THE ELECTRONIC STATES OF LINEAR METHYLENE (CH_2)

CALCULATION OF THE ELECTRONIC STATES OF THE LINEAR METHYLENE (CH_2) RADICAL BY THE LCAO/ASMO/CI METHOD

by

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SCOPE AND CONTENTS:

The electronic energy levels of the linear CH_2 radical are calculated by the LCAO/ASMO/CI method and it is definitely established that $^3\Sigma_g^-$ is the ground state. Various electronic transitions are predicted as being spectroscopically accessible. Possible electronic states involved in the spectral transitions observed so far for CH_2 are also suggested. The role of "Configuration Interaction" and the effect of including doubly excited configurations in calculating energy levels by the Molecular Orbital method are discussed.

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TABLE OF CONTENTS

Page

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

Page

TABLES

APPENDICES

FIGURES

CHAPTER 1.

I. INTRODUCTION

Dirac[1] in 1929 stated that the whole of chemistry is implicit in the laws of Quantum Mechanics.

Quantum Mechanics has been applied to the problems of molecular structure by two main methods, the Valence Bond[2] (V.B.) method and the Molecular Orbital[3] (M.O.) method.

Until a few years ago, comparatively little attention was given to the M.O. method for investigating the electronic structure of atoms and molecules as contrasted with the V.B. method. However, as the interest of quantum chemists turned to more and more complicated molecules, it became clear that the V.B. approximation was too unwieldy to provide l a convenient structural theory of large molecules; the M.O. theory on the other hand provided a more manageable technique.

During the last decade there have emerged two main approaches in the framework of M.O. theory: the Self-Consistent Field Scheme (SCF) and the Configuration Interaction Scheme (CI). The scheme "SCF anti-symmetrised product of M.O.'s in the approximation of Linear Combination of Atomic Orbitals" (LCAO/ASMO/SCF) developed by Roothaan[4], in its usual form can be applied with great success to the closed-shell ground states of molecules, and also by using approximations to some lower excited electronic states.

The scheme "Configuration Interaction anti-symmetrized product of Molecular Orbitals in the LCAO approximation" (LCAO/ASMO/CI), developed by Craig,[5a] Coulson et al[5b] and others[5c] in general can be used for describing not only the ground electronic states, but also the excited electronic states of polyatomic molecules.

In recent years, when large electronic computers are available to help work out the complicated computations required in Molecular Orbital Calculations, many attempts have been made to calculate rigorously the electronic energies and wave-functions for simple molecules by the Molecular Orbital method, with considerable success.

In this thesis, the LCAO/ASMO/CI method is used to calculate the electronic energy levels of the linear CH_2 radical, a very reactive and unstable species which has only recently been observed spectroscopically by Herzberg and Shoosmith.[6] The results obtained here enable predictions to be made as to the electronic states involved both in the transition observed by these authors, which they have not yet identified, and in further transitions hitherto unobserved spectroscopically.

II. SPECTROSCOPIC INVESTIGATIONS OF THE METHYLENE RADICAL

Herzberg[7] in 1942 attributed the so-called 'Cometary emission bands' at 4050 Å to the methylene radical. Later he[8] excited these bands in methane by means of an electrical discharge. In 1946 Herman[9] succeeded in photographing the above bands with higher dispersion. Two years later Goldfinger et al,[10] also reported the presence of the 4050 Å group in an electrical discharge through diazomethane (CH_2N_2) and ketene (CH_2CO).

However, until 1949 no analysis of these bands had been attempted. In order to make a detailed study of these bands, Monfils and Rosen[11] developed a new method of exciting them. They found that the 4050 Å group was strongly emitted in a hollow cathode discharge through various hydrocarbons such as toluene, benzene, methane, and very strongly in a discharge through pure hydrogen using graphite electrodes. From the analysis of these bands, they concluded that the moment of inertia deduced from the observed fine structure indicated the presence of a much heavier molecule than CH_2. Moreover, the bands excited in deuterium showed no noticeable frequency shifts with respect to those excited in the hydrogen. This was another argument against CH_2 being the emitter of these bands.

