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A STUDY OF CH₂.

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DIFFERENT ORBITALS FOR DIFFERENT SPINS,

A STUDY OF CH₂

by
Lois Cederberg Leffler

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To
"The Bears"

PREFACE

"Quantum chemistry is like a progression with an upper limit: the Schrödinger equation is good for atomic and molecular systems--if only we could solve it accurately! So all we do is search for better and better approximations to the Schrödinger equation for a given system, and we should say for a given system in a given environment. We are trying to fill a given frame; there cannot be any sensational discoveries ahead of us; all we may expect is hard work."

From C. Sandorfy, Electronic Spectra and Quantum Chemistry, (Prentice-Hall, Inc., New Jersey, 1964), p. 312.

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INTRODUCTION

The proper method of including electron correlation has been a persistent problem throughout the history of quantum mechanics. The most common way of treating this tendency for electrons to avoid each other has been the use of the method of Configuration Interaction (CI), that is to say the expression of the total wave function as a minimized linear combination of determinantal wave functions representing as many as practical of the possible configurations, thus allowing electrons to avoid each other by permitting them to spend time in other energy levels. In their treatment of CH_2 for instance Foster and Boys¹ used 128 such terms. Difficulties immediately arise because of the magnitude of the number of possible configurations arising given N electrons and the problem of deciding a priori which configurations are of most importance in lowering the energy. Löwdin² has proposed another method corresponding to a limited configuration interaction treatment which he and others³ have worked out and applied to the π electrons of alternant systems--the so-called

¹J. M. Foster, S. F. Boys, Rev. Mod. Phys. **32**, 305 (1960).

²P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

³See, for example, R. Pauncz, J. de Heer, P.-O. Löwdin, J. Chem. Phys. **36**, 2247 (1962); R. Pauncz, J. de Heer, P.-O. Löwdin, J. Chem. Phys. **36**, 2257 (1962); J. de Heer, J. Chem. Phys. **37**, 2080 (1962); R. Pauncz, J. Chem. Phys. **37**, 2739 (1962); J. de Heer, R. Pauncz, J. Chem. Phys. **39**, 2314 (1963).

Alternant Molecular Orbital (AMO) method. This has been paralleled by the unrestricted Hartree-Fock scheme as worked out by Slater and his collaborators.⁴ In the last two treatments two entirely different sets of orbitals are used, one for the electrons having α spins and one for those having β spins, thus allowing antiparallel electrons to avoid each other also. Slater uses a single determinant corresponding to a mixture of spin states. This is not a disadvantage in the systems so far considered although the physical picture is confused.⁵ A second possibility is the so-called extended Hartree-Fock scheme where the correct spin function is projected out of a determinant whose elements allow for different orbitals for different spins.² These methods have been called "Different Orbitals for Different Spins" or simply D.O.D.S. methods. There are still others such as the NPSO method (Non-Paired Spatial Orbitals). (See R. Pauncz, J. Chem. Phys. 43, 569 (1965) for a short discussion.)

These attempts to allow the electrons to avoid one another when in the same spacial orbital are not new nor are the subjects of these studies. Hylleraas⁶ and Eckart⁷ used such a method in their treatments of He by allowing

⁴See, for example, J. C. Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951); Rev. Mod. Phys. 25, 199 (1953); R. E. Watson, A. J. Freeman, Phys. Rev. 120, 1125 (1960); Phys. Rev. 120, 1134 (1960).

⁵P.-O. Löwdin, Adv. Chem. Phys. 2, 207 (1959).

⁶E. A. Hylleraas, Z. Physik 54, 347 (1929).

⁷C. Eckart, Phys. Rev. 36, 878 (1930).

the two 1s orbitals to have different orbital exponents. Hylleraas also used a similar method on H_2 .⁸ A modern attempt to apply a D.O.D.S. treatment to the singlet S state of He has only recently been reported⁹, which accounts for 94% of the radial correlation energy. This might be cited as still another example of the quality of early work and the fertile imagination of the early workers.

In the present work the results of an attempt to apply an AMO-DODS treatment to the CH_2 molecule is reported. The mathematical treatment followed Pauncz *et. al.*³ including the use of different mixing parameters. Simple one-electron LCAO-MO orbitals were used with all overlaps explicitly included as a starting point in the formation of the AMO's. The pairing was chosen by "geometrical intuition" at first and limited trial runs were made using other pairings. These other pairings appeared to be of higher energy so were not studied extensively. The results obtained seem quite different from the results characteristic of alternant conjugated systems for which the method has previously been used and naturally reflect the molecular orbitals used as a basis set. A discussion of the results follows a description of the treatment.

