

# *V-N* Vertical Transition of Planar Ethylene

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The *V-N* vertical transition of planar ethylene has been investigated by means of a large Gaussian basis set, taking into account both the SCF and correlation energies. It is shown that in this case the SCF function, which would lead to a valuation of the Rydberg character at around 80%, does not provide an adequate description of the *V* state. The correlative effects bring about a lowering of the percentage of the Rydberg character to 38%. The calculated value for the transition energy is in excellent accord with the experimental data.

**Key words:** Correlation energy – Ethylene, *V-N* transition

## 1. Introduction

Analysing the spectrum of ethylene, Mulliken [1, 7] attributed the series of diffuse bands, the maximum intensity of which is found at about 7.66 eV, to a valence electronic transition *V-N*, due to the excitation of an electron from a  $1b_{3u}$  ( $\pi$ ) to a  $1b_{2g}$  ( $\pi^*$ ) molecular orbital. This interpretation has even recently been consolidated by means of absorption spectra in a condensed phase [8, 9]. In recent years, on the other hand, numerous SCF calculations have been carried out using very large basis sets [10-16], the peculiarity of which is that they do not confirm the valence character of the transition: for example the value of  $\langle b_{2g} | x^2 | b_{2g} \rangle$  (the *x*-axis is taken perpendicular to the plane of the molecule, and the *z*-axis through the two carbon atoms) is approximately 40 a.u., a value a long way off what one expects for a valence-type orbital. Some authors have employed a configuration interaction (CI) treatment taking into account a part (however rather modest) of the correlation energy; their results lead one to believe that the SCF method is in some way inadequate to describe the *V* state.

It actually seems reasonable to think that in this case the correlation energy plays a notable and, in a certain sense, unusual role. Using a minimal set, the  $\pi$  part of the approximate wave function can be written

$$\Psi_N = \mathcal{N} \{ P_{xc_1}(1) P_{xc_1}(2) + P_{xc_2}(1) P_{xc_2}(2) + P_{xc_1}(1) P_{xc_2}(2) + P_{xc_2}(1) P_{xc_1}(2) \}$$

for the ground state *N*, while for the *V* state (one electron in the  $\pi$  orbital and one in the  $\pi^*$ ) the approximate wave function is

$$\Psi_V = \mathcal{N}' \{ P_{xc_1}(1) P_{xc_1}(2) - P_{xc_2}(1) P_{xc_2}(2) \}.$$

Based upon these approximate functions, one would have to conclude that the correlation energy is a little larger in the excited state than in the ground state, the latter being made of ionic and covalent structures of equal weight and the other only of ionic structures. The correlative effects are indeed more sizeable in the ionic structures than in the covalent ones, because the latter are already correlated in part. Therefore we can suppose that for a valence transition there is not the same loss of correlation energy as for the other transitions (1 eV). The SCF method is unable to account for effects of this type and this fact is the basis of its inadequacy in describing the  $V$  state of ethylene.

An MC method, in turn, would not have to lead to believable results, at least while limited to a small number of configurations. It is well known, in fact, that thousands, and even tens of thousands of configurations are necessary to obtain at least 90–95% of the correlation energy. For this reason, considering also that the ethylene is the first member of a very important class of chemical compounds, we found it suitable to re-analyze the problem, taking into consideration both SCF and total energies (without relativistic). The latter was obtained by adding to the SCF energy the correlation energy, calculated with a previously developed formula [17], which in the cases taken as examples had provided about 98% of the total correlation energy.

## 2. Basis Functions

In our calculations, we have used  $s$ ,  $p$  and  $d$  modified Gaussian functions [18, 19]. As far as  $s$  and  $p$  functions are concerned, if the orbital exponents  $\alpha$  are sufficiently large ( $\alpha > 0.3$ ) there are not particular considerations to make, except those obvious ones about the necessity of a sufficiently dense basis set to obtain accurate values of energy. For the more expanded functions, however, there arises the problem of their excessive overlap, a drawback which can cause an even considerable loss of precision in the calculation; on the other hand, every contribution of two  $s$  or  $p$  functions on the carbon atoms can be approximated by suitable  $s$ ,  $p$  or  $d$  functions in the middle of the C-C bond. That is the same as using the united atom approximation for the more expanded region of the wave function. The accuracy of this approximation is shown in Table 1. It is noticeable that the overlap of the united atom orbital with the suitable combination of separated atomic orbitals is larger than 0.99 for orbital exponents lower than 0.5.

The basis functions we have chosen are shown in Table 2. These functions, in great measure, are the same as those employed by McKoy [13], which in turn lead up to the calculations worked out by Huzinaga and other authors [20, 21]. The overlap among close orbitals is normally ranged from 0.8 to 0.9, which makes us confident that the results are reasonably accurate.

