About the Calculation of Electronic Transitions in the Original CNDO/2 Treatment

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The original CNDO/2 method is adapted to the open shell case in order to calculate the first singlet-triplet electronic transition. The molecular wave functions are optimized, minimizing the fundamental and excited state energies. Some linear hydrocarbons and monocyclic azines are calculated. The results are improved compared with those obtained by means of the virtual orbital approximation. The modifications in the energy levels are discussed.

I. Introduction

Among the different attempts to improve the original CNDO/2 treatment[1] of electronic transitions, we are concerned with the following ones: DEL BENE and JAFFÉ[2] successfully modified the parametrization and introduced configuration interaction. However, ARRIAU et. al.[3] found that Jaffé's parametrization could still be modified in some cases in order to improve the agreement with experiment. GIESSNER-PRETTRE and PULLMAN[4] introduced CI but retained the Pople parametrization. KROTO and SANTRY[5] formulated an approximate open shell theory for singlets based on CNDO.

We intend to resume the original treatment, avoiding for the moment CI as well as the change in parametrization. We shall instead remember that virtual orbitals cease to be such, and undergo therefore a change, when occupied[6]. We shall confine ourselves to the open-shell first triplet case (which is straightforward) of a few linear hydrocarbons and monocyclic azines.

II — Open Shell Calculation

Let us remember that the transitions to the lowest triplet states are usually calculated as arising from the promotion of one electron from orbital $\boldsymbol{i}$ to the virtual orbital $\boldsymbol{a}$; following ROOTHAAN[7]:

$$\boldsymbol{E}({}^3\Phi_{ia}) - \boldsymbol{E}({}^1\Phi_o) = \varepsilon_a - \varepsilon_i - \boldsymbol{J}_{ia}$$

where $\varepsilon_i(\varepsilon_a)$ is the energy of orbital $\boldsymbol{i}(\boldsymbol{a})$, and $\boldsymbol{J}_{ia}$ the corresponding molecular Coulomb integral. ${}^1\Phi_o$ is the shorthand notation for the ground state wave function. $\boldsymbol{E}({}^3\Phi_{ia})$ is the energy of the triplet state.

The excited state energy thus obtained is indeed the energy of what we may call a "virtual molecule". It is calculated without altering the molecular orbitals belonging to the fundamental state.

We shall also calculate the total energies for the molecule, but with allowance for the variation in the excited state orbitals, minimizing self-consistently the energy. We should thus improve the results, for actually all levels change.

We use the virtual orbital as a starting point for the calculation of the excited molecule geometry. We obtain first the molecule's fundamental state with the CNDO/2 method, having values for wave function coefficients $\boldsymbol{c}_{i\mu}$ and therefore the properties of the fundamental state. We build the excited state bond order matrix starting from these $\boldsymbol{c}_{i\mu}$, with the corresponding occupation numbers. The π bond orders $\boldsymbol{p}_{\mu\nu}$ are introduced into a formula — suitable for excited states — relating them to new interatomic distances[8]. This geometry is introduced as basis for the first iteration in the elements of the SCF Hamiltonian $\boldsymbol{F}$[1]

$$\begin{aligned}\boldsymbol{F}_{\mu\mu} &= -\tfrac{1}{2}(\boldsymbol{I}_\mu + \boldsymbol{A}_\mu) + [(\boldsymbol{p}_{AA} - \boldsymbol{Z}_A) - \tfrac{1}{2}(\boldsymbol{p}_{\mu\mu} - 1)]\,\gamma_{AA} \\ &\quad + \sum_{B \neq A} (\boldsymbol{p}_{BB} - \boldsymbol{Z}_B)\,\gamma_{AB}\end{aligned}$$

$$\boldsymbol{F}_{\mu\nu} = \tfrac{1}{2}(\beta_A^0 + \beta_B^0)\,\boldsymbol{S}_{\mu\nu} - \tfrac{1}{2}\,\boldsymbol{p}_{\mu\nu}\,\gamma_{AB}$$

following then CNDO/2 until attaining a self-consistent energy. We are thus using a Hamiltonian corresponding to the excited state.

The transition is then given by the difference in the corresponding total energies, supposing as usual, that the excitation does not alter the vibrational state.