⁸E. A. Hylleraas, Z. Physik 71, 739 (1931).

⁹D. P. Chong, J. Chem. Phys. 45, 3317 (1966).

HISTORICAL DEVELOPMENT

The experimental history of methylene, that is, the production of substances called methylene, started as early as 1835¹⁰ but the "modern" history of the substance can be said to originate about 1912 with the work of Staudinger¹¹ and his co-workers. The theoretical history began in 1932 with the one-electron treatment of Mulliken¹² and interest has continued to the present time due to the evident inadequacies of the quantum mechanical approximations which must be applied to many-electron problems.

Methylene, or carbene as it is also called, is an eight electron molecule having as its formula CH₂. One would expect a linear triplet ground state for the electronic configuration of $1s^2(sp)_I^2(sp)_{II}^2p_Y^1p_Z^1$ of carbon or, alternatively, if one used the sp₂ hybridized carbon orbitals, an electronic configuration of $1s^2(sp_2)_I^2(sp_2)_{II}^2(sp_2)_{III}^2$, a H-C-H angle of 120°, and a singlet state. One could

- ¹⁰a. J. B. Dumas, E. Péligot, Ann. chim. phys. 58, 5 (1835).
- b. M. V. Regnault, Ann. chim. phys. 71, 353 (1839).
- c. A. Perrot, Ann. 101, 375 (1857).
- d. A. M. Butlerov, Ann. 120, 356 (1861).
- e. J. V. Neff, Ann. 298, 202 (1897).
- ¹¹a. H. Staudinger, O. Kupfer, Ber. Deut. Chem. Ges. 44, 2197 (1911).
- b. H. Staudinger, O. Kupfer, Ber. Deut. Chem. Ges. 45, 501 (1912).
- c. H. Staudinger, R. Endle, Ber. Deut. Chem. Ges. 46, 1437 (1913).
- d. H. Staudinger, J. Goldstein, Ber. Deut. Chem. Ges. 49, 1923 (1916).
- e. H. Staudinger, E. Anthes, F. Pfenninger, Ber. Deut. Chem. Ges. 49, 1928 (1916).
- ¹²R. S. Mulliken, Phys. Rev. 41, 751 (1932); 43, 279 (1933).

imagine other possibilities also, especially $1s^2 2s^2 2p_x^2 2p_y^2$ giving rise to a 90° angle and a singlet state.

The first spectroscopic evidence for methylene was reported in 1942 by Herzberg¹³ but this was later corrected by Douglas¹⁴ who indicated that the observed bands were caused by the linear triatomic molecule C_3 . In 1959 and 1961 Herzberg^{15,16} reported the spectra and structure of methylene and cited an absorption about 1400 \AA as due to a triplet ($^3\Sigma_g^-$) species which is approximately linear and which has an C-H distance of about 1.03 \AA . The species absorbing in the region $5500\text{--}9500 \text{ \AA}$ was shown to be singlet (1A_1) with an angle of 103° and a C-H distance of 1.12 \AA . The triplet species was suggested to be the ground state since the singlet state decays to the triplet. A later paper¹⁷ gave the ionization potential of free CH_2 to be $83,851 \text{ cm}^{-1}$ (10.396 e.v.) with the lower limit of $D(CH-H)$ to be 98 kcal/mole , that of $D(CH_2-H) = 113 \text{ kcal/mole}$.

The spin state of methylene is of considerable interest to the mechanician but the question has been impossible to settle experimentally. In their chapter in Kirmse's book Gasper and Hammond¹⁸ state that they feel that the

¹³G. Herzberg, Rev. Mod. Phys. 14, 195 (1942).

¹⁴A. E. Douglas, Astrophys. J. 114, 466 (1951).

¹⁵G. Herzberg, J. Shoosmith, Nature(London) 183, 1801(1959).

¹⁶G. Herzberg, Proc. Roy. Soc. (London) A262, 291 (1961).

¹⁷G. Herzberg, Can. J. Phys. 39, 1511 (1961).