## 3. SCF Energy

The SCF energy of the ground state, calculated with the previously described basis set, is  $-78.0382$  a.u., and it is of an accuracy comparable to the best values reported in the literature. A further lowering of the energy is obtainable, above all, by increasing the

Table 1. Optimized values of overlap  $S$  between two Gaussian functions with orbital exponent  $\alpha$  at a distance of  $2R$ , and a single Gaussian function with orbital exponent  $\alpha' = k\alpha$  in the middle point

$\alpha R^2$	$s_A + s_B \rightarrow s'$		$s_A - s_B \rightarrow p_z$		$p_{xA} + p_{xB} \rightarrow p'_x$		$p_{xA} - p_{xB} \rightarrow d_{xz}$	
	$k$	$S$	$k$	$S$	$k$	$S$	$k$	$S$
0.1	0.983	0.9999	0.990	1.0	0.990	0.9999	0.993	1.0
0.2	0.967	0.9996	0.980	0.9999	0.980	0.9995	0.986	0.9999
0.5	0.920	0.9974	0.951	0.9995	0.951	0.9969	0.965	0.9993
1.0	0.847	0.9898	0.905	0.9979	0.905	0.9877	0.931	0.9970
5.0	0.468	0.8212	0.618	0.9530	0.618	0.7850	0.705	0.9333

Table 2. Basis functions

Centre	Type	Orbital exponent
C	<i>s</i>	(16067.118, 2365.8824, 542.29752, 148.23131) <sup>a</sup> (46.007872, 15.853338, 5.8801611) <sup>b</sup>
		2.2821385, 4.1833454, 0.6169005, 0.2742436
	<i>p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub></i>	(42.0201, 8.90332) <sup>c</sup> 2.57917, 0.89487, 0.338303
	<i>d<sub>xz</sub>, d<sub>yz</sub></i>	1.1429, 0.35945, 0.1146
C-C	<i>s</i>	1.0, 0.5, 0.116, 0.058, 0.012, 0.0035, 0.0010
	<i>p<sub>x</sub></i>	0.126, 0.054
	<i>p<sub>z</sub></i>	0.5, 0.123, 0.059
	<i>d<sub>xz</sub></i>	0.7, 0.129, 0.054, 0.0225, 0.0091, 0.0037
H	<i>s</i>	18.61, 4.239, 0.6577, 0.1483
	<i>p<sub>x</sub></i>	0.57, 0.24

<sup>a</sup> Contracted; coefficients 0.0048811, 0.036662, 0.19236, 0.83227.

<sup>b</sup> Contracted; coefficients 0.1405, 0.3317, 0.4481.

<sup>c</sup> Contracted; coefficients 0.13, 1.0.

density of the basis set in the description of the  $\sigma$  bonds and of the  $1s$  orbitals of the C atoms, but this would have a purely numerical significance and would in no way modify the substance of the conclusions.

As far as the energy of the  $V$  state is concerned, the calculated value of  $-77.7702$  a.u. already appears in fairly good accord with the experimental data. From the analysis of the coefficients of the functions in the  $b_{2g}$  orbital, for the  $V$  state there seems to be evidence of a substantial Rydberg character; in fact, the entire orbital has an overlap of about 0.8 with a  $d_{xz}$  orbital with  $\alpha = 0.016$  in the centre of the C-C bond. It appears therefore like an hydrogenoid  $d_{xz}$  orbital corresponding to a nuclear charge of a little above 1, and this is in agreement with that obtained by other authors.

At this point we have considered it essential to analyse how the energy varies in relation to the change of the Rydberg character of the  $b_{2g}$  orbital.

For this purpose let us consider the function:

$$\Psi = c_V \Psi_V + c_R (\Psi_R - S \Psi_V) (1 - S^2)^{-1/2}, \quad S = \langle \Psi_V | \Psi_R \rangle$$

where  $\Psi_R$  is essentially the Rydberg part of the  $b_{2g}$  orbital, that is, the part made up of the central  $d_{xz}$  functions with  $\alpha \leq 0.054$ . The remaining part of the  $b_{2g}$  orbital may be considered as having a valence character; in fact it provides an  $\langle x^2 \rangle$  value equal to  $4.81 \text{ a.u.}^2$ , which is what one must expect for an orbital of this type. The behaviour of the calculated SCF energy versus  $c_R^2$  is shown in Fig. 1.

It is noticeable that for a value of  $c_R^2$  between 0.2 and 0.8, the variation of energy is less than 0.5 eV. This leads one to believe that an SCF calculation cannot really be used in order to estimate the percentage of the Rydberg character of the  $V$  state; it is clear, in fact, that in this case even a modest variation of correlation energy can completely modify its character.

#### 4. Calculation of the Correlation Energy

In a preceding paper [17] it is shown how the calculation of the correlation energy can be usefully worked out, integrating a suitable function of the density matrix. The final formula [(19) in the Reference] can be applied to the calculation of the correlation energy only for the ground state, while for the  $V$  state it is necessary to bring about some modifications. The factor  $\rho(R)$  in the formula cited has been obtained, applying the simplification:

$$P_{2HF}(\mathbf{R}, \mathbf{R})/\rho_{HF}(\mathbf{R}) = \frac{1}{2}\rho_{HF}(\mathbf{R})$$

Because this is no longer true in the case of open shells, (19) will have to be modified, substituting for  $\rho(\mathbf{R})$  the expression:

$$2P_{2HF}(\mathbf{R}, \mathbf{R})/\rho_{HF}(\mathbf{R}).$$

The correlation energy thus calculated for the ground state is  $-0.492$  a.u.; that of the  $V$  state varies with the Rydberg character in the range  $-0.50$  -  $-0.459$ , as shown in Fig. 2. The value corresponding to the SCF  $V$  state is  $-0.466$  a.u.

