

MULTICONFIGURATION WAVEFUNCTIONS FOR THE LOWEST ($\pi\pi^*$) EXCITED STATES OF ETHYLENE

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Ab initio calculations have been carried out for the $T(^3B_{1u})$ and $V(^1B_{1u})$ states of ethylene in a planar nuclear configuration. A "double-zeta" gaussian basis, augmented by diffuse functions, was used. A wide variety of configuration interaction wavefunctions (including as many as 1605 configurations), optimized by the iterative natural orbital method, were computed. The calculations predict the $^1B_{1u}$ state to lie 3.8–4.1 eV above the $^3B_{1u}$ state. The spatial extent of the triplet state is that of a normal valence state with $\langle r^2 \rangle \approx 12 \text{ bohr}^2$. The singlet state, on the other hand, is found to be quite diffuse or Rydberg-like, $\langle r^2 \rangle \approx 35 \text{ bohr}^2$; electron correlation was found to decrease $\langle r^2 \rangle$ by 30% from the Hartree–Fock value (52 bohr²). This result is not consistent with simple notions concerning π -electron theory.

1. Introduction

The low-lying ($\pi\pi^*$) states of ethylene are of great interest, both theoretically and experimentally, because they serve as prototypes for the description of the low-lying excited states of larger unsaturated systems [1]. With the ethylene molecule in the yz -plane,

z being the carbon–carbon axis, the Hartree–Fock configuration for the ground state (planar, D_{2h} symmetry) is [2,3]

$$N(^1A_g) : 1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2 \quad (1)$$

This state is often denoted as $N(\pi^+)$. Replacing one of the $1b_{3u}(\pi)$ orbitals with a $1b_{2g}(\pi^*)$ orbital gives rise to the triplet, $T(\pi\pi^*)$, and singlet, $V(\pi\pi^*)$, states. The

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Hartree-Fock configuration for these excited states is

$$T(^3B_{1u}), V(^1B_{1u}): 1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 \\ 1b_{3g}^2 1b_{3u} 1b_{2g} \quad (2)$$

The experimental results have been interpreted in terms of a vertical excitation energy of 4.4–4.6 eV for the T state [4] and 7.6 eV for the V state [5].

Of particular interest here is the controversy which has arisen since the theoretical prediction of Dunning et al. [6] that in the planar geometry the V state is a diffuse, Rydberg-like state. The stimulus for the calculations of Dunning et al. was the fact that earlier ab initio calculations [7] had predicted the $V(^1B_{1u})$ state to lie 10–13 eV above the ground state, in marked contrast to the experimental result of 7.6 eV. By including diffuse $2p\pi$ functions in the basis set, Dunning et al. [6] found that the calculated excitation energy decreases drastically, to 8.28 eV. The planar V state was clearly Rydberg-like, the $\langle x^2 \rangle$ (with \hat{x} normal to the plane of the molecule[†]) ranging from 50.6 bohr² (SCF) to 49.0 bohr² (π -electron CI). By comparison, for the N and T states $\langle x^2 \rangle = 12.0$ and 11.8 bohr² (SCF)^{††}. The diffuse character of the V state had been noted much earlier by Huzinaga [8], but the approximate nature of the calculation left the matter in doubt.

Although the calculations of Dunning et al. [6] are certainly correct, there has been considerable controversy concerning whether in fact the $V(\pi\pi^*)$ state is Rydberg-like. Arguing that the experimental evidence

[†] Note that the coordinate system used by Dunning et al. [6] differs from that used here, the \hat{x} and \hat{z} coordinates being interchanged.

^{††} In an orbital model such as the Hartree-Fock model, it is instructive to analyze the orbital contributions to a given property. Thus, for the V state we find that $\langle \pi|x^2|\pi \rangle = 2.2$ bohr² and $\langle \pi^*|x^2|\pi^* \rangle = 42.1$ bohr², while for the T state $\langle \pi|x^2|\pi \rangle = 2.3$ bohr² and $\langle \pi^*|x^2|\pi^* \rangle = 2.7$ bohr². The contribution of the σ core to $\langle x^2 \rangle$ is 6.4 bohr² in the V state and 6.8 bohr² in the T state. It is clear that the Rydberg-like character of the V state is directly attributable to the diffuse π^* -orbital.