Douglas[12] in 1951 suggested that these bands might be attributed to C_3, a linear triatomic carbon molecule. To establish this fact, Clusius and Douglas[13] excited the spectrum of $C^{13}H_4$ by the method of Herman[9], and on the basis of the observed isotopic effects, in agreement with those expected theoretically[16], when C^{13} isotope replaces C^{12} isotope in the C_3^{12} molecule, they postulated that the emitter of the 4050 Å bands was the C_3 molecule. However the problem of analyzing and explaining the many complex bands of the 4050 Å group still remains unsolved.

Since the original misassignment by Herzberg[7] of 4050 Å group to CH_2, Herzberg and many other workers have been very active in searching for the spectrum of the CH_2 radical, and it was only very recently that some success appears to have been achieved by two groups.

In 1958 McCarty Jr. and Robinson,[14] on condensing the products of an electrical discharge through ethane plus krypton (krypton being in excess by a factor of 30), in a liquid-helium cooled quartz tube observed three sharp lines near 2600 Å in absorption through the deposit, and attributed them to the CH_2 radical. They also reported an isotopic shift in the photo-catalyzed product from ethane-d6, the vibrational spacing changing from 900 ± 50 cm^{-1} in the hydrogenic compound to 725 ± 50 $cm.^{-1}$ for the product from the fully deuterated ethane. Although from their analysis there is very little information either on the nature of the ground state or on the molecular geometry of CH_2, they have emphasized that at least one of the states involved in the transition is bent, because the 900 cm^{-1} spacing probably corresponds to the ν_2' bending mode, which is expected to appear strongly when there is a large difference in angle between the two states. However, they are by no means certain that these bands are due to CH_2, as some impurity might be responsible for them.

Very recently Herzberg and Shoosmith[6] have positively identified certain bands near 1400 Å, obtained during the flash-photolysis of diazomethane (CH_2N_2), as due to the methylene (CH_2) radical. They observed six "diffuse lines" in one of the 1400 Å groups, which showed a marked frequency shift on substitution with deuterium, thus establishing the presence of one or more hydrogen atoms in the molecule responsible for this spectrum.

The strongest feature in the flash-photolysis of ordinary diazomethane (CH_2N_2) occurred at 1414.5 Å, but in fully deuterated diazomethane (CD_2N_2) at 1415.8 Å. Also, when partly deuterated diazomethane ($CHDN_2$) was flash-photolysed, a third feature was observed at 1415.5 Å. This indicated that the molecule responsible for spectrum contained two hydrogen atoms. It was likely that CH_2, CHD and CD_2 were responsible for the spectra observed at 1414.5 Å, 1415.5 Å and 1415.8 Å respectively. However, conclusive proof could only be obtained by a study of the rotational fine structure of some of the systems mentioned above.

Unfortunately, in the 4th order of a vacuum-spectrograph, all the features observed in the flash-photolysis of CH_2N_2 were diffuse. The 1415.8 Å system obtained from the flash-photolysis of CD_2N_2 showed a rather well-defined fine structure. This difference between the deuterated (CD_2) and the non-deuterated (CH_2) molecule was very similar to that for the 2600 Å band system of CD_3 and CH_3 radicals observed earlier by Herzberg and Shoosmith[15], and is apparently due to the fact that a deuterated molecule predissociates less than a non-deuterated molecule.

The fine structure of the 1415.8 Å feature in the flash-photolysis of CD_2N_2 consisted of a simple P and R branch, each of which showed a clear intensity alternation. The presence of this alternation proved undoubtedly that there must be two symmetrically placed identical atoms (deuterium atoms) in the molecule. Moreover, the absence of a Q branch proved that this fine structure was either a parallel band of a linear molecule or the $K''=0$ sub-bands of a nearly symmetrical top. See Herzberg[16] for the meaning of these terms.

