl. <sup>h</sup> All values relative to the triplet ground state. <sup>i</sup> Several other states with small oscillator strengths between this state and the next lower state shown have been omitted from the table. <sup>j</sup> Type of selection: 3M3S. <sup>k</sup> Assumed to be planar on the basis of MINDO/3 and MNDO results. <sup>l</sup> MNDO optimized geometry used. <sup>m</sup> Type of selection: 4M4S. <sup>n</sup> Assignment based on the present calculations. <sup>oo</sup> Assignment in accordance with the ab initio CI results of ref 99. <sup>bb</sup> Band attributed from its fine structure to the CH<sub>3</sub> group. Assigned to a σσ\* excitation on the base of CNDO/2 results.<sup>46</sup> <sup>cc</sup> The first three calculated states involve the e' MOs and VOs (referred to as σ<sub>ext</sub> in ref 55) which split after CI into the <sup>1</sup>A', <sup>1</sup>A<sub>1</sub>, and <sup>1</sup>E' states. This assignment agrees with that of ref 55 based on ab initio SCF calculations. The literature assignment of the second observed band to an <sup>1</sup>E' state (e' (σ<sub>ext</sub>) → a<sub>2</sub> (σ<sub>ext</sub>')) disagrees with the one found in the present calculations, <sup>1</sup>E' (e' (σ<sub>ext</sub>) → a<sub>1</sub> (σ<sub>int</sub>')). <sup>dd</sup> Suggested, on the basis of ab initio SCF data, to be of σπ\* type.<sup>58</sup> <sup>ee</sup> Assignment in accordance with the ab initio SCF data of ref 58. <sup>ff</sup> Band assigned in ref 67 to at least two transitions including a forbidden one of A<sub>2</sub> symmetry. <sup>gg</sup> The first band of Dewar benzene was assigned to the <sup>1</sup>A<sub>2</sub> (ππ\*) state.<sup>79</sup> <sup>hh</sup> Assigned to a <sup>1</sup>B<sub>1</sub> state of either σπ\* or πσ\* type on the basis of intuitive arguments.<sup>79</sup> <sup>ii</sup> No assignments made in ref 84. <sup>jj</sup> Observed band assigned to the <sup>1</sup>B<sub>2</sub> (ππ\*) state from π-VESCF calculations.<sup>86</sup> <sup>kk</sup> All energies are given in electron volts. Values marked by an asterisk have been used in the parameter optimization process.

fulvene) two or more ionizations were assigned to one band in the spectrum on intensity considerations. These assignments are confirmed. The only example where the inclusion of CI seems to be unreasonable is hydrogen. Here, in a minimal basis set, no CI is possible for the ion state whereas the ground state

is stabilized by mixing in a double excitation (-0.35 eV). Consequently, the LNDO/S as well as ab initio CI calculations yield the Koopmans' defect with the wrong sign.

The comparison of theoretical and experimental ETEs is often quite complicated by the fact that frequently a larger

number of computed states than experimental bands are obtained. While the assignment of  $\pi\pi^*$  states is often unambiguous, the location of  $\pi\sigma^*$ ,  $\sigma\pi^*$ , or  $\sigma\sigma^*$  transitions in the spectra presents problems. For ethylene, propene, cyclopropane, and cyclopropene such states appear to have been identified.<sup>46,55,57,99</sup>

A further remark concerns cyclobutadiene. Here the VIPs as well as ETEs favor the existence of a rectangular singlet ground state.<sup>101</sup>

Finally it appears worth mentioning that the ETEs for all molecules listed in Table III were also calculated using the CNDO/S SECI method. The essence of the results follows. The method works only satisfactorily for  $\pi\pi^*$  singlet excitations of planar  $\pi$  systems except for ethylene, its alkyl derivatives, and small ring compounds. These shortcomings may be a consequence of the CNDO approximation used as well as of using just one reference molecule (benzene) in the parametrization process.

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## A MINDO/3 Study of the Norrish Type II Reaction of Butanal

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**Abstract:** The MINDO/3 semiempirical SCF MO method, although parametrized to fit ground-state ( $S_0$ ) energies and geometries of molecules, has been found to give useful estimates of the energies of the lowest singlet ( $S_1$ ) and triplet ( $T_1$ ) excited states. It has accordingly been used to study the Norrish type II reactions of butanal, by calculating relevant parts of the  $S_0$ ,  $S_1$ , and  $T_1$  potential surfaces. The triplet reaction is predicted to take place via a stable biradical intermediate. The singlet reaction can, however, by-pass the biradical by a mechanism involving direct conversion to the product, via a narrowly avoided  $S_0$ - $S_1$  crossing. These conclusions are in agreement with the results of published photochemical and pyrolytic studies.

