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A $2p\pi$, $3d\pi$ Valence Bond Wave Function for the $^1B_{1u}$ State of Ethylene

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A $2p\pi$, $3d\pi$ valence bond wave function for the lowest $^1B_{1u}$ state of the π-system of ethylene is variationally optimized with respect to the atomic orbital exponents using a non-empirical π-approximation. The resulting energy compares favourably with previous calculations and leads to a satisfactory value for the lowest $^1A_{1g} - {}^1B_{1u}$ transition energy. The optimized exponent for the $2p\pi$ orbital is close to the Slater value whereas the exponent for the $3d\pi$ orbital is found to be nearly hydrogenic. The implications of this result are discussed in some detail.

Für den tiefsten $^1B_{1u}$-Zustand des π-Elektronensystems des Äthylens wird nach der Variationsmethode eine $2p\pi$, $3d\pi$-Valenzbindungs-Wellenfunktion bezüglich der Orbitalkoeffizienten optimiert, wobei eine nicht-empirische π-Approximation zugrunde gelegt wird. Die berechnete Energie stimmt gut mit den Ergebnissen vorausgegangener Rechnungen überein. Für den tiefsten $^1A_{1g} - {}^1B_{1u}$-Übergang ergibt sich ein befriedigender Energiewert. Der optimierte Orbitalkoeffizient für das $2p\pi$-Orbital stimmt gut mit dem nach der Slaterschen Regel bestimmten Koeffizient überein, während man für den $3d\pi$-Orbitalkoeffizienten einen Wert findet, der dem des Wasserstoffs ähnlich ist.

Une founction d'onde V.B.$(2p_\pi, 3d_\pi)$ est optimée pour l'état $^1B_{1u}$ d'aethylen. L'energie calculé aussi que l'energie de transition la plus basse $^1A_{1g} - {}^1B_{1u}$ est en bon accord avec des valeurs connues.

1. Introduction

A $1s$, $2p\sigma$ valence bond wave function has recently [1, 2] been employed with some success for the $B\,{}^1\Sigma_u^+$ state of the hydrogen molecule. The analogy between the hydrogen molecule and the π-system of ethylene suggests a similar treatment of the lowest $^1B_{1u}(V)$ state of ethylene using a $2p\pi$, $3d\pi$ valence bond wave function. In this note we shall report the results of such a calculation in which the atomic orbital exponents for the $2p\pi$ and $3d\pi$ orbitals in the π-system are variationally optimized. The calculations are performed entirely within the conventional non-empirical π-approximation [3] with neglect of exchange interactions between core-electrons and π-electrons.

The low-lying excited states of ethylene have been extensively studied (see Refs. [3, 4 and 5] for bibliographies). The treatment which is most akin to the present is the molecular orbital calculation by Huzinaga [6] where the $2p\pi$ atomic orbital exponents in the bonding and antibonding molecular orbitals are used as independent variational parameters. For the $^1B_{1u}$ state this leads to an unexpectedly low value for the orbital exponent in the antibonding molecular orbital. The figure quoted [6] is 0.4 (compared to 1.6 in the bonding orbital), however, computational difficulties did not allow a determination of the actual energy minimum which apparently occurs at an even lower value of the orbital exponent (see footnote 9 of Ref. [6]).

The present valence bond approach leads to a rather satisfactory agreement with the experimental transition energy, but again at the expense of producing a very diffuse atomic orbital, namely a nearly hydrogenic $3d\pi$ orbital.

2. Wave Function and Energies

The Hamiltonian operator for the two mobile electrons in the planar ethylene molecule can in the π-approximation [3] be written (in atomic units):

$$\mathscr{H} = \mathscr{H}_{\mathrm{CC}} + \sum_{i=1}^{2} V_{\mathrm{H}}(i) \tag{1}$$

where

$$\mathscr{H}_{\mathrm{CC}} = \sum_{i=1}^{2} \left[-\frac{1}{2} \nabla_i^2 + V_{\mathrm{C}}(i) \right] + \frac{1}{r_{12}} \,. \tag{2}$$

$V_{\mathrm{C}}(i)$ represents the coulomb potential energy of electron i in the field of the two carbon cores, each consisting of a nuclear core of charge $+4$ and three electrons; $V_{\mathrm{H}}(i)$ is the coulomb potential due to the four hydrogen atoms. Each of the core-electrons is assigned to a simple Slater orbital. In the case of a carbon atom these core orbitals are a (nodeless) $2s$ orbital and two $2p$ orbitals in the molecular plane all with orbital exponent 1.59; in the hydrogen atom the electron is assigned to a $1s$ orbital with exponent 1.0. Since exchange potentials from the core are neglected the operator (2) becomes independent of the state of hybridization of the carbon orbitals. The explicit separation of the total π-Hamiltonian, Eq. (1), into a carbon-carbon part and a hydrogenic part is made for computational reasons (*vide infra*).