[‡] The second moments, x^2 , y^2 and z^2 , of the charge distribution have been used, since the first moments vanish by symmetry. The second moments quoted include a nuclear contribution (for $\langle y^2 \rangle$ and $\langle z^2 \rangle$): the electronic contribution is taken as positive, the nuclear contribution as negative.

mitigated against a diffuse V state, Basch and McKoy [9] suggested that this result was due to a deficiency in the Hartree-Fock model. Their interpretation of the available data, both theoretical and experimental, led them to conclude that the "true" V state is a normal valence state "unrelated to any bound state obtained in the Hartree-Fock approximation ...".

Prompted by the theoretical activity, Miron et al. [10] reviewed a variety of experimental results relevant to the nature of the V state. In addition, they carried out an investigation of the $N \rightarrow V$ transition in liquid and solid krypton. On the basis of a small liquid-solid shift (≈ 100 cm⁻¹) Miron et al. concluded that the V state of ethylene is a valence state and not the diffuse, Rydberg-like state predicted by theory. In summary, they remark that the "experimental information seems to be somewhat more reliable than the current theoretical analysis of the problem". The earlier results of Robin and Kuebler [11] on the effects of moderate pressures of N₂ on the $N \rightarrow V$ transition were also taken to indicate that the V state is valence in character.

A complication in describing the V state of ethylene was pointed out by Dunning et al. [6] who noted that the π^* -orbital should tighten up as the molecule is twisted from planar to equilibrium nuclear configuration (with the two CH₂ groups rotated 90° relative to one another). This implies a more valence-like charge distribution at the equilibrium configuration of the V state. Indeed, Basch and McKoy [9] reported unconverged Hartree-Fock calculations for this configuration and found that the resulting π orbitals were valence-like. This conclusion was confirmed by Hunt et al. [12]^{‡‡}. Further, Hunt et al. solved for the self-consistent orbitals for various twisting angles (0°, 30°, 60° and 90°) and found that the π^* orbital changes smoothly from Rydberg-like to valence-like as the molecule is twisted. This change in the character of the V state upon twisting must, of course, be taken into account in interpreting the experimental data.

^{‡‡} Basch and McKoy [9] located the twisted V state 0.6 eV below the planar state. Hunt et al. [12], solving for the states self-consistently [13], find a twisting barrier of 1.2 eV. This discrepancy may be due to the approximate way Basch and McKoy solved the Hartree-Fock equations at $\theta = 90^\circ$.

The calculations discussed above, however, serve to clarify rather than answer the question of interest: is the V state of ethylene Rydberg-like *for the planar geometry*? To help answer this question we present here the results of an extensive series of CI calculations on the T and V states of planar ethylene.

2. Method of calculation

The basis set used on the two carbon atoms in ethylene was the (9s5p)/[4s2p] contracted gaussian double zeta basis proposed by Dunning [14]. In addition, two sets of diffuse 2p functions, with exponents $\zeta = 0.0250$ and 0.0077 , were added to each carbon atom[†]. These diffuse functions allow the wavefunction the freedom to take on that degree of Rydberg character consistent with the lowest total energy obtainable. The hydrogen basis was the (4s)/[2s] set [14]. The most serious deficiency in the present basis set is the lack of a set of 3d functions centered on each carbon. It is, however, very unlikely that our results would be qualitatively changed by a further expansion of the basis set.

All calculations were carried out at the equilibrium geometry of the ground state of ethylene [2] with $R_{CH} = 1.086 \text{ \AA}$, $R_{CC} = 1.339 \text{ \AA}$ and $\angle HCH = 117.6^\circ$. The molecule lies in the yz-plane with z along the carbon-carbon bond axis and x perpendicular to the molecular plane.

To obtain a nearly optimum set of orbitals for the CI calculations, the iterative natural orbital procedure [15] was used. That is, both the configuration coefficients and the orbitals were allowed to vary during the calculations. The configurations included in the present calculations were selected on the basis of the following two criteria:

(1) *Number of orbitals doubly occupied.* Holding the carbon 1s orbitals ($1a_g$ and $1b_{1u}$) doubly occupied in all configurations is a chemically reasonable approximation [16]. However, the number of configurations included may be further reduced by also doubly occupying the next two orbitals ($2a_g$ and $2b_{1u}$). Even more severe approximations are to correlate only the $3a_g^2 1b_{3u} 1b_{2g}$ or the $1b_{3u} 1b_{2g}$ configura-

tions. (In the latter case, only the π and π^* orbitals have been included in CI.)