A more rigorous approach could consist of attaining self-consistency in geometry for the excited state starting from a fundamental state which is in turn self-consistent in geometry (i.e. repeating the above mentioned procedure with the $p_{\mu\nu}$ obtained in each step). However, in our case this is not worthwhile since the energy values do not change significantly. For example, in pyrazine the total energy is affected by 10^{-4} in self-consistency, and the transition changes by 2%.

III — Discussion

Figure 1 reports the ethylene energy levels for the fundamental state, which are occupied as shown building the "virtual molecule", together with the triplet levels corresponding to α and β spins in the self-consistent open shell calculation. The most affected levels are, obviously, the HOMO and the LEMO. That is, when the LEMO of the fundamental state becomes HOMO for the α state, its value changes drastically, and this also occurs with the ground state HOMO which becomes a β LEMO.

Apart from these, all energy levels are affected, as mentioned, on changing the occupation numbers. The most sensitive are the π levels, as seen in Figure 2, showing the energy levels in butadiene. For example the 7 ground state level, which is π, becomes more stable in the α state; in the β state it becomes so much less stable that it falls between the two σ levels which were labelled 8 and 9 for the ground state (now 7 and 9), and are

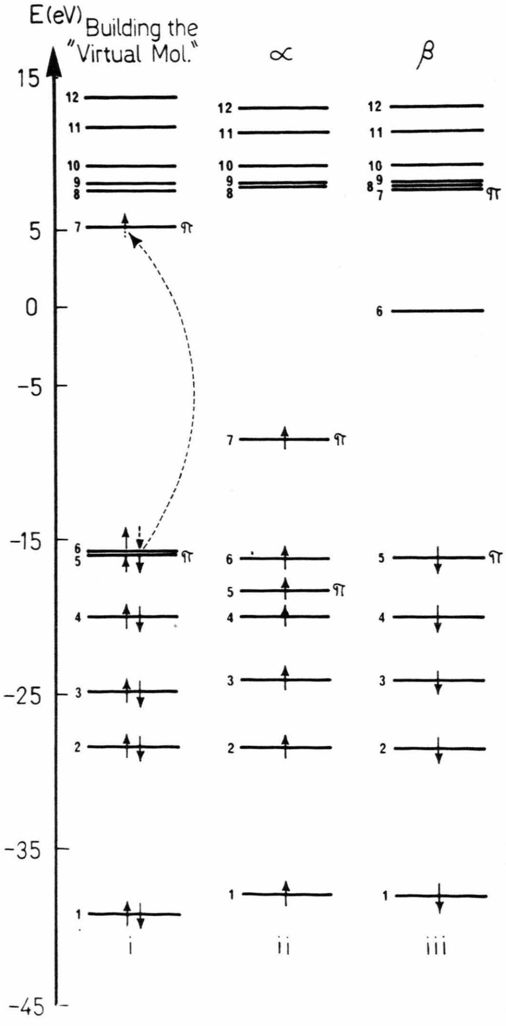

Fig. 1. Energy levels for ethylene: (i) when building the "virtual molecule" (↑) starting from the fundamental state (↓); (ii)α; (iii)β levels for the open-shell calculation.