In the present approach the trial wave function for the lowest ${}^1B_{1u}$ state is a valence bond function constructed from $2p\pi$ and $3d\pi$ atomic orbitals on the two carbon atoms. The proper combination of these orbitals which transforms as ${}^1B_{1u}$ is:

$$\Psi = N[p_a(1)\, d_b(2) + d_b(1)\, p_a(2) - d_a(1)\, p_b(2) - p_b(1)\, d_a(2)] \tag{3}$$

where we have omitted the two-electron spin-function for the singlet state. N is a normalisation factor and the orbitals are:

$$p_a = (\zeta_p^5/\pi)^{\frac{1}{2}}\, r_a \sin\theta_a \cos\varphi\, e^{-\zeta_p r_a},$$

$$d_a = (2\zeta_d^7/3\pi)^{\frac{1}{2}}\, r_a^2 \sin\theta_a \cos\theta_a \cos\varphi\, e^{-\zeta_d r_a}$$

with similar expressions for the orbitals centered on atom b. The phases in Eq. (3) correspond to local co-ordinate systems with z-axes pointing towards each other. We have used the same molecular geometry as Huzinaga [6] in order to allow direct comparison of the results[1].

The optimal values of the orbital exponents ζ_p and ζ_d are found by minimizing the energy

$$E_{\mathrm{CC}} = \langle \Psi | \mathscr{H}_{\mathrm{CC}} | \Psi \rangle / \langle \Psi | \Psi \rangle \tag{4}$$

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[1] Carbon-carbon distance equal to 1.353 Å, carbon-hydrogen distance equal to 1.071 Å.

with respect to these two non-linear parameters. The neglect of the potentials due to the four hydrogen atoms in the optimization is dictated by want of computer programs which allow an accurate calculation of three-center integrals involving $3d$-orbitals. All the remaining one- and two-center integrals in (4) are calculated exactly with the *DIATOM* program of Corbato and Switendick [7] for a systematic variation of the two orbital exponents. Table 1 shows the total energy of the two π-electrons according to Eq. (4) as function of the orbital exponents in the vicinity of the minimum ($\zeta_p = 1.55$ and $\zeta_d = 0.32$). The resulting minimum energy is -20.321 eV which is a slight improvement over Huzinaga's -20.095 eV (also without the hydrogenic potentials) [6].

Table 1. *Energy of the $2p\pi$, $3d\pi$ wave function as function of the orbital exponents*[a]

ζ_d \ ζ_p	1.50	1.55	1.60
0.20		−20.164	
0.25		−20.270[b]	
0.30	−20.301	−20.317	−20.285
0.32	−20.306	−20.321	−20.289
0.34	−20.304	−20.317	−20.285
0.36		−20.307	
0.38		−20.290	

[a] All energies in eV.

[b] The stability of the results has been checked by calculating this value twice, first with 193 points of integration in the numerical calculation of the integrals yielding -20.2699 eV. and subsequently with 385 points yielding -20.2697 eV.

It is important to note that the procedure leads to a definite extremum albeit a shallow one. We emphasize this point since Yaris, Moscowitz, and Berry [5] have recently warned against the use of very expanded atomic orbitals in the basis set because of the danger of generating unbound functions. The accuracy of the present computations is tested as explained in a footnote to the table and the existence of a definite minimum shows that the optimized function does indeed represent a bound state.

The effect of the four hydrogen atoms can now be taken into account by simple first order perturbation using $V_{\mathrm{H}}(i)$ as the perturbation operator. The necessary approximations in the integral evaluation are outlined in the appendix. The resulting π-electron energy is -21.618 eV which is again slightly lower than Huzinaga's -21.512 eV (including hydrogen potentials), however, the approximations in the calculation of the three-center integrals are somewhat different in the two cases (see appendix).

Table 2 summarizes the results of the present approach and of the molecular orbital calculations by Parr and Crawford [8] and by Huzinaga [6]. The transition energies quoted for the present $2p\pi$, $3d\pi$ valence bond function are obtained by use of the appropriate ground state energies from Huzinaga's calculation. It is observed that the computed transition energy is in rather satisfactory agreement with the experimental value when the hydrogenic potentials are taken into account.

Table 2. *Comparison of calculated energies*[a]

	Parr and Crawford [8]	Huzinaga [6]		Present calculation		Experimental
		without V_H	with V_H	without V_H	with V_H	
${}^1A_{1g}(N)$		-26.413	-28.788			
${}^1B_{1u}(V)$		-20.095	-21.512	-20.321	-21.618	
$E(N-V)$	11.5	6.32	7.28	6.09[b]	7.17[b]	7.6

[a] All energies in eV.