(2) *Classes of configurations included.* Three different types of CI wavefunctions, labeled MC1, MC2 and MC3 in an earlier paper [17], were investigated. In order to explain the structure of wavefunctions MC1 and MC2, it is necessary to enumerate the symmetries of the molecular orbitals which can be constructed for ethylene from a minimum basis set. In addition to the occupied Hartree-Fock ground state orbitals, eq. (1), a minimum basis set yields $4a_g$, $3b_{1u}$, $4b_{1u}$, $2b_{2u}$, $2b_{3g}$ and $1b_{2g}$ orbitals. Then, MC1 includes the Hartree-Fock configuration plus all single and double excitations into the above six valence orbitals. MC2 includes all configurations differing by no more than two orbitals from the Hartree-Fock configuration, in which no more than a single electron occupies an orbital outside the above set (the first order wavefunction) [18]. Finally, MC3 includes the SCF function plus *all* singly- and doubly-excited configurations.

It is known from accurate calculations on atoms [19] that, if the coefficient of the SCF configuration is 0.9 or greater, then MC3, i.e., Hartree-Fock plus all singles and doubles, will recover 95% or more of the correlation energy obtainable with a given basis set. MC1 and MC2 are designed, not to account for all of the correlation energy, but to account, in varying degrees, for those correlation effects unique to the states of interest. It has been found that MC1 and MC2 contain the most important features of MC3 [17].

3. Results and discussion

Tables 1 and 2 summarize the present calculations on the ethylene molecule. Table 1 contains selected results from all of the CI calculations carried out on the V state; table 2 is a summary of the results of selected calculations on both the T and V states.

The Hartree-Fock calculation reported in table 1 agrees with the finding of Dunning et al. [6] that in the Hartree-Fock approximation the (planar) V state is diffuse and Rydberg-like. The calculated excitation energies [6] are $\Delta E(T \leftarrow N) = 3.33 \text{ eV}$ and $\Delta E(V \leftarrow N) = 7.41 \text{ eV}$. The Hartree-Fock excitation energies are too low because the π orbitals of the N state are not as well correlated as those of the T and V states.

To obtain a more consistent description of the N,

[†] All three components of the 2p functions, ($2p_x$, $2p_y$, $2p_z$), were added to the basis set.

Table 1
Convergence of CI calculations on the $V(\pi\pi^*)$ state of ethylene. Ground state geometry (all quantities in atomic units)

Number of SCF orbitals doubly occupied	Type of CI	Number of configurations	Energy	$\langle x^2 \rangle$
	Hartree-Fock	1	-77.7363	51.8
6	MC1	17	-77.7465	-
6	MC2	167	-77.7584	44.7
6	MC3	492	-77.7610	41.1
4	MC2	479	-77.8005	38.8
4	MC2 + all singles ^{a)}	539	-77.8015	-
4	MC3	1394	-77.8182	35.4
2	MC1	124	-77.8312	-
2	MC2	1018	-77.8716	38.3

a) Singles from all 4 inner orbitals.

T, and V states, we can carry out π -electron CI calculations on all three states. Using the σ cores obtained from the Hartree-Fock calculations on the corresponding states, the π -electron CI calculations of Dunning et al. [6] gave excitation energies of $\Delta E(T \leftarrow N) = 4.22$ eV and $\Delta E(V \leftarrow N) = 8.28$ eV. The π -electron CI calculations (even the one including 3d δ functions[†], i.e., 3d functions of symmetry b_{2g} and a_u ; see table 2) had little effect on the charge distribution of the V state. Similar calculations were later reported by Buenker et al. [20], who also carried out calculations on a number of other excited states of ethylene.

The many-electron CI calculations reported in tables 1 and 2 correlate the following orbital configurations

$$3a_g^2 1b_{3u} 1b_{2g},$$

$$1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u} 1b_{2g},$$

$$2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u} 1b_{2g}.$$

In all cases except the last, MC1, MC2 and MC3 calculations were carried out on both the T and V states (see, e.g., table 1). For the last configuration, which involves correlating all but the carbon inner shell orbitals, only MC1 and MC2 calculations were carried out. However, we include in table 2 estimates for an MC3

[†] Two 3d δ functions, $\zeta = 0.4712$ and 0.1396 , were added to each carbon basis. The exponents were scale optimized.

calculation on this configuration.