Further evidence was obtained by the observation of a similar band without an alternation of intensity in the flash-photolysis of partly deuterated diazomethane ($CHDN_2$).

Herzberg and Shoosmith[6] deduced the following values for the rotational constants (reciprocal moments of inertia) in the upper (B') and lower (B'') states of the two molecules, CD_2 and CHD.

B' (CD_2)	3.59 cm.$^{-1}$	B'' (CD_2)	3.95 cm.$^{-1}$
B' (CHD)	4.80 cm.$^{-1}$	B'' (CHD)	5.33 cm.$^{-1}$

For the definition of B', B'' and other rotational constants see Herzberg[16]. The magnitudes of these rotational constands are compatible only with the molecules of the type XD_2 and XHD. However, the ground state and the first excited state of NH_2 are known, and these were definitely not involved in the transition responsible for the bands under investigation. Thus they concluded that the species emitting the spectrum was definitely the methylene radical and suggested that the simplest and most obvious explanation of the observed fine structure, would point to the molecule being linear in both the upper and lower states of the transition.

Assuming this, they obtained the following two independent values for C-H or C-D bond distance from the rotational constants (B") of CD_2 and CHD respectively.

$$r_o" = 1.029 \text{ Å and } 1.034 \text{ Å}$$

If, however, the molecule was assumed to be non-linear, then using the two moments of inertia to determine $r_o"$ and $\angle$HCH they found $r_o"=1.071$ Å and $\angle HCH=140°$. But this would imply that the rotational constant A" for CD_2 would be 41.7 $cm.^{-1}$, and therefore several other sub-bands with $K" = 1,2,3$ .... would be expected, for which no evidence was found. The absence of these sub-bands could be accounted for, if it was assumed that the upper state was linear or that levels with $K"=0$, in the upper state were strongly pre-dissociated and therefore escaped observation. Although it was hard to say definitely whether the molecule was linear or non-linear in the ground state, it was concluded that in all probability the $\angle$HCH was between 140° and 180°.

Moreover, from the fact that in CD_2 spectrum, the strong lines were of odd J, it was concluded that the lower electronic state of the transition was not totally symmetrical.

So, while the actual nature of the ground state remains undecided, it has been definitely established that the spectrum under consideration was due to the methylene radical and that in the lower state of the observed transition, the species has an angle between 140° and 180° and a non-totally symmetrical electronic state. Most recently, Herzberg[17] has obtained a second band system in the near infra-red and visible regions of the spectrum. According to Herzberg, this presumably is a system similar to the well-known system of NH_2 and most probably is a singlet system. So far, the relative positions of the states involved in the transition and their exact nature are unknown.

III. THEORETICAL INVESTIGATIONS OF THE METHYLENE RADICAL

Lennard-Jones[18] in 1934 discussed this species using molecular orbital theory and correlated the various electronic states of the non-linear CH_2 radical with the energy levels of the oxygen atom and the electronic states of the NH radical, which are both iso-electronic with CH_2. He assumed the C_{2v} point group for the non-linear CH_2 and by means of Group Theory found $1A_1$ as the ground state.

For the symmetry point groups, and meaning of the irreducible representations, etc. of non-linear and linear centro-symmetric molecules, such as CH_2, non-linear and linear, see Lennard-Jones,[18] Walsh,[19] Eyring et al,[20a] Wilson et al.[20b]

Walsh[19] also discussed CH_2 semi-empirically and gave two alternative schemes for the electronic transitions of the bent (C_{2v} point group) and linear CH_2 radical ($D_{\infty h}$ point group). He concluded that if CH_2 should have a strong spectral transition at wave-lengths longer than 2500 Å, then the ground state is singlet ($1A_1$), and the molecule is non-linear. This agrees with Lennard-Jones'[18] prediction, discussed earlier.