[b] These transition energies are calculated with the appropriate ground state energies from Huzinaga's calculations.

3. Discussion

The classic non-empirical π-approximation treatment of the low-exited states of ethylene is the Parr and Crawford [8] molecular orbital calculation in which the basis orbitals are taken as strict Slater orbitals. Their wave function for the ${}^1B_{1u}$ state is therefore purely ionic with no variational parameters, and it is characteristic that the calculation grossly overestimates the energy of this state and hence the lowest singlet-singlet transition energy (see Table 2). In Huzinaga's calculation [6] the orbital exponents in the bonding and antibonding molecular orbitals are treated as independent, nonlinear variational parameters. The calculated singlet-singlet transition energy is thereby improved to virtual agreement with the experimental value. However, the resulting orbital exponents in the two molecular orbitals turn out to differ strongly (see the introduction).

The present $2p\pi$, $3d\pi$ wave function leads to nearly the same energy as Huzinaga's molecular orbital function, and the two approaches have furthermore one feature in common, namely the appearance of very diffuse atomic orbitals (respectively a $3d\pi$ orbital with $\zeta_d = 0.32$ and a $2p\pi$ orbital with $\zeta_p = 0.4$). These orbital exponents are curiously close to the pure hydrogenic values which means that both approaches assign a high degree of Rydberg character to this state. Furthermore, the effect of having two very different orbital exponents in a two-electron wave function is that one electron stays near the nuclei while the other moves further out, so to speak. A major part of the improvement (relative to Parr's and Crawford's results) which is found in the present treatment and by Huzinaga is therefore undoubtedly associated with an in-out (or vertical) type correlation of the electronic motion[2].

The left-right (or horizontal) correlation of the electrons can be estimated by use of the similarity between the ${}^1B_{1u}$ state of the ethylenic π-system and the ${}^1\Sigma_u^+$ state of the hydrogen molecule. In a previous communication [2] we have analyzed the hydrogenic counterparts to the three types of wave functions considered here for the ${}^1B_{1u}$ state. This analysis placed particular emphasis on the covalent and/or ionic nature of the wave functions (which is just another way of saying electron correlation). The results of the analysis are contained in Fig. 1 of Ref. [2] which shows that the $1s$, $2p\sigma$ valence bond function for the ${}^1\Sigma_u^+$ state leads to a highly ionic electron distribution in spite of its covalent construction.

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[2] It should be noted that we use the word correlation in its literal sense, no reference to a Hartree-Fock scheme is implied.

The important prerequisite for this result is the low value of the $2p\sigma$ orbital exponent which means that a $2p\sigma$ orbital centered at one of the hydrogen nuclei will have its radial maximum in the vicinity of the other nucleus. In the present $2p\pi$, $3d\pi$ valence bond function we encounter essentially the same feature, namely the diffuse $3d\pi$ orbital. By analogy, the electron distribution predicted by the optimized wave function (3) will therefore be expected to be largely ionic again in contrast to its formally covalent appearance.

Table 3. *Overlap integrals between* ${}^1B_{1u}(V)$ *wave functions*

	A	*B*	*C*
A	1.00	0.37	0.30
B		1.00	0.78
C			1.00

A: Parr and Crawford [8] (molecular orbital).
B: Huzinaga [6] (molecular orbital).
C: $2p\pi$, $3d\pi$ valence bond (Eq. (3)).

We shall terminate this section by considering the overlap integrals between the three types of ${}^1B_{1u}$ wave functions we have been discussing. The values of these overlap integrals are given in Table 3 which shows that the present valence bond function and Huzinaga's function have an overlap of about 80%. Since the two wave functions lead to very nearly the same expectation value for the energy we can take the remaining 20% as a crude estimate of the magnitude of the deviation from the lowest exact solution (of ${}^1B_{1u}$ symmetry) for the π-Hamiltonian (1).

4. Concluding Remarks

The results of the preceding sections are obtained within the pure π-approximation which means in particular that excitations of the core electrons have been neglected completely. Recent work on the near ultra-violet spectrum of ethylene, especially by Yaris, Moscowitz, and Berry [5], has shown that the details of the spectrum can be understood only by taking the core-peel transitions explicitly into account. However, the main component of the band (from an intensity point of view) can still be identified with the ${}^1B_{1u}$ π-electron state. The fact that the energy of this transition is so well accounted for in the present calculation supports Huzinaga's claim [6] that a large part of the inaccuracies of previous non-empirical π-electron calculations is associated with the choice of too crude a wave function and not with inherent errors in the π-model. A small number of non-linear variational parameters seems particularly expedient for an improvement of the wave function.