¹⁸W. Kirmse, Carbene Chemistry, (Academic Press, New York, 1964), p. 251.

singlet and triplet states show "significantly different" behaviour and that chemical evidence, i.e. at study of insertion and addition reactions, can distinguish between the species. However, in the same paragraph, they cite an opposite point of view. This is typical of the state of the art--even the name of the substance is subject to disagreement.

Theoretical attempts to settle the matter of the ground state multiplicity and geometry started in 1934 when Mulliken¹² considered the substance. He assumed it belonged to the point group C_{2v} , ignored electron repulsion, and arrived at a singlet A_1 ground state with a triplet B_1 excited state.

Lennard-Jones¹⁹ then did a treatment whereby he took the 3P , 1D and 1S terms of the oxygen atom and contemplated the splitting of these levels as the oxygen was subjected to a strong axial perturbation and the symmetry became C_{2v} , progressing from oxygen through NH to CH_2 . This united atom approach also gave a 1A_1 ground state with a 3B_1 excited state.

Further early work was done by Norrish.²⁰ In a study of the photodecomposition of diazomethane and ketene he concluded that molecular CH_2 (in contrast to a diradical) was the logical result. He attributed a gain of reorganization

¹⁹J. E. Lennard-Jones, Trans. Faraday Soc. 30, 70 (1934).

²⁰R. G. W. Norrish, Trans. Faraday Soc. 30, 103 (1934).

energy to the process of repairing formerly promoted electrons in the C_{2s} orbital ($^3S \rightarrow ^3P$) to the step $CH_3 \rightarrow CH_2 + H$ and argued that this would dictate the formation of a bent singlet ground state.

Voge²¹ did a detailed semiempirical valence bond treatment of CH_4 and then incidently considered CH_2 . He especially pointed out that the stronger bond formed by C_{sp} hybrid orbitals might very well cause CH_2 to be linear.

The first paper in which Walsh considered CH_2 ²² stated that the more s character in a carbon valency the more electronegative is this carbon and the stronger the C-H bond formed as shown by the acidic character of acetylene, a consideration of the stretching force constants of various C bonds, and bond energies. He then discussed why H-H repulsion in a 90° H-C-H configuration would lead to a hybridization of the carbon orbitals and H-C-H angles greater than 90° . If the angle then is greater than 90° Walsh predicted a triplet ground state. Walsh considered available thermal data and decided that the reorganization to divalent carbon occurs at the step $CH_2 \rightarrow CH + H$ giving rise to a triplet ground state, in contrast to the conclusion reached by Norrish. Work in this period was strongly influenced by the early incorrect data on CH_2 ¹³ but much of the discussion was general.

²¹H. H. Voge, J. Chem. Phys. 4, 581 (1936).

²²A. D. Walsh, Disc. Faraday Soc. 2, 18 (1947).

Laidler and Casey²³ considered resonance possible between singlet or triplet CH_2 and the corresponding singlet or triplet ionized states and concluded that an observed angle of 140° implies a bent singlet state even though it seemed that a linear triplet state should be the lower. This provoked a reply by Duffy²⁴ in which he suggested that sp^3 orbitals might be used for the unshared electrons implying an angle of 109° for the triplet state. However, Gasper and Hammond¹⁸ point out that combining the tetrahedral orbitals into symmetric and anti-symmetric states would break the degeneracy. Laidler and Casey²⁵ then returned with an analysis of thermal data based on the kinetics of a reaction between sodium and methylene chloride which was assumed to produce methylene. They obtained a value of 19 kcal/mole as the energy of promotion from the singlet to the triplet states assuming that the singlet state was obtained using pure p orbitals and the triplet sp hybrids.

Lennard-Jones and Pople²⁶ considered only electrostatic forces and the antisymmetry principle to arrive at a qualitative picture of molecular structure and a subsequent triangular singlet state and linear triplet state with no prediction as to ground state.

²³K. J. Laidler, E. J. Casey, J. Chem. Phys. 17, 213 (1949).

²⁴G. H. Duffy, J. Chem. Phys. 17, 840 (1949).

²⁵K. J. Laidler, E. J. Casey, J. Chem. Phys. 17, 1087 (1949).

²⁶J. Lennard-Jones, J. A. Pople, Disc. Faraday Soc. 10, 9 (1951).

