

THE THEORETICAL DESCRIPTION OF
THE $(\pi\pi^*)$ EXCITED STATES OF ETHYLENE†

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Received 19 August 1969

It is shown that the excited singlet $(\pi\pi^*)$ state (V) of planar ethylene in both the Hartree-Fock and π -electron configuration interaction descriptions is quite diffuse. The extent of the π^* -orbital in the π -direction as measured by $\langle z^2 \rangle$ is $42 a_0^2$ in the V state as compared to $2.7 a_0^2$ in the corresponding triplet state (T). In addition, we find that the Hartree-Fock vertical excitation energy for the V state is 7.42 eV as compared to the experimental value of 7.6 eV.

The excited states of ethylene which are of most interest both experimentally and theoretically are the singlet and triplet states arising from the $(\pi\pi^*)$ configuration. If the molecule lies in the xy -plane with \hat{x} along the CC bond axis, these states are of B_{3u} symmetry and have been designated $V(^1B_{3u})$ and $T(^3B_{3u})$ by Mulliken. The $(\pi)^2$ ground state is denoted as $N(^1A_{1g})$. The experimental results have been interpreted as involving a vertical excitation energy of 4.6 eV for the T state [1] and 7.6 eV for the V state [2]. Previous theoretical calculations [3-5] (Hartree-Fock) for planar ethylene with the ground state geometry have given ≈ 3.4 eV as the excitation energy (ΔE) for the T state and 9.3 - 12.0 eV for the V state. The low ΔE for the T state is understandable since there should be about 1 eV less correlation energy in the triplet state than in the ground state. However, these results imply that the V state has 1.7 eV *more* correlation energy than the ground state. One would normally expect the correlation energy for an open-shell state to be less than a closed-shell state of similar electronic structure, so there have been a number of attempts to determine the origin of the extra correlation in the V state [6]. We shall see below that previous SCF calculations on the V state used inadequate basis sets and that the use of a more flexible set leads to $\Delta E(V) = 7.42$ eV and, thus,

a correlation energy for the V state slightly less than that in the ground state.

In table 1 we present the results of our self-consistent restricted Hartree-Fock# calculations on the ground and excited T and V states of ethylene (using the same geometry as for the ground state [3,4]). Here we have considered basis sets appropriate for the ground state (as in most previous calculations [3-5]), as well as more complete sets obtained by addition of the necessary diffuse basis functions##.

From table 1 we see that the spatial extent of the π^* -orbital in the triplet state is comparable to that of the π -orbital in the ground state, being significantly more diffuse only along the CC bond axis, as expected from its nodal structure. This is a reflection of the basic similarities in the electronic structure of the lowest (ground) singlet and triplet states as discussed below.

In the V state, on the other hand, the π^* -orbital is quite diffuse, $\langle z^2 \rangle = 42.08$ au, and is bound by only 1.6 eV. In addition, the calculated excitation energy (7.42 eV) is now in good agree-

For these states, the Lagrange multipliers coupling the open-shell orbitals to the closed-shell orbitals and to each other are zero by symmetry.

The "valence" basis sets were the carbon (9s 5p) and hydrogen (4s), $\zeta = 1.2$, Gaussian sets of Huzinaga optimally contracted to a [4s 3p/2s] set. This valence set was used in the calculation on the ground state; for the triplet state this set was augmented with a diffuse $2p_\pi$ basis function ($\zeta = 0.0365$) on each carbon; for the singlet state the carbon $2p_\pi$ basis was further expanded by the addition of two basis functions with $\zeta = 0.0116, 0.0037$. These sets were obtained by adding more and more diffuse basis functions until the wave functions converged.

† Partially supported by a grant (GP-6965) from the National Science Foundation.

‡ NSF Predoctoral Fellow 1966-1969.

‡‡ NDEA Trainee 1967-1969.

‡‡‡ Alfred P. Sloan Fellow.

‡ Contribution No. 3924.