Appendix

The influence of the hydrogen atoms on the μ-electron energy is calculated by first order perturbation theory which gives an energy contribution of

$$\Delta E_{\mathrm{H}} = \langle \Psi \mid V_{\mathrm{H}}(1) + V_{\mathrm{H}}(2) \mid \Psi \rangle / \langle \Psi \mid \Psi \rangle = 2 \langle \Psi \mid V_{\mathrm{H}}(1) \mid \Psi \rangle / \langle \Psi \mid \Psi \rangle . \quad \text{(A.1)}$$

The four hydrogen atoms will for symmetry reasons give identical contributions to ΔE_H in which case Eq. (A.1) can be written:

$$\Delta E_H = 8\langle\Psi \mid V_1(1) \mid \Psi\rangle / \langle\Psi \mid \Psi\rangle \tag{A.2}$$

where $V_1(i)$ is the coulomb potential due to the nucleus and $1s$-electron of hydrogen atom 1:

$$V_1(i) = -\frac{1}{r_{1i}} + \int \frac{1}{r_{ji}} (1s)_1^2(j)\, dv_j\,.$$

Expansion of the energy integral in Eq. (A.2) by use of the wave function (3) gives an expression containing the two-center integrals:

$$\langle p_a \mid V_1 \mid p_a\rangle = \int p_a(1)\, V_1(1)\, p_a(1)\, dv_1\,, \tag{A.3a}$$

$$\langle d_a \mid V_1 \mid d_a\rangle = \int d_a(1)\, V_1(1)\, d_a(1)\, dv_1\,, \tag{A.3b}$$

plus the corresponding terms for the orbitals on atom b, and the three-center integrals:

$$\langle p_a \mid V_1 \mid p_b\rangle = \int p_a(1)\, V_1(1)\, p_b(1)\, dv_1\,, \tag{A.4a}$$

$$\langle d_a \mid V_1 \mid d_b\rangle = \int d_a(1)\, V_1(1)\, d_b(1)\, dv_1\,, \tag{A.4b}$$

$$\langle p_a \mid V_1 \mid d_b\rangle = \int p_a(1)\, V_1(1)\, d_b(1)\, dv_1\,, \tag{A.4c}$$

$$\langle d_a \mid V_1 \mid p_b\rangle = \int d_a(1)\, V_1(1)\, p_b(1)\, dv_1\,. \tag{A.4d}$$

The three-center integrals represent the electrostatic energy of a two-center charge-distribution $\chi_a(1)\,\chi_b(1)$ in the field of a hydrogen atom. These integrals can be evaluated by making the following approximation for the charge-distribution:

$$\chi_a(1)\,\chi_b(1) = \lambda_a \chi_a(1)\,\chi_a(1) + \lambda_b \chi_b(1)\,\chi_b(1)\,. \tag{A.5}$$

The best values for the numerical coefficients λ_a and λ_b are determined by requiring that the total electric charge and the electric dipole moment of the charge-distribution be conserved in the approximation [9]. If the orbitals are equivalent, as in Eqs. (A.4a, b), the center of gravity of the distribution falls halfway between the centers and the result is obviously $\lambda_a = \lambda_b$ which gives the familiar Mulliken approximation [10]:

$$p_a(1)\, p_b(1) = \frac{1}{2} \langle p_a \mid p_b\rangle\, [p_a(1) p_a(1) + p_b(1) p_b(1)] \tag{A.6}$$

and similarly for the distribution $d_a(1)\, d_b(1)$.

In the case of the non-equivalent orbitals, in Eqs. (A.4c, d), the center of gravity of the distribution will be located close to the atom where the $2p\pi$ orbital is centered. This follows from the fact that the $3d\pi$ orbital will have a nearly flat radial function in the region of the neighbouring $2p\pi$ orbital (due to its low orbital exponent). Following Dahl and Ballhausen [11] we shall accordingly use the approximations

$$p_a(1)\, d_b(1) = \langle p_a \mid d_b\rangle\, p_a(1)\, p_a(1)\,, \tag{A.7a}$$

$$p_b(1)\, d_a(1) = \langle p_b \mid d_a\rangle\, p_b(1)\, p_b(1)\,, \tag{A.7b}$$

where the conservation of the dipole moment is only approximately fulfilled. In the notation of Dahl and Ballhausen [11] the charge distributions in Eqs. (A.6) and (A.7) are termed respectively class I and class II distributions.

Eqs. (A.6) and (A.7) allow a reduction of the integrals (A.4) to the integrals (A.3) and the perturbation energy ΔE_{H} can therefore be expressed solely in terms of overlap integrals and the two-center integrals (A.3). These integrals are calculated exactly by the *DIATOM* program [8] and the result is $\Delta E_{\mathrm{H}} = -1.297$ eV (Table 2).

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