The above electronic transition may be represented as

$$(a_1)^2\ (b_2)^2\ (a_1)\ (b_1)\ 1B_1 \longleftarrow (a_1)^2\ (b_2)^2\ (a_1)^2\ 1A_1$$

However, Walsh also suggested the possibility of a transition at wave-lengths below 2500 Å as

$$(\sigma_g)(\sigma_u)^2(\pi_u)^2(\pi_u)\ 3\Pi_u \leftarrow (\sigma_g)^2(\sigma_u)^2(\pi_u)(\pi_u)\ 3$$

This would point to the CH_2 being linear with $^3\Sigma_g^-$ as the ground state.*

Laidler and Casey[21] treated the electronic states of CH_2 qualitatively, and gave a schematic representation of energy levels of various pure ionic and pure covalent states of this species for the singlet (both non-linear and linear geometry) and the triplet states (linear geometry). They suggested that if the ground state was a singlet, then there was resonance mainly between the 90 degree covalent structure and the two singlet ionic states, while if it was in a triplet state, there was resonance between the Sp-hybridised linear covalent state, and the two triplet ionic states.

Recently Gallup[22] reported the results using the LCAO/MO approximation and concluded on the basis of his calculations that CH_2 exists in a triplet ground state, the calculated angle being 160°. Moreover, calculations of the electronic energies of singlet and triplet states as a function of bond angle showed minima in both the cases at 160°. His work was criticized by Gray[23] and in his reply to this Gallup[24] cited unpublished work by Noyes, which indicates the presence of CH_2 fragments in photo-catalyzed gas reactions of hydrocarbons, which appear to have triplet ($^3B_1$) as their ground state.

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* Here small letters denote M.O.'s and capitals denote electronic states as suggested by Lennard-Jones.[18] The M.O.'s have the same character scheme (Eyring et al[20a]) as the states denoted by the same letter and sub-script.

Very recently, after the theoretical work on linear CH_2 reported in this thesis was completed, an LCAO/MO/SCF study of CH_2 was published by Padgett and Krauss.[25] They also performed a second-order perturbation Configuration Interaction calculation and found, before as well as after the second order CI, the $^3\Sigma_g^-$ state to be the lowest for linear CH_2, in agreement with the results reported in this thesis where a complete CI calculation was done. Although from their results for bent CH_2, after the second order perturbation CI calculation, the $^3B_1$ state showed a minimum at about 120°, yet the $^1A_1$ state at this bond angle was too close to the $^3B_1$ state to decide which of the two was the ground state in this case.

Moreover, they assumed the C-H bond distance equal to 2.12 a.u., which is much larger in magnitude than the values given by Herzberg and Shoosmith[6] from their spectroscopic work on the CH_2 radical.

So, it appears that at least for linear CH_2, the ground state is $^3\Sigma_g^-$, but whether the actual ground state molecular geometry of CH_2 is bent or linear, and if it is bent whether the ground state is $^3B_1$ or $^1A_1$, remains undecided.

CHAPTER 2

THE LCAO/ASMO/CI METHOD

There are two main methods for attacking chemical problems quantum-mechanically. The first one is termed the Valence-Bond (V.B.) method, developed by Heitler, London, Slater, and Pauling, hence also called the HLSP method.[2a-c] In this method the atoms are considered as the starting materials from which the molecule is built up and the molecular wave-functions are constructed from the wave-function of the individual atoms.

The second method, known as the Molecular Orbital (M.O.) method, was developed by Hund, Mulliken and Lennard-Jones almost simultaneously.[3a-c] Although both the methods have been in use for nearly three decades, it is only recently that the molecular orbital method has attracted the attention of more quantum-chemists and molecular spectroscopists than the valence bond method. This is due to the fact that for electronic energy levels, electronic transitions, etc., the M.O. method gives theoretical results in much better agreement with those experimentally observed than the valence bond method.