Table 1
 Restricted Hartree-Fock calculations on the ground, $N(^1A_{1g})$, and $(\pi\pi^*)$ excited, $T(^3B_{3u})$ and $V(^1B_{3u})$, states of ethylene. Calculations were for the ground state geometry. Except as noted, all quantities are in atomic units. a)

Basis set	Ground state b)		Excited states		
	$N(^1A_{1g})$ Valence c)	$T(^3B_{3u})$ Valence c)	$T(^3B_{3u})$ Augm*td d)	$V(^1B_{3u})$ Valence c)	$V(^1B_{3u})$ Augm*td e)
E_{HF}	-78.0140	-77.8913	-77.8917	-77.6794	-77.7415
ΔE (eV)	-	3.33	3.33	9.10	7.41
f f)	-	-	-	0.89	0.15
$\epsilon(\pi)$ g)	-0.3729	-0.5167	-0.5175	-0.3527	-0.5995
$\epsilon(\pi^*)$ g)	-	-0.2422	-0.2419	-0.0113	-0.0593
$\langle\pi x^2 \pi\rangle$	2.1540	2.0592	2.0634	2.1064	2.0294
$\langle\pi y^2 \pi\rangle$	0.8809	0.7523	0.7559	0.8215	0.7246
$\langle\pi z^2 \pi\rangle$	2.6428	2.2570	2.2678	2.4646	2.1739
$\langle\pi^* x^2 \pi^*\rangle$	-	3.6828	3.8468	5.6603	43.0190
$\langle\pi^* y^2 \pi^*\rangle$	-	0.8614	0.9149	1.5555	14.0272
$\langle\pi^* z^2 \pi^*\rangle$	-	2.5842	2.7446	4.6664	42.0815

a) 1 au of energy = 27.2107 eV and 1 au of length = 0.529167×10^{-9} cm.

b) T. H. Dunning and V. McKoy, unpublished calculations.

c) The valence set is the [4s 3p/2s] Gaussian basis, see ref. [7].

d) This is the valence set augmented with one diffuse $2p_z$ carbon function, see ref. [7].

e) This is the valence set augmented with three diffuse $2p_z$ carbon functions, see ref. [7].

f) The oscillator strength is $f = \frac{2}{3} \Delta E |D|^2$ where D is the transition moment, $D = \langle\Psi_f|r|\Psi_i\rangle$, and all quantities are in atomic units.

g) ϵ is the orbital energy.

ment with the experimental vertical excitation energy (7.6 eV)[†] and, in contrast to previous calculations, is below it. Thus, the correlation energy of the open-shell state is less than that of the closed-shell ground state as we might reasonably expect. The calculated oscillator strength of the transition is $f_{HF} = 0.15$ whereas the experimental is $f_{exp} \approx 0.3$. Thus the use of the usual valence-type basis set to describe this state is a severe restriction. As we shall see below, the planar V state is just *not* a valence state.

It is of interest to note that the $n\pi^*$ orbitals of the $1\pi^*$ Hamiltonian for the excited singlet state closely correspond to the self-consistent orbitals of the higher excited states^{††}. Using these orbitals we predict additional $^1B_{3u}$ states at 8.11 eV and 8.78 eV^{†††} (all other states were unbound). The oscillator strength for the transition to the 2^1B_{3u} ($\pi\pi^*$) state is $f_{HF} = 0.06$ and the $\langle z^2 \rangle$ for

[†] Assuming, of course, that the experimental value does indeed correspond to the vertical excitation energy.

^{††} In fact, within the restriction that the core does not change, these orbitals are the variationally correct orbitals.

^{†††} More diffuse basis functions would be required to adequately describe the 3^1B_{3u} ($\pi\pi^*$) state.

the $2\pi^*$ orbital is 186.668 au. Both of these states are Rydberg states as would be expected.

To better understand the relationship between the N, T and V states, we will examine the orbital representations of the excited states. First consider a minimum basis set representation of the π - and π^* -orbitals. Then, in terms of the atomic basis set $\{2p_a, 2p_b\}$, we obtain for the spatial part of the π wavefunctions

$$T : 2p_a(1)2p_b(2) - 2p_b(1)2p_a(2)$$

$$V : 2p_a(1)2p_a(2) - 2p_b(1)2p_b(2)$$

The triplet state is just the antibonding state corresponding to the valence bond ground state; hence, its charge distribution should be somewhat similar to that of the ground state, in agreement with the above calculation. The excited singlet state, however is an *ionic* state [8] and as such would be poorly represented by the above wavefunction - we clearly must allow the orbital exponents of the basis functions in the π - and π^* -orbitals to be different. If $\zeta_{\pi^*} \neq \zeta_{\pi}$, then the wavefunction for the V state is a sum of two terms: (1) a split-shell ionic component, $[2p_a(1)2p'_a(2) +$