#### 5. Results and Conclusion

Figs. 1 and 2 show the different behaviour of the SCF energy and of the correlation energy versus the Rydberg character of the  $b_{2g}$  orbital. The lowering of the absolute value of the correlation energy as the Rydberg character is increased comes within the predicted results since it corresponds to a progressive separation between two electrons.

The behaviour of the total energy is shown in Fig. 3; the minimum arises at  $c_R^2 = 0.38$  and the total energy is  $-78.243$  a.u.

A total energy of  $-78.530$  a.u. having been obtained for the ground state, the energy of the vertical transition  $V-N$  has a product equal to  $0.287$  a.u. ( $7.8$  eV), in excellent accord with the experimental data.

Fig. 4 shows the  $\langle b_{2g} | x^2 | b_{2g} \rangle$  value as a function of  $c_R^2$ ; the value corresponding to the minimum energy is  $22$  a.u.<sup>2</sup>, while that corresponding to the SCF  $b_{2g}$  orbital is  $36.57$  a.u.<sup>2</sup>.

Though this value is higher than that of a pure valence orbital, we hold that it is not in contrast with the experimental evidence, since it is clearly lower than that relative to a Rydberg orbital. Furthermore, we estimate the  $b_{2g}$  orbital as built up with 62% of valence character, and only with 38% of Rydberg character. In comparison with the value obtained by the SCF method (80% Rydberg character), the change is very noticeable; this fact shows that the correlation energy plays a fundamental role.

We think that these conclusions are not peculiar to the transition we have analysed, but that they can be extended to all the  $V-N$ -type transitions [7]; probably in these cases not only the two-electron SCF density matrix but the one-electron as well is affected with a great error, which makes the role of the correlation energy determinant.

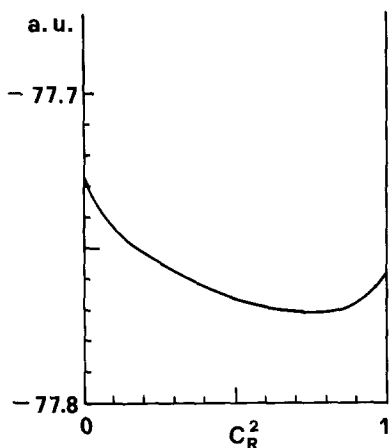


Fig. 1.

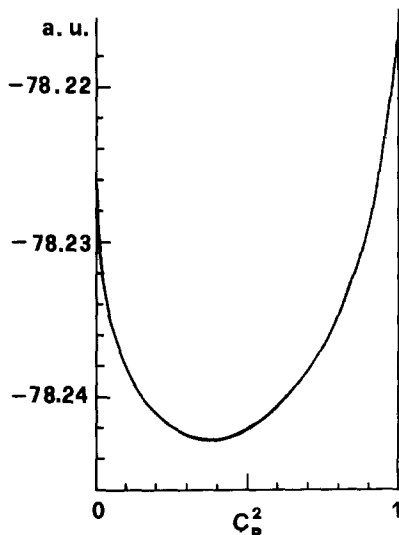


Fig. 3.

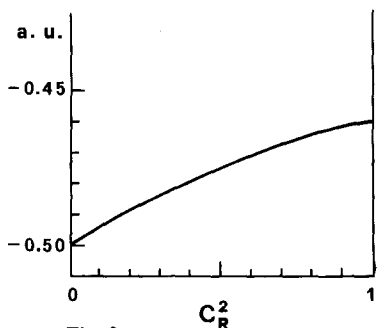


Fig. 2.

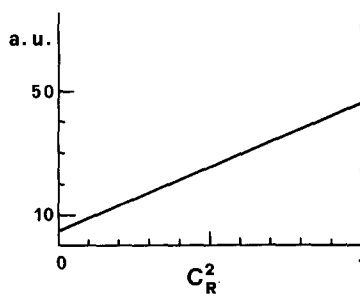


Fig. 4.

Fig. 1. SCF energy of the  $V$  state versus  $c_R^2$  (fraction of Rydberg character)

Fig. 2. Correlation energy of the  $V$  state versus  $c_R^2$

Fig. 3. Total (SCF + correlation) energy of the  $V$  state versus  $c_R^2$

Fig. 4.  $\langle b_{2g} | x^2 | b_{2g} \rangle$  value in the  $V$  state versus  $c_R^2$

This is not true in the other type transitions. For instance, in the  $\pi - 4a_g$  transition of the ethylene we obtain, by means of the basis set cited, a value of  $-77.8098$  a.u. for the SCF energy of the excited state, and a value of  $-78.269$  for the total energy. Hence, the transition energy is  $0.261$  a.u. ( $7.1$  eV), in complete accord with the experimental data, without any modification of the one-electron density matrix.

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