was compensated for automatically by an increase in the magnitude of other interactions. Except for δ_1, the values of these integrals are small and may not be significant. However, some type of 1,4 interaction must be introduced; otherwise, certain accidental degeneracies in isobutane (1 a_2 and 4 e) and neopentane (1 t_1 and 1 e) cannot be lifted. The inclusion of a single parameter δ_1 resolves this difficulty.

Eigenvectors of Topological and Bond Orbitals. The coefficients of the eigenvectors of the starting topological orbitals only differ by small amounts (usually less than 10%) from the final bond orbital coefficients (see paragraph at end of paper regarding supplementary material). Also, we remarked previously on the close correspondence of the topological functions to those obtained by Jorgensen and Salem[26] using the LCAO–MO method. This significant result indicates that the molecular connectedness is the main factor determining the molecular wave function, at least for these saturated hydrocarbons.

Applications. We plan to extend the calculations on saturated hydrocarbons to larger acyclic and cyclic alkanes. Calculations on substituted saturated compounds are being carried out, and questions regarding through-bond or through-space interactions between heteroatom or unsaturated moieties are under investigation.

Supplementary Material Available: Listings of topological eigenvector coefficients and the bond orbital wave functions for methane, ethane, propane, isobutane, and neopentane (9 pages). Ordering information is given on any current masthead page.

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Ionization Potentials of H₂O from Valence Bond and Molecular Orbital Wave Functions[1]

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Abstract: A comparison is presented of the H_2O ionization potentials calculated from molecular orbital wave functions using Koopmans' theorem with those calculated from valence bond wave functions using the extended Koopmans' theorem. It is found that the two methods give closely comparable results for the main peaks in the photoelectron spectrum. In addition, the valence bond calculation predicts two additional weak, closely spaced, shake up states which may correspond to a previously unassigned feature near 48 eV in the experimental photoionization spectrum.

I. Introduction

The recent revival of the valence bond (VB) model, both in its traditional form[2] and in various self-consistent-field (SCF) versions either with[3] or without[4,5] artificial orthogonality constraints, has provided a useful alternative to the molecular orbital (MO) model for the interpretation of many molecular properties from ab initio calculations. However, ionization potentials, which are easily obtained from MO wave functions by means of Koopmans' theorem,[6] have not hitherto been obtained as directly from VB calculations. The recently proposed extended Koopmans' theorem[7] (EKT) appears to provide a simple and appealing procedure to extract ionization

potentials directly from arbitrary parent state wave functions. Thus, it is of some interest to combine these methods to determine how well ionization potentials can be obtained from VB wave functions by use of the EKT.

In this paper we report the results of such calculations on the ionization potentials of H_2O. It is found that MO and VB wave functions obtained from the same basis set give very similar results for the main peaks in the photoionization spectrum, both being roughly 1 eV higher than experiment for the three valence ionizations, about 4 eV too high for the corelike fourth ionization, and about 20 eV too high for the core ionization. In addition, the valence bond calculation predicts the presence of two other weak, closely spaced, valence shake up states. These may correspond to a previously unassigned feature near 48 eV in the experimental photoionization spectrum.

II. Theory

Let $\Psi(x_1 \ldots x_N)$ be a wave function for the N-electron parent ground state and $\Phi_a(x_1 \ldots x_{N-1})$ a wave function for state a of the $(N - 1)$-electron system after ionization. According to the extended Koopmans' theorem,[7] a reasonable approximate wave function Φ_a can be generated by annihilating a single spin orbital $\chi_a(x)$ from the given (fixed) parent wave function Ψ:

$$\Phi_a(x_1 \ldots x_{N-1}) = \int dx_N \chi_a^*(x_N) \Psi(x_1 \ldots x_N) \quad (1)$$

The optimum spin orbital χ_a is determined variationally to minimize the expectation value of the $(N - 1)$-electron Hamiltonian with respect to Φ_a. This leads[6a] to the equation[8]

$$\int dx' V(xx') \chi_a(x') = \epsilon_a \int dx' \gamma(xx') \chi_a(x') \quad (2)$$

for the determination of χ_a, where

$$V(xx') = -N \int dx_1 \ldots dx_{N-1} \Psi^*(x_1 \ldots x_{N-1}x')$$
$$\times \left[h(x) + \sum_i^{N-1} g(x_i x) \right] \Psi(x_1 \ldots x_{N-1}x) \quad (3)$$