Table 2

Complete pi-electron configuration interaction calculations on the ground, $N(^1A_{1g})$, and $(\pi\pi^*)$ excited, $T(^3B_{3u})$ and $V(^1B_{3u})$, states of ethylene. For each state the core is obtained from the corresponding restricted Hartree-Fock wavefunction. Calculations were for the ground state geometry. Except as noted, all quantities are in atomic units. a)

Basis sets ^{b)}	Ground state	Excited states	
	$N(^1A_{1g})$	$T(^3B_{3u})$	$V(^1B_{3u})$
	Valence	Augm*td	Augm*td
E_{CI}	-78.0463	-77.8919	-77.7422
ΔE (eV)	-	4.22	8.28
f	-	-	0.12
$\langle \pi^* x^2 \pi^* \rangle^c$	-	3.8539	41.4570
$\langle \pi^* y^2 \pi^* \rangle^c$	-	0.9172	13.5050
$\langle \pi^* z^2 \pi^* \rangle^c$	-	2.7517	40.5151

a) See footnote a of table 1.

b) See ref. [7] and footnotes c, d and e of table 1.

c) Expectation values correspond to the $1\pi^*$ natural orbital in the CI expansion.

+ $2p'_a(1)2p_a(2)$] - [$2p_b(1)2p'_b(2) + 2p'_b(1)2p_b(2)$] and (2) a covalent component, [$2p_a(1)2p'_b(2) + 2p'_b(1)2p_a(2)$] + [$2p'_a(1)2p_b(2) - 2p_b(1)2p'_a(2)$]. Because of the ionic nature of the wavefunction, we expect $\zeta\pi^* \ll \zeta\pi$, as is indeed found. All previous *ab initio* calculations [3-5] on the V state either explicitly or implicitly (i.e., by the choice of basis set) assumed that $\zeta\pi^* \approx \zeta\pi$.

Since the diffuse nature of the V state of ethylene is a consequence of the ionic character of the wavefunction, such behavior is expected to be general. In fact, calculations by Phillipson and Mulliken [9] on the lowest $1,3\Sigma_u$ state of H_2 first indicated this trend of T and V states over a decade ago. More recently, in calculations invoking the π -electron approximation, Huzinaga [10] obtained a diffuse π^* -orbital for the V state of ethylene and Taketa et al. [11] found a low exponent for the π_g -orbital in the $3\Sigma_u^+$ state of O_2 (but, as expected, only after they dropped the equivalence restrictions on the π_g -orbitals). However, the neglect of the (attractive) exchange interaction inherent in the Goepfert-Mayer-Sklar formulation of the σ -core potential used by both of these authors may cause the very loosely bound π^* (or π_g)-orbital to be unbound, in which case the optimum orbital exponent would be zero. In fact, neglect of the exchange interaction with the σ -core for the *ab initio* calculations on ethylene presented here does indeed lead to an unbound π^* -orbital.

Robin, Hart and Kuebler [12] have also suggested that diffuse basis functions might be required in excited state calculations. However, they based their analysis of the problem on a virtual orbital approximation for the excited states. Such a representation of the excited state wavefunction is completely inadequate [13]. For example, in the present case the $1\pi^*$ -(virtual) orbital from the ground state calculation using the valence basis set augmented with three diffuse functions had $\epsilon = +0.0122$ au and $\langle z^2 \rangle = 224.519$ au and led to excitation energies of 9.1863 and 9.1868 eV for the T and V states, respectively[†]. In fact, were the molecular Hartree-Fock equations for the ground state of such a neutral system to be solved exactly, all the virtual orbitals would probably correspond to continuum states[†].