This was followed by a consideration of electronic configurations of maximum probability by Linnet and Poë²⁷ using determinantal wave functions and minimizing $\langle \Psi | \Psi \rangle$ as a function of electronic spacial coordinate while ignoring electronic repulsion, assuming then that a molecule would be made up of orbitals from the central atom having maximum probability. For triplet CH_2 this would imply a tetrahedral C configuration tending toward an oxygen (the CH_2 united atom) configuration having an angle of 130° between the two pairs of electrons in the valence shell. This would then suggest a triplet angle between 109° and 130° . Similarly for singlet CH_2 the corresponding united atom is oxygen having three valence electron pairs at the corners of an equilateral triangle while carbon having a pair of valence electrons and two single electrons would exhibit an angle of 118° in this treatment. They conclude that single CH_2 would have a physical angle of 118 to 120° .

Niira and Oohata²⁸ considered sp^3 and s^2p^2 carbon states and C_{2v} symmetry from singlet and triplet linear combinations of thirteen possible orbital wave functions. They included interactions between all pairs of particles in their Hamiltonian and did a variation treatment, taking advantage of partitioning between symmetry and spin states. The energy terms were evaluated from spectroscopic data and tables of

²⁷J. W. Linnett, A. J. Poë, Trans. Faraday Soc. 47, 1033 (1951).

²⁸K. Niira, K. Oohata, J. Phys. Soc. (Japan) 7, 61 (1952).

integrals of Zener type functions using 1.12 \AA for $R_{\text{C-H}}$. They obtained energy curves as a function of H-C-H angle and deduced that $^3\text{B}_1$ is the lowest state for all angles followed by $^1\text{B}_1$ and $^1\text{A}_1$ in that order.

Walsh returned to the arena with a correlation study between the orbitals of linear and non-linear AH_2 .²⁹ He concluded that molecules having more than four valence electrons would be bent in the ground state and predicted long wavelength transition for the bent singlet state and short wavelength transitions (less than 2500 \AA) for the linear triplet. Interestingly enough the transition assigned by Herzberg to the approximately linear species occurs at 1400 \AA .¹⁶ Walsh's results come from considering the variation of energy with H-C-H angle as C_{2v} orbitals pass over into those of $\text{D}_{\infty h}$ and pure p orbitals become sp hybrids with the resultant increase in binding energy.

The modern quantitative theoretical history of methylene began with a note by Gallup³⁰ in which an extended-Hückel type treatment including overlap was used to study the singlet and triplet states as a function of H-C-H angle. This was challenged by Gray³¹ and a rebuttal published by Gallup.³²

²⁹A. D. Walsh, J. Chem. Soc. 2260 (1953).

³⁰G. A. Gallup, J. Chem. Phys. 26, 716 (1957).

³¹B. F. Gray, J. Chem. Phys. 28, 1252 (1958).

³²G. A. Gallup, J. Chem. Phys. 28, 1252 (1958)

The definitive theoretical study of CH_2 was done by Foster and Boys¹. Their study was based on a full configuration scheme based on eight expansion functions including e^{-4r_c} , e^{-3r_c} , $r_c e^{-r_c}$, $x_c e^{-r_c}$, $y_c e^{-r_c}$, $z_c e^{-r_c}$, and the two hydrogen orbitals, each of the form $e^{-.75r_c}$, using integral evaluation programs written by the authors and I. Jones. The results in atomic units are summarized in Figure 7.

FIGURE 7. RESULTS OF FOSTER AND BOYS¹

	3B_1	1A_1	1B_1
Total Energy (a.u.)	-38.904	-38.865	-38.808
H-C-H Angle	129°	90°	132°
C-H distance (a.u.)	2.11	2.21	2.11

A LCAO-SCF calculation by Padgett and Krauss³³ for a series of H-C-H angles used Slater atomic orbitals, including the C_{1s} orbitals and the orthogonalized C_{2s} orbitals, arranged in symmetry orbitals and $R_{C-H} = 1.12 \text{ \AA}$. Coulson's³⁴ method was used for $\int \frac{\psi_a \psi_b}{r_c} d\tau$ integrals and Mulliken's approximation³⁵ used on the three and four center integrals. They emphasized the qualitative character of the work and stated that they did not feel that their work defined a ground state although they did obtain energy diagrams as a

³³A. Padgett, M. Krauss, J. Chem. Phys. **32**, 189 (1960).

³⁴C. A. Coulson, Proc. Camb. Phil. Soc. **33**, 104 (1937).