$$\gamma(xx') = N \int dx_1 \ldots dx_{N-1} \Psi^*(x_1 \ldots x_{N-1}x')$$
$$\times \Psi(x_1 \ldots x_{N-1}x) \quad (4)$$

and where $h(x_i)$ and $g(x_i x_j)$ are the one- and two-particle operators, respectively, occurring in the Hamiltonian. The eigenvalue ϵ_a in eq 2, called the "orbital energy" of χ_a, is just the negative of the ionization energy from state Ψ to state Φ_a. If Ψ is an SCF–MO wave function, then eq 2 is simply the Hartree–Fock equation for the canonical molecular orbital χ_a and we recover the usual Koopmans' theorem.[6] Thus, eq 2 provides a natural extension of Koopmans' theorem to an arbitrary parent state wave function Ψ. Previous calculations[7,9] have indicated that the procedure is capable of giving accurate results, at least for valence ionization, when used with accurate parent wave functions Ψ.

We note in passing that the problem of calculating photoionization cross sections within the EKT framework has also been solved.[10]

Most molecular calculations are performed by expanding the wave function in terms of determinants constructed from some basis set of spin orbitals, say $\{\xi_p\}$. The EKT development is quite flexible with regard to the choice of the $\{\xi_p\}$. For example, they might be taken as the actual optimized orbitals occurring in the determinants, or they might be taken as the elementary basis functions from which those orbitals are constructed; either will lead to the same final results.[11] It is convenient to define the matrices Δ, γ, and V according to

$$\Delta_{pq} = \langle \xi_p | \xi_q \rangle \quad (5)$$

$$\gamma(xx') = \sum_{pq} \xi_p(x) \gamma_{pq} \xi_q^*(x') \quad (6)$$

$$\frac{N(N - 1)}{2} \int dx_1 \ldots dx_{N-2} \Psi^*(x_1 \ldots x_{N-2}x'x''')$$

$$\times \Psi(x_1 \ldots x_{N-2}xx'') = \sum_{pqrs} \xi_p(x) \xi_q(x'')$$
$$\times \Gamma_{pqrs} \xi_r^*(x') \xi_s^*(x''') \quad (7)$$

$$V_{pu} = -\sum_{qs} \langle \xi_p | h | \xi_q \rangle \gamma_{qs} \Delta_{su}$$
$$- 2 \sum_{qrst} \langle \xi_p \xi_t | g | \xi_q \xi_r \rangle \Gamma_{qrst} \Delta_{su} \quad (8)$$

or, symbolically,

$$V = -(h\gamma + 2g{:}\Gamma)\Delta \quad (8')$$

The spin orbital χ_a can also be expanded in this same basis:

$$\chi_a = \sum_p \xi_p c_{pa} \quad (9)$$

Collecting the coefficients c_{pa} into a column vector c_a, we can now write eq 2 in matrix form:[11]

$$V c_a = \epsilon_a (\Delta \gamma \Delta) c_a \quad (10)$$

Equation 10 can be easily solved by standard matrix diagonalization techniques to obtain both the desired eigenvalues ϵ_a and eigenvectors c_a. We emphasize that this is not an iterative procedure. The matrices Δ, γ, and V are directly constructed from the basis set $\{\xi_p\}$ and the parent state wave function Ψ, and the desired results are then obtained from eq 10 by a simple matrix calculation.

Finally, we should mention that in going beyond a single determinant level of approximation the operator $V(xx')$, and the corresponding matrix V, may not be Hermitian unless Ψ corresponds to a complete CI or fully converged MC–SCF wave function. Only a Hermitian V should be used in the EKT procedure. This is most simply accomplished by replacing V with $1/2(V + V^{\mp})$ prior to use in eq 10.

III. Computational Details

The foregoing theory has been used to calculate vertical ionization energies for H_2O at its experimental equilibrium geometry[12] ($R = 0.9584$ Å, $\theta = 104°27'$). The molecular orbital (MO) wave function used can be represented in terms of localized molecular orbitals[13] (LMO) as

$$\Psi^{LMO} = \mathcal{A}[1s\overline{1s}\ b_1\overline{b_1}\ b_2\overline{b_2}\ \ell_1\overline{\ell_1}\ \ell_2\overline{\ell_2}] \quad (11)$$