The calculated singlet-triplet splitting is 3.9 ± 0.1 eV (based on the estimate and the last four calculations in table 2). Although comparable calculations were not carried out on the ground state, the triplet excitation energy, $\Delta E(N \rightarrow T) = 4.22$ eV, obtained from the π -electron CI calculation [6] should be fairly reliable (± 0.2 eV). Adding the calculated singlet-triplet splitting to this, we obtain $\Delta E = 8.1$ eV for the $N \rightarrow V$ transition. Although this value is somewhat higher than the assigned experimental vertical excitation energy, $\Delta E_{\text{exp}} = 7.6$ eV, it should be near the limit of that obtainable with the present basis set.

One of our main concerns was to determine whether, as predicted by Basch and McKoy [9], the inclusion of electron correlation would yield a valence-like V state. The results given in table 2 suggest that this is not the case. However, the size of the V state does decrease significantly upon inclusion of electron correlation. For example, the expectation value of x^2 decreases from 52 bohr² to ≈ 35 bohr², a decrease of 30%. For comparison, the second moments for the T state are essentially unchanged. Since the T state value of $\langle x^2 \rangle$ is calculated to be ≈ 12 bohr², we see that the V state has a charge distribution considerably more diffuse, or Rydberg-like, than a normal valence state. As stressed by Dunning et al. [6], "... the planar V state is just *not* a valence state" (original italics). Neither can the $V(\pi\pi^*)$ state be considered a normal Rydberg state [6, 12], e.g., it is significantly less diffuse than the $2^1A_g(1\pi 2\pi)$ Rydberg state (for which

SCF calculations [12] give $\langle x^2 \rangle \approx 65 \text{ bohr}^2$ even though this latter state belongs to the $n = 3$ Rydberg complex ($3p\pi$), and it is undoubtedly affected by electron correlation to a greater extent than is a normal Rydberg state.

The present results suggest that the Hartree-Fock description of the V state of ethylene is roughly correct. Thus, the CI calculations corroborate the earlier finding that the charge distributions of the iso-configurational T($\pi\pi^*$) and V($\pi\pi^*$) states are markedly different[†]. In addition, the calculated singlet-triplet separations are in good agreement: 3.8–4.1 eV for the CI calculations versus 4.0–4.1 eV from the Hartree-Fock calculations [6]. Although the effects of electron correlation certainly cannot be neglected, the basic characteristics of the ($\pi\pi^*$) states of ethylene are those predicted by the Hartree-Fock model.

A possible objection to our theoretical procedure involves our use of the iterative natural orbital procedure. Although four iterations were typically used, it could be argued that by starting with the Hartree-Fock orbitals for the V state, the diffuse π^* orbital never had a chance to contract to a reasonable size. Therefore, we carried out an additional calculation on the V state, but starting with the SCF orbitals for the T state. This calculation included 539 configurations, being structurally identical to the sixth line of table 1. With these initial orbitals the iterative natural orbital procedure converged much more slowly, requiring 10 iterations to stabilize the energy to 10^{-4} hartree. In essence, the ten iterations were required to change the π^* orbital from valence to diffuse in character. For the final wavefunction the energy was -77.8032 hartree and the calculated values of $\langle x^2 \rangle$, $\langle y^2 \rangle$ and $\langle z^2 \rangle$ were 33.4, 16.0 and 36.2 bohr².

While the present work was in progress, we discovered that two other groups were carrying out calculations on the V state of ethylene. Both Buenker et al. [20], whose calculations were discussed earlier, and Morokuma [21] used basis sets similar to ours. The calculations of both Buenker et al. and Morokuma led to a description of the V state in agreement with that given here. These calculations are, however, less exhaustive than those presented here. CI calculations

on a number of states of ethylene, including σ - π correlation effects, have recently been reported by Buenker et al. [23]. Buenker et al. also obtain a diffuse ($\pi\pi^*$) singlet state in the planar configuration, although these calculations are more limited than those presented herein. In fact, Buenker et al. make the perhaps startling suggestion that the state termed V by Merer and Mulliken [3] is not the ${}^1B_{1u}(\pi\pi^*)$ state, but rather a ${}^1B_{1g}(\pi 3p_{CH})$ Rydberg state. However, Hunt et al. [12] have also studied these states and reach conclusions more in agreement with the usual assignment.