The all-electron calculations on ethylene by both Schulman, Moskowitz and Hollister [3] and Kaldor and Shavitt [4] used a valence basis set and the virtual orbital approximation for the excited state^{††}. Thus, they obtained excitation energies for the V state which are far too high. Basch, Robin and Kuebler [5], in an attempt to circumvent the use of virtual orbitals, proposed that the restricted Hartree-Fock equations be solved for the triplet state and the set of orbitals so obtained be used to construct the corresponding singlet wavefunction. However, as we have seen, the spatial distributions of the $(\pi\pi^*)$ singlet and triplet states are vastly different. To see why this is so, we note that the Hartree-Fock Hamiltonians for the π^* -orbital in the T and V states are

$$h_{\pi^*} = h + 2J_C - K_C + J_{\pi} - K_{\pi} \quad \text{Triplet}$$

$$h_{\pi^*} = h + 2J_C - K_C + J_{\pi} + K_{\pi} \quad \text{Singlet}$$

where h contains the kinetic energy and nuclear attraction terms, $2J_C - K_C$ represents the averaged electron-electron interaction with the σ -core, and J_{π} and K_{π} are the usual Coulomb and exchange operators. Thus, the singlet and triplet Hamil-

[†] Improved virtual orbitals [13] (which within the restriction that the core does not change, are the correct variational orbitals) lead to much improved results. Thus, with this expanded basis set such frozen core SCF wavefunctions predict excitation energies of 3.45 and 8.33 eV for the T and V states, and $\langle z^2 \rangle$ for the π^* -orbital of 2.7506 and 26.3407 au, respectively.

^{††} Although the results were never reported, self-consistent open-shell calculations on the V state were carried out by Schulman, Moskowitz and Hollister (see footnote 16 in ref. [3]). Presumably, only a valence basis set was employed.

tonians for the π^* orbital differ by $2K_{\pi}$. If this exchange interaction is large, as it is in the lowest ($\pi\pi^*$) states, we expect the singlet π^* -orbital to be significantly more diffuse than the triplet orbital since this interaction is repulsive in the singlet Hamiltonian.

On the other hand, for some states, such as Rydberg states as well as some valence states, the exchange interaction is quite small and it is a better approximation to assume that the singlet and triplet orbitals are the same.

From calculations on the negative ions of such atoms as hydrogen and lithium [14], we know that split-shell wavefunctions tend to exaggerate the diffuse nature of the loosely bound orbital. Inclusion of angular correlation produces a much more accurate charge distribution. In molecules a dominant type of correlation is left-right correlation along a bond or, in valence bond language, the optimum mixing of the covalent and ionic components of the wavefunction. To assess the effects of this type of correlation on the nature of the V state, we carried out a complete configuration interaction (CI) calculation on the π -electron system. In each case the σ -core was that obtained from the corresponding SCF calculation and only the configurations arising from the π - and π^* -orbitals were considered. The results of these calculations are presented in table 2 (the orbital expectation values are for the appropriate natural orbital in the CI expansion).

From table 2 we see that although π -electron CI has a pronounced effect on the ground state, lowering the energy by 0.88 eV, it has a negligible effect on the T and V excited states. Thus, the excitation energy for the triplet state is now in rather good agreement with experiment (4.2 versus 4.6 eV), while for the singlet it is slightly too high (8.28 eV versus 7.6 eV)†. Evidently, ionic-covalent (or left-right) mixing is not nearly as important in these excited states as it is in the ground state. From table 1 we also note that CI on the V state caused only a slight contraction in the π^* -orbital. It is, however, possible that "angular" correlation around the bond is important in describing the π -charge distribution and would lead to some contraction of the V state. Of course, the spatial extent of the V state in its equilibrium configuration with two CH_2 groups rotated 90° relative to each other need not be as

diffuse as it is for the planar configuration.

We should point out here that if the σ -core from the ground state is used in the V state CI calculation, we obtain $\Delta E(V) = 8.90$ eV, $f = 0.25$ and $\langle z^2 \rangle = 27.09$ au. This is an indication of the minimum, unavoidable error involved in calculations (such as those based on the π -electron approximation) which assume a frozen σ -core (e.g. [15]).

Frozen core SCF calculations have also been carried out on the $1,^3\text{B}_{3g}(1b_{1g} \rightarrow \pi^*)$ and $1,^3\text{B}_{2g}(3a_g \rightarrow \pi^*)$ excited states. The corresponding excitation energies are (9.50, 8.92 eV) and (10.22, 9.50 eV). In each case the π^* -orbital was found to be valence like. More complete calculations will be presented at a later time.

Further work on the T and V states of ethylene (including the effects of changes in geometry (particularly twisting) and the use of further CI) as well as on other important valence and Rydberg states is in progress and will be reported in due course.

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† See footnote on p. 49.