where $\mathcal{A}$ is the antisymmetrizer, 1s represents the oxygen core, b_1 represents a bonding orbital between oxygen and one hydrogen, b_2 represents an equivalent bond to the other hydrogen, ℓ_1 and ℓ_2 represent the two symmetrically related lone pairs, and a bar (lack of a bar) indicates $\beta(\alpha)$ spin. By contrast, the perfect pairing valence bond (VB) wave function used can be depicted[4b] as

$$\Psi^{VB} = \mathcal{A}[(1s\overline{1s} - \delta_1 1s^*\overline{1s^*})(b_1\overline{b_1} - \delta_2 b_1^*\overline{b_1^*})(b_2\overline{b_2} - \delta_2 b_2^*\overline{b_2^*})(\ell_1\overline{\ell_1} - \delta_3 \ell_1^*\overline{\ell_1^*})(\ell_2\overline{\ell_2} - \delta_3 \ell_2^*\overline{\ell_2^*})] \quad (12)$$

where the asterisks indicate higher energy orbitals localized in the same general regions of space as the corresponding orbitals without asterisks. The optimum coefficients δ_1, δ_2, and δ_3 are small, typically 0.1 or less. Since the orbitals having the same symbol in both the LMO and VB wave functions turn out to be qualitatively quite similar, we do not clutter up the notation by distinguishing them.

All the orbitals in the above wave functions were optimized by expressing them as linear combinations of basis sets of

Table I. Vertical Ionization Potentials of H_2O Calculated from Molecular Orbital (MO), Nonorthogonal Valence Bond (VB), and Strongly Orthogonal VB Wave Functions with Various Basis Sets of Slater-Type Orbitals (STO)

	MO 14 STO	MO 19 STO	MO 28 STO	VB 14 STO	Strongly orthogonal VB 19 STO	VB 19 STO	VB 28 STO	Experiment
				Total Energy, au				
E_{total}	−75.993	−76.034	−76.060	−76.069	−76.102	−76.108	−76.138	−76.481[a]
				Ionization Energy, eV				
H_2O^+ symmetry								
$^2B_1$	14.29	13.82	13.75	14.48	13.66	13.96	13.48	12.62[b]
$^2A_1$	15.76	15.79	15.84	15.59	15.77	15.54	15.40	14.74[b]
$^2B_2$	19.56	19.34	19.45	19.96	19.78	19.61	19.59	18.51[b]
$^2A_1$	37.35	36.59	36.70	36.81	36.32	36.00	35.53	32.2[b]
$^2B_2$				47.03	50.48	48.38	48.80⎫	48(?)[c]
$^2A_1$				47.44	53.41	48.69	48.93⎭	
$^2A_1$	560.0	559.5	559.4	558.9	559.0	558.5	558.7	539.7[d]

[a] Reference 19. [b] Reference 22. [c] Reference 23. [d] Reference 24.

Slater-type orbitals (STO). Examined were a 14 STO "double ζ" set, a 19 STO set identical to the 14 STO set except for the addition of d polarization functions on the oxygen atom, and a 28 STO set having p functions on the hydrogen atoms as well as d functions and an extra set of p functions on the oxygen.[5d]

The MO wave function was obtained by standard basis set SCF techniques.[14] The VB wave function, having no artificial orthogonality constraints on the orbitals, was optimized by the approximate SCF procedure described in detail elsewhere.[5a,b] With the 19 STO basis, we also obtained for comparison a completely optimized perfect pairing valence bond wave function with strong orthogonality constraints imposed on the orbitals. The total energy of each wave function is included in Table I.

The matrices Δ, γ, and V of eq 5–8 were then obtained for each wave function in terms of the optimized orbitals appearing in eq 11 and 12. For the MO and strongly orthogonal VB wave functions, the V matrix was exactly Hermitian. However, with the nonorthogonal VB wave functions, V was not exactly Hermitian due to incomplete SCF convergence owing to our approximate optimization procedure.[5a,b] For this reason, the Hermitian component of V was projected before applying eq 10. As noted by Ellenbogen et al.,[9c] this could lead to unreliable results if substantial changes in the elements of V are required to make it Hermitian. In this calculation, symmetrization changed the nonorthogonal VB matrix elements of V by less than 0.05 eV in all cases except for the off-diagonal elements connecting b_1 with b_1* (or b_2 with b_2*), which elements changed by 0.12 eV (14 STO), 0.12 eV (19 STO), and 0.18 eV (28 STO), and the off-diagonal elements connecting 1s with 1s*, which changed by 0.10 eV (14 STO), 0.10 eV (19 STO), and 0.11 eV (28 STO). From this, we estimate the error introduced into the VB ionization potentials by the incomplete SCF optimization to be on the order of 0.2–0.3 eV or less.