³⁵R. S. Mulliken, J. Chem. Phys. **46**, 497 (1949).

function of angle and minima with respect to angle at 90° and 120° for the 1A_1 and the 3B_1 states respectively.

King and Malli³⁶ studied linear methylene extensively using a C-H bond length of 1.0295 \AA and a LCAO-MO-CI procedure. Their basic molecular spin orbitals were symmetry orbitals constructed from Slater atomic orbitals with fixed parameters and a "large" number of configurations were considered to compensate for errors arising from the simplifications used. A secular determinant of unmanageable proportions was reduced by considering symmetry classifications and multiplicity. They conclude that the spectral results are indeed consistent with a linear ground state.

Ellison³⁷ used a semi-empirical valence bond method to predict a linear 3B_1 ground state and a 1A_1 state with an H-C-H angle of 100° using $R_{C-H} = 1.12 \text{ \AA}$. The method is similar to Jordan and Longuet-Higgins³⁸ and is valuable for the insight it gives into the origin of energy terms. The Hamiltonian is expressed as the sum of the Hamiltonian for free carbon, that for a sum of n hydrogen atoms and the one representing the interaction between the carbon and the hydrogen systems. The resulting energy expression then contains terms which can be identified as belonging to promotional energy, Coulomb energy, bond exchange energy,

³⁶G. W. King, G. L. Malli, Can. J. Chem. 39, 1652 (1961).

³⁷F. O. Ellison, J. Chem. Phys. 36, 3112 (1962).

³⁸P. C. H. Jordan, H. C. Longuet-Higgins, Mol. Phys. 5, 121 (1962).

exchange energy corresponding to non-bonded interactions, and resonance energy. It is then seen for CH_2 that the geometry is a compromise between the 90° and 180° states with the triplet linear state becoming the ground state because of the maximum bond-overlap resulting from a sp hybrid, low promotional energy to form a 3B_1 state, and the influence of non-bonded interactions.

A semiempirical treatment of the series CH , CH_2 , CH_3 , NH , NH_2 , BH , BH_2 , and BH_3 combining some aspects of atoms-in-molecules and valence bond theory was done by Jordan and Longuet-Higgins.³⁸ They assumed that the hydrogen atoms formed two-electron bonds with the carbon, considered fixed bond lengths, and allowed for bond bending. The energy expression was considered to be a function of the H-C-H angle and the hybridization parameter and was minimized with respect to the latter for a series of bond angles. Energy was expressed as a linear combination of E_C , E_{CH} , and E_H :

$$E_{\text{total}} = E_C + 2E_{\text{C-H}} + 2E_H$$

where E_C is the valence state energy of carbon and depends upon the electronic and hybridizational state.

E_H is the ground state energy of the hydrogen atom, and E_{CH} , the C-H bond energy which is a function of the bond angle, the hybridization state and the degree of angular distortion from the "ideal" configuration of the hybrid orbitals. The terms in E_{total} were determined as a function of the physical angle and hybridization by recourse to

experimental data. Results for CH_2 showed 105.5° for $^1\text{A}_1$, 180° for $^3\text{B}_1$, some agreement with spectral results. and a lower triplet state.

Pedley³⁹ calculated dissociation energies of C-H bonds as a function of H-C-H angle and concluded that the ground state is linear by considering the interplay of valence state energies, C-C and C-H bond strengths and steric repulsions between non-bonded atoms. His value of $D(\text{CH}_2\text{-H})$ is 116 kcal/mole. (The experimental value is 113 kcal/mole).¹⁷

An interesting recent treatment of CH_2 by Pauling uses different orbitals for α and β spins in a structural theory⁴⁰ He divides the six valence electrons into four with α spin and two with β spin. He assumes sp hybrid orbitals on the carbon and places two α and two β -spins in them. The remaining two α spins go into the unhybridized p orbitals. The hydrogens are each assumed to be bonded to the carbon by means of one-electron sp_σ bonds while the electrons in the p -orbitals are assumed to form one-electron p_+ bonds with the hydrogens. By considering electronegativity differences he is able to assign percent of s character to the sp hybrids. As a first approximation, the competition between the 180° sp_- and the 90° p_+ bonds with the two hydrogens would lead to a resultant triplet state with an

³⁹J. B. Pedley, Trans. Faraday Soc. 58, 23 (1962).

⁴⁰Linus Pauling, Molecular Orbitals in Chemistry, Physics, and Biology, (Academic Press, New York, 1964), p. 207.