### Introduction

Work in these laboratories<sup>2</sup> over the last 13 years led to the development of a semiempirical SCF MO treatment (MINDO/3<sup>3</sup>) which has proved remarkably effective in the study of organic reaction mechanisms.<sup>4</sup> While MINDO/3 was parametrized solely to fit experimental heats of formation and geometries of molecules, it has been found to reproduce a very wide variety of other ground-state properties (dipole moments,<sup>3</sup> molecular polarizabilities<sup>4</sup> and hyperpolarizabilities,<sup>5</sup> first ionization potentials,<sup>3</sup> ESCA chemical shifts,<sup>6</sup> molecular vibration frequencies<sup>7</sup> and isotopic shifts,<sup>8</sup> entropies<sup>9</sup> and specific heats,<sup>9</sup> kinetic isotope effects,<sup>8,9</sup> nuclear quadrupole coupling constants,<sup>10</sup> NMR<sup>11</sup> and ESR<sup>12</sup> parameters, and the electronic band structure of polymers<sup>13</sup>). This versatility is rather remarkable, because most of these properties are unrelated to the ones used in the parametrization.

MINDO/3 also reproduces the relative energies of the lowest singlet and triplet states both of methylene<sup>14,15</sup> and of the oxygen molecule ( $O_2$ )<sup>15</sup> satisfactorily, the results being indeed as good as, or better than, those given by rather sophisticated ab initio procedures. While these molecules both have triplet ground states, the success of MINDO/3 in this connection suggested that it might be equally effective in predicting the energies of the lowest triplet excited ( $T_1$ ) states of normal closed-shell molecules and extensive tests have shown that this is indeed the case.<sup>16</sup>

These calculations involved use of the "half-electron" (h-e) method,<sup>17</sup> which indeed had already been shown<sup>18</sup> to reproduce the energies of  $\pi \rightarrow \pi^*$  triplets for a variety of conjugated hydrocarbons, using the  $\pi$  SCF MO treatment developed in these laboratories.<sup>19</sup> The latter calculations also led to reasonable estimates of the energies of the lowest  $\pi \rightarrow \pi^*$  singlet excited states ( $S_1$ ) of the molecules in question, using a simple extension of the h-e treatment of triplets.

In view of this, it seemed likely that MINDO/3 should be able to provide useful estimates of the energies of singlet excited ( $S_1$ ) states in general and so prove useful in the study of photochemical reactions. Such an extension could prove extremely useful because the mechanisms of photochemical reactions are much less well understood than those involving ground-state species and because MINDO/3 has proved of

major value in the latter area. Moreover, studies of several chemiluminescent reactions have already led to novel and important conclusions.<sup>20</sup> When, however, we began to study  $S_1$  energies in a systematic way, we found that the methods used previously to estimate them by the h-e approximation were in error. Here we describe a rigorous procedure for the purpose and results for a number of molecules.

Since this approach seemed encouraging, we decided to apply it to a standard photochemical reaction. We chose the Norrish type II reaction, for three reasons. First, it is one of the best known and most investigated photochemical processes.<sup>21-24</sup> Second, in spite of all this study, its mechanism is still not fully established. Third, as far as we know, no quantitative theoretical study of the Norrish type II reaction has as yet been carried out.<sup>25</sup> This is not in fact surprising, because even the simplest such reaction, i.e., that of butanal (**1**), involves a system with 13 atoms (and hence 33 degrees of freedom) and 28 valence electrons. The calculations must, moreover, be carried out for three distinct potential surfaces, the two lowest singlets ( $S_0$ ,  $S_1$ ) and the lowest triplet ( $T_1$ ). An adequate study by the Roothaan-Hall (RH: "ab initio SCF") method would be out of the question, even if a minimum basis set were used (when the results would in any case be quite unreliable). This indeed is quite a formidable problem even for MINDO/3, because the necessary geometry optimizations are much slower for open-shell systems than for closed-shell ones (vide infra). Since our primary purpose was in any case to explore the applicability of MINDO/3 in this kind of connection, we therefore confined our study to the most salient features of the reaction, seeking in particular to establish whether or not a biradical intermediate is involved and the differences, if any, between the mechanisms of reactions involving the  $S_1$  and  $T_1$  surfaces.

### Method

The calculations were based upon the half-electron<sup>17</sup> (h-e) method, modified by inclusion of configuration interaction (CI). In the h-e method, the standard closed-shell SCF procedure for ground states is adapted for calculating open-shell excited singlet or triplet states.