No spatial symmetry constraints were imposed on the calculation of the annihilated spin orbitals χ_a. However, in searching for the optimum orbitals, the extended Koopmans' theorem procedure automatically selected orbitals reflecting the point group symmetry of the molecule, thereby leading to pure symmetry states of H_2O^+.

IV. Discussion of Results

In lieu of a detailed discussion of previous H_2O ionization potential calculations, we refer to the excellent critical discussion in the review article by Schwartz[15] and mention here only some of the very recent studies. These include the ΔE_{SCF} and closely related transition operator calculations by Goscinski, Hehenberger, Roos, and Siegbahn,[16] the ΔE_{SCF} cal-

culation of Deutsch and Curtiss,[17] a series of studies on the core-hole satellite states by Ågren, Svensson, and Wahlgren,[18] the ΔE_{SCF} and large CI calculations on valence ionization by Rosenberg and Shavitt,[19] the one-body Green's function calculation by Yamakawa, Aoyama, and Ichikawa,[20] and the many-body perturbation theory calculation of Prime and Robb.[21] These studies all differ in philosophy from the present one in that they seek very high accuracy (with varying degrees of success), thus necessitating a good deal more work (and computer time) in performing separate, independent calculations on the final states, on hypothetical transition states, or on perturbation theory corrections. In contrast, the extended Koopmans' theorem allows one to obtain semiquantitative ionization potential information almost "for free" once the wave function for the parent state is obtained.[7,9]

The results of our ionization potential calculations are presented in Table I. For the five main peaks in the photoionization spectrum it is seen that the MO and VB methods give very similar results when the same basis set is used for each, all the calculated results being somewhat above the experimental results. Deviations from experiment are, typically, about 1 eV for the three valence ionization potentials, about 4 eV for the corelike fourth ionization, and about 20 eV for the core ionization. Improvements in basis set lead to only small changes in the ionization potentials and do not necessarily improve the agreement with experiment. According to Pickup,[25] the large error encountered with core ionization is due to orbital and correlation relaxation effects which cannot be adequately described within the framework of the EKT, although this interpretation does not seem to be supported by the formal analysis of Anderson and Simons.[26]

Examination of the wave functions led us to an important new insight into the workings of the extended Koopmans' theorem. To keep the discussion simple, we illustrate the point by considering only the 19 STO-MO and strongly orthogonal VB results for the first ionization potential, leading to a $^2B_1$ state of H_2O^+. The MO wave function is most conveniently discussed in terms of localized molecular orbitals, as in eq 11. The VB wave function of eq 12 can be expanded into 32 determinants, the leading terms being

$$\Psi^{VB} = \Psi^{LMO} - 0.10[\Psi^{LMO}(b_1\overline{b_1} \rightarrow b_1^*\overline{b_1}^*)$$
$$+ \Psi^{LMO}(b_2\overline{b_2} \rightarrow b_2^*\overline{b_2}^*)] - 0.05[\Psi^{LMO}(\ell_1\overline{\ell_1} \rightarrow \ell_1^*\overline{\ell_1}^*)$$
$$+ \Psi^{LMO}(\ell_2\overline{\ell_2} \rightarrow \ell_2^*\overline{\ell_2}^*)] + \ldots \quad (13)$$

where the notation indicates explicitly only the excitations required to produce the various configurations from the LMO wave function. The $^2B_1$ ionic wave function is obtained in the MO calculation by annihilating the orbital

$$\chi^{LMO} = (\overline{\ell_1} - \overline{\ell_2})/\sqrt{2} \qquad (14)$$

from Ψ^{LMO} and in the VB calculation by annihilating

$$\chi^{VB} = 0.48(\overline{\ell_1} - \overline{\ell_2})/\sqrt{2} + 0.88(\overline{\ell_1{}^*} - \overline{\ell_2{}^*})/\sqrt{2} \qquad (15)$$

from Ψ^{VB}. Evidently χ^{MO} and χ^{VB} are quite different orbitals, yet they lead to final states differing in energy by only 0.16 eV and having very similar wave functions! The explanation of this can be seen by examining the parent wave functions. Since Ψ^{LMO} is the dominant contribution to Ψ^{VB}, the first term of χ^{VB} in eq 15 leads to a final state configuration differing only in its norm from that produced by the MO calculation. The contribution to the final state from the configuration arising from the second term of χ^{VB} is small (its coefficient being an order of magnitude smaller than that of the leading configuration), despite the fact that this term dominates χ^{VB}, since the configurations in Ψ^{VB} having $\ell_1{}^*$ and $\ell_2{}^*$ occupied occur only with small weights. Thus, the MO and VB approaches produce very similar final state wave functions from very different annihilated orbitals, due to small differences in the parent state wave function.