More recently we have learned of CI calculations by Whitten [23] which place the V state of ethylene at 8.1 eV with $\langle x^2 \rangle = 10$ –15 bohr². Although such a result would be in good agreement with the predictions of Basch and McKoy, it is not consistent with the results of the calculations presented here.

The diffuse, Rydberg-like V($\pi\pi^*$) state obtained here is also inconsistent with the results obtained by McKoy and co-workers [24,25] using the excitation operator method. Although their calculations predict excitation energies of 9.4 eV [24] and 7.9 eV [25], the latter being in good agreement with that obtained here, they also find that "the π^* orbital of the V state, although somewhat more diffuse than the π^* orbital of the T state, is a valence-like molecular orbital" with $\langle \pi^* | x^2 | \pi^* \rangle = 9.0 \text{ bohr}^2$ [25]. From the present CI calculations we estimate that for the π^* principal natural orbital $\langle \pi^* | x^2 | \pi^* \rangle \approx 27 \text{ bohr}^2$. The excitation operator approach for calculating the excited states of atomic and molecular systems has also been discussed by Dunning [26] and, more recently, by Ostlund and Karplus [27].

Following Whitten's suggestion we also carried out calculations excluding the diffuse 2p-functions from the basis set. Doubly occupying only the two carbon inner shell orbitals, MC1 and MC2 calculations were carried out. The SCF, MC1 and MC2 energies are given in table 3. Here we see that the basis set error is 1.72 eV for the SCF calculation and 0.84 eV for the CI calculation (MC2). The above trend is consistent with the observed changes in the charge distribution upon inclusion of correlation effects.

It has been suggested [9,22,24,25] that there is a valence V($\pi\pi^*$) state of ethylene distinct from the diffuse, Rydberg-like V($\pi\pi^*$) state such as is found here. Although eliminating the diffuse functions nec-

[†] The reason for the marked difference in the charge distributions of the T and V states has been discussed by Dunning et al. [6]. See also [12].

Table 3
Comparison of Hartree-Fock and CI calculations on the $V(\pi\pi^*)$ state with and without diffuse 2p-functions. The CI calculations correlate the $2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u} 1b_{1g}$ configuration

Type of calculation	Energies		Energy differences ^{c)}	
	without diffuse functions ^{a)}	with diffuse functions ^{b)}		
SCF	-77.6731 H	-77.7363 H	0.0632 H	1.72 eV
MC1	-77.7978	-77.8312	0.0334	0.91
MC2	-77.8408	-77.8716	0.0308	0.84

a) The [4s2p/2s] basis set was used.

b) The full [4s2p/2s] basis augmented with two sets of diffuse 2p-functions was used.

c) 1 hartree = 27.2117 eV.

essarily leads to a state with a valence-like charge distribution 0.84 eV above the diffuse $V(\pi\pi^*)$ state, this does not imply the presence of a higher-lying valence ($\pi\pi^*$) state. For example, the wavefunction for the ($\pi\pi^*$) state obtained with the double zeta basis is not orthogonal to the wavefunction obtained with the augmented basis set and, thus, the resulting energy is not an upper bound on the energy of a higher excited state (Hylleraas-Undheim-MacDonald theorem [28]). In fact, the wavefunctions obtained with the double zeta and augmented double zeta basis are expected to have high overlap, so that the former wavefunction is no more than a restricted representation of the latter. Confirmation of the occurrence of a higher-lying valence ($\pi\pi^*$) state would require the simultaneous calculation of the wavefunctions of at least the lowest two states of $^1B_{1u}$ symmetry. Since the orbitals of such a valence state would be quite different from those of the lower-lying diffuse state(s), a very, very large CI, including several thousand configurations, would be necessary.

4. Concluding remarks

An extensive series of CI calculations on the $V(\pi\pi^*)$ state of ethylene indicate that in the planar configuration the $V(\pi\pi^*)$ state is a diffuse, Rydberg-like state with a vertical excitation energy of ≈ 8.1 eV. Since the $T(\pi\pi^*)$ state is a normal valence state, there exists a gross disparity in the description of the electronic structure of these two iso-configurational states. Although electron correlation was found to be of impor-

tance in the description of the $V(\pi\pi^*)$ state, the Hartree-Fock wavefunction does describe the essential characteristics of the state.

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