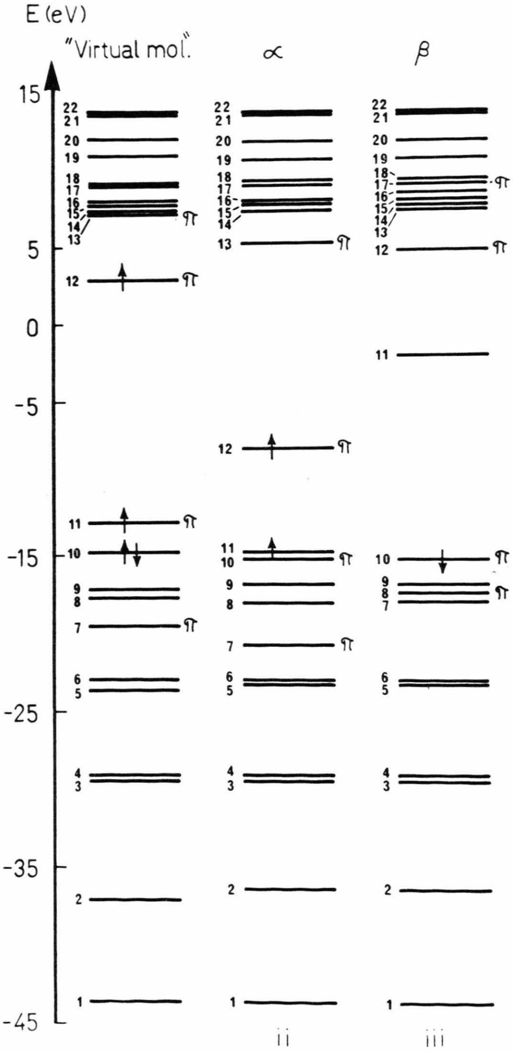

Fig. 2. Energy levels for butadiene: (i) "Virtual molecule" built with the fundamental state levels; (ii)α; (iii)β levels for the open-shell calculation.

much less affected. Something very similar occurs with the highest π level, the 13 ground state level.

Pyridine (Table 1) shows an example of the most general expected trend, the α being different from the β levels. Again, orbital No. 16 is no more virtual for the α spins, and orbital No. 15 becomes in turn virtual for the β spins. For pyridine's triplet, the α levels are lower than the β levels, but this is not a general feature.

Table 1. Energy levels for pyridine (in $-$eV).

Orbital No.	Fundamental	Triplet state α spins	Triplet state β spins
1	51.42	50.57	50.53
2	39.07	38.02	37.80
3	37.25	37.38	37.34
4	30.79	30.74	30.62
5	30.17	29.88	29.73
6	28.39	27.85	26.83
7	23.53 π	24.38 π	23.16 π
8	22.14	22.05	21.82
9	19.98	19.99	19.86
10	18.56	19.26	18.98
11	18.06	17.96	16.36
12	14.46 π	16.65 π	14.35
13	14.34	15.20 π	14.21 π
14	13.86 π	14.43	14.06 π
15	13.02	13.07	$-$0.09
16	$-$3.50 π	7.12 π	
17		$-$4.10 π	

Table 2 reports the first singlet-triplet transition. Our assignments are the same as those of the V.O. approximation. The present calculation, unlike the CIS-INDO one, predicts for ethylene a Berry-like transition. The σ or π character of the ethylene's highest occupied level has been the subject of discussions[9]. Even if the σ CNDO assignment has been ascribed to a fault of this method[10], it can be remarked that the σ–π mixing is not more pronounced in CNDO than in other AVE methods[11, 12].

The assignments in azines are $\sigma \to \pi^*$ which, leaving open the exact meaning of the n levels (see below), coincide with experiment except perhaps for pyridine, where Evans[13] is $\pi \to \pi^*$. The recent lowest triplet experimental result for s-tetrazine[14] clears the uncertainties about this molecule. In spite of its unusual emission properties[15], the triplet is also lower than the first singlet in this case.

We said that we were interested mainly in the comparison with the V.O. calculation. In this sense, we see that our estimation reduces the V.O. results by 12% to 30%. This sounds as a reasonable relative improvement, the differences being always in the right direction. We may point out that the improvement is at least of the same order as that obtained by introducing configuration interaction in the INDO method, no doubt more sophisticated than the one applied here. The agreement obtained is of course far from satisfactory taking an absolute point of view (Let us recall that naïve π methods may be quite successful in predicting the usual $n \to \pi^*$ transitions in azines[20]). However, the way chosen seems quite promising when considering that we have not taken into account several factors which may have had a negative influence:

The CNDO Coulomb integrals, which are estimated following Roothaan's[21] formulae, are not the most suitable for energy calculations. Following the Del Bene-Jaffé[2] criterium, it is likely that semiempirical integrals improve the situation.

Geometry has a critical importance. Cheung et. al. have argued[22] that CNDO/2 appears insufficiently accurate for many direct quantitative applications, particulary when subtile geometrical effects may be involved. These authors optimize some geometries of the fundamental state. Further improvement could perhaps be obtained by applying the procedure to the excited state geometry, about which there is little experimental knowledge.