The behavior just discussed is typical of all the states studied. The annihilated orbital is very sensitive to small changes in the correlation configurations included in the parent wave function and so does not, by itself, provide a useful description of the final state ion. Speaking roughly, a knowledge of "what is there" is just as important as a knowledge of "what is removed" in describing how ionic wave functions are produced by the extended Koopmans' theorem.

There are ten occupied spatial orbitals in the VB wave function, in contrast to five for the MO case, so five additional solutions of eq 10 are obtained in the VB calculation. Three of these cannot be given physical significance in the present determination since their positions show large fluctuations (more than 15 eV) with basis set size, probably because of the lack of diffuse functions in the basis. The other two (near 48 eV) are quite stable with respect to basis set size and are included in Table I. These can be interpreted as valence shake up states, corresponding to ionization to excited states of H_2O^+. A qualitative description can be given in terms of a one-electron picture based on annihilating a single spin orbital from the VB wave function:

$$\chi^{VB}(^2B_2 \text{ ion}) = \overline{b_1{}^*} - \overline{b_2{}^*} \qquad (16)$$

$$\chi^{VB}(^2A_1 \text{ ion}) = \overline{b_1{}^*} + \overline{b_2{}^*} \qquad (17)$$

(cf. eq 4), or, equivalently, in terms of a two-electron (annihilation plus excitation) picture based on the MO wave function:

$$\Psi^{VB}(^2B_2 \text{ ion}) = \Psi^{LMO}(\cancel{b_1}, b_1 \rightarrow b_1{}^*)$$
$$- \Psi^{LMO}(\cancel{b_2}, b_2 \rightarrow b_2{}^*) \qquad (18)$$

$$\Psi^{VB}(^2A_1 \text{ ion}) = \Psi^{LMO}(\cancel{b_1}, b_1 \rightarrow b_1{}^*)$$
$$+ \Psi^{LMO}(\cancel{b_2}, b_2 \rightarrow b_2{}^*) \qquad (19)$$

where our notation in the latter case indicates the orbitals annihilated by crossing them out with a slash. Note the close similarity of the two states; they differ only in the relative phases of the two contributing terms. Inasmuch as the high-energy orbitals $b_1{}^*$ and $b_2{}^*$ have little interaction with each other or with the other occupied orbitals, the close energy of the two states is readily understood. It is also noteworthy that the ordering of these two states ($^2B_2$ below $^2A_1$) is maintained in all of our calculations.

These shake up states represent the only case where there is a substantial difference between the nonorthogonal VB and the strongly orthogonal VB results. The reason for this difference is not completely clear, but it is probably due to the orthogonality constraints pushing the strongly orthogonal

orbitals marked with asterisks to higher energy than is necessary. In this connection, we note that the EKT procedure guarantees that the H_2O^+ states will be mutually orthogonal regardless of the type of parent state wave function.

Judging from the behavior of the other states studied, the calculated results for the two shake up states are probably higher than the experimental positions. The error may in fact be quite large if either or both of the final states are strongly affected by configurations not included in the VB model. More elaborate calculations will be required to determine the accuracy of the present results on the shake up states. This could still be done within the EKT framework by using a more accurate CI or MC–SCF parent state wave function.

Neither the total photoabsorption spectrum for H_2O of de Reilhac and Damany[27] nor the electron impact spectrum of Lassettre and White[28] show any features which might be attributed to these shake up states. However, the data points are spaced widely enough in this region (42.2 and 49.6 eV in the former study and 45.0 and 50.0 eV in the latter study) that a weak feature up to several volts wide might easily have been missed. On the other hand, the photoionization spectrum of Cairns, Harrison, and Schoen[23] shows a point at 260 Å (48 eV) which rises noticeably from the smooth curve passing through the neighboring points. The authors mention, but do not discuss, this point in the text of their article, apparently to indicate that it is real and not merely due to "noise."

The near coincidence of the unassigned experimental peak[23] with the two calculated shake up states near 48 eV suggests that the calculations may, in fact, be accurate and that the peak can be assigned to the threshold for ionization to one or both of these shake up states. More detailed theoretical and experimental work is clearly called for to confirm this tentative assignment. To aid a possible experimental study, we estimate, on the basis of the sudden approximation,[10,29] that the $^2A_1$ peak may be up to twice as intense as the $^2B_1$ peak, but should only be about one-tenth as intense as the main valence peaks in a high-energy photoelectron spectrum.

Note Added in Proof. Recent calculations on ionization potentials of H_2O have been reported from a perturbation theory-CI method (C. B. Bacskay, *Chem. Phys.*, **26**, 47 (1977)) and from another Green's function method (V. Carravetta and R. Moccia, *Mol. Phys.*, **35**, 129 (1978)). The latter work finds that the peak observed near 32 eV is composed of three states of roughly equal intensity spread over several eV, a not at all unexpected result (see L. S. Cederbaum, J. Schirmer, W. Domcke, and W. von Niessen, *J. Phys. B: Atom. Molec. Phys.*, **15**, L549 (1977)). The former work finds a series of weak higher energy shake up states associated with the main 32-eV peak. These shake up states are probably not experimentally observable given the present state of art, each being well under 1% of the intensity of the main peak. The shake up states found in the present calculation are distinguished by their relatively high predicted intensities.

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Ab Initio Calculation of the Reaction Path for the Addition of Singlet ($^1A_1$) Methylene to Ethylene

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Abstract: Ab initio calculations at the SCF level and with the inclusion of valence shell electron correlation in the CEPA (coupled electron pair approximation) scheme with a double ζ type basis plus polarization functions on carbon have been performed for the reaction path of the addition of singlet ($\tilde{a}$ $^1A_1$) methylene to ethylene to yield cyclopropane. The energy is minimized with respect to all relevant geometrical parameters for fixed values of the approximate reaction coordinate. The reaction energy is accounted for to within the uncertainty of the experimental energy of CH_2 ($\tilde{a}$ $^1A_1$). The energy along the reaction path decreases monotonically without a barrier. Hoffmann's prediction that the reaction path should be nonsymmetric is confirmed. The reaction starts with an electrophilic phase and is accomplished with a nucleophilic phase. In the two phases different geometrical arrangements and different internal geometries of the partners are favored.

I. Introduction

Methylene (CH_2) plays an important role as an intermediate in chemical reactions. Therefore, its electronic structure has received much attention.[2-7] The properties of CH_2 in low-lying electronic states as well as the difference in reactivity in these states were of particular interest.[4,5,8-13]

It is known from experimental studies[9,14-20] that the photolysis of ketene vapor or diazomethane leads primarily to methylene in highly excited singlet states. It is then deexcited in collisions with inert gas molecules to a mixture of CH_2 ($^1A_1$) and CH_2 ($^3B_1$). The ratio of these two components depends on the conditions under which the photolysis is performed.

The CH_2 species is very reactive.[9,20,21] For example, with ethylene it reacts to form propylene and cyclopropane.[14-19] The relative yields of the products depend on the conditions of the reaction and it is possible to limit the yield of propylene to a very small fraction.[15] Furthermore, the attack of the CH_2 on the double bond in ethylene, which leads to cyclopropane, is sometimes stereospecific. The stereospecificity, or lack of it, depends on which of the two electronic states of CH_2 is in-

volved.[17-21] Some authors suggest that the singlet species should react in a single-step process to yield the three-membered ring stereospecifically while the triplet species should initially form a diradical intermediate which possesses only a small rotational barrier about single bonds, so that there is no stereospecificity in the second case.[5,8,10,16-23] This idea was probably first formulated by Skell and Garner[24] whereas Benson et al.[25,26] have suggested that an open-chain trimethylene is also involved in the singlet reaction. That the addition of triplet methylene to ethylene takes place via the trimethylene biradical[27,28] has been confirmed by theoretical investigations at the semiempirical[5,8] as well as at the ab initio level,[10,22] although the geometry of approach is not known in all its details.

For the addition of singlet methylene to double bonds the situation is not so straightforward from the theoretical point of view. According to the Woodward–Hoffmann rules cycloaddition of methylene to ethylene is forbidden if C_{2v} symmetry is preserved.[8] The orbital phase continuity principle of Goddard III leads to the same conclusions.[10] Bodor et al.[5] have