It is well established that CNDO predicts that for pyridine, for example, the HOMO is not confined to the nitrogen lone pair (as the classical picture describes) but is delocalized over the other σ orbitals[2, 23]. Figure 3 illustrates this delocalization, which is due predominantly to the carbon $2p_y$ orbitals[2] and to the hydrogens.

Rehybridization of the n level under excitation has been discussed in literature[18, 19, 24]. Goodman[18] says that its s character decreases, but his value is perhaps too low. Mason[24] claims instead that the s character of

Table 2. First singlet-triplet transition (in eV).

Molecule	This work	CNDO/2 V.O.	CIS INDO[4]	Experimental
Ethylene	7.38 ($\sigma \to \pi^*$)	10.29	7.89 ($\pi \to \pi^*$)	4.6 [16]
Butadiene	5.03 ($\pi \to \pi^*$)	6.44	6.05 ($\pi \to \pi^*$)	3.5 [17]
Hexatriene	3.64 ($\pi \to \pi^*$)	5.76	4.62 ($\pi \to \pi^*$)	
Pyridine	5.05 ($\sigma \to \pi^*$)	7.48	4.87 ($n \to \pi^*$)	3.66 ($\pi \to \pi^*$) [13]
Pyridazine	4.58 ($\sigma \to \pi^*$)	6.57		2.91 ($n \to \pi^*$) [18]
Pyrimidine	5.61 ($\sigma \to \pi^*$)	6.75		3.51 ($n \to \pi^*$) [18]
Pyrazine	4.99 ($\sigma \to \pi^*$)	5.67		3.22 ($n \to \pi^*$) [19]
S-Tetrazine	3.73 ($\sigma \to \pi^*$)	4.37		1.69 ($n \to \pi^*$) [14]

the ***n*** level increases ("On the promotion of a lonepair electron to a π orbital, the ***s*** character of the "hole" left behind is shared amongst the remaining σ electrons, notably those of the σ bonds") together with the N angles. Due to our way of calculating the transition, we found it more natural to consider the hybridization of the whole fundamental state or the whole triplet state. We obtain that the ***s*** character increases for N in all azines. For pyrimidine, e.g., we have N($sp^{1.81}$) in the ground state and N($sp^{1.57}$) in the excited state.

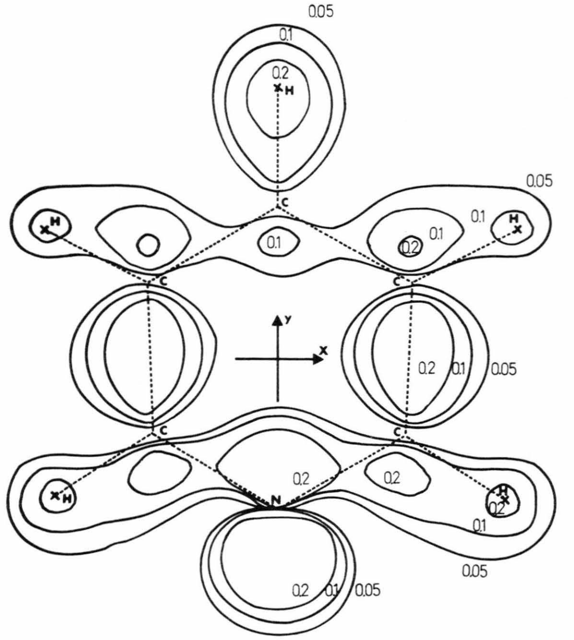

Fig. 3. Contour charge density lines for the HOMO in pyridine, ground state

The electronic distributions of the triplet state following the V.O. approximation and the open-shell treatment are quite close, the only significant difference being that for ethylene, where

$$q_C = -0.344 \text{ (V.O.)}; \quad -0.034 \text{ (open shell)}$$

and

$$q_H = +0.173 \text{ (V.O.)}; \quad +0.017 \text{ (open shell)}.$$

A striking feature of Kroto and Santry's work about the first singlet excited state of some molecules is the qualitative difference which they obtain between the excited state charge densities following both approximations. May be the lack of orthogonality which they mention for the open shell theory causes some difficulties in this respect.

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