The M.O. method is actually an extension of the Bohr theory of electron configurations from atoms to molecules. A brief account of the method of Molecular Orbitals in the approximation of "Linear Combination of Atomic Orbitals" (abbreviated to LCAO/MO is as follows.[3,4]

Consider a molecule containing N electrons, and give each electron a wave-function called a Molecular Orbital (M.O.), depending upon the space or orbital co-ordinates of that electron only, i.e.

$$\phi i^{u} = \phi i \; (x^{u},\, y^{u},\, z^{u}) \qquad (1)$$
$$= \phi i \; (r^{u}).$$

where x^u, y^u and z^u are the space co-ordinates and r^u is the position-vector of the uth electron, the subscript i signifies the ith M.O. The M.O. is called so because it may be thought of as representing the orbit of the electron in the molecule and is essentially polycentric, i.e. it extends over the whole molecule.

The M.O.'s (ϕi) are usually constructed as linear combinations of A.O.'s (X_i) where the A.O. (X_i) is a one-electron wave-function of one of the atoms which constitute the molecule, i.e. it is an eigen-function of the Schrödinger wave-equation for an atom, obtained by the Hartree procedure or some other similar technique, then

$$\phi i = \sum_{n} C_{in} X_{n} \qquad (2)$$

The M.O.'s are constructed so as to form an orthonormal set, i.e.

$$\int \phi_i^* \phi_j \, dv = S_{ij} \qquad (3)$$

where S_{ij} is the Kroneker delta symbol which is equal to one, if $i=j$ and equal to zero if $i \neq j$.

Moreover, it is convenient to construct the M.O.'s so that they transform like the irreducible representations of the symmetry point group of the molecule under consideration.

In addition to space or orbital co-ordinates, every electron has spin co-ordinates, and a one-electron molecular wave-function depending upon the space as well as the spin co-ordinates is called a Molecular Spin Orbital (M.S.O.) ψ for that particular electron. The M.S.O.'s are also constructed to form an orthonormal set, i.e.

$\int \psi i^* \psi j \; d\tau = S_{ij}$ where $d\tau$ is the volume element depending upon the space as well as spin co-ordinates.

In what follows, the spin-orbital coupling is neglected; and so a M.S.O. factors into a M.O. and a spin function, i.e.

$$\begin{aligned} \psi K^u &= \psi k \, (r^u, s^u) \\ &= \psi k \, (qk^u) \qquad (5) \\ &= \phi_{i(k)} \, (r^u) \, \eta k^u \end{aligned}$$

where q_u is the scalar product of the vector r^u and basic spin functions α^u or β^u for the uth electron. Then the total N-electron Molecular wave-function is written as the anti-symmetrized product (Φ_u) of M.S.O.'s (ASMO or AP), which is also often called the Slater determinant, i.e.

$$\Phi_u = (N!)^{-\frac{1}{2}} \left| \psi 1(q_1) \psi 2 \, (q_2) \, \psi 3 \, (q_3) \, .. \psi N \, (q_N) \right|$$

where $(N!)^{-\frac{1}{2}}$ is the normalisation factor, and where only the terms in the leading diagonal of the Slater determinant are written between the bars.

The reason for writing the total N-electron Molecular Wave-function as an antisymmetrized product is as follows. Consider the quantum-mechanical situation of a system of N particles, say N electrons in the case of a molecule. Then the total wave-function, ψ total, for this assembly is described fully by a wave-function ψ, i.e.

$$\psi = \psi\,(q_1,\ q_2,\ q_3,\ \ldots.\ q_N) \qquad (7)$$

where each q_i as before is the combination of the space as well as the spin co-ordinates of the ith particle, i.e. the ith electron in the case considered here. Now the physical meaning of ψ is that $|\psi^2|$ gives the probability-density for finding the particles in the point $(q_1,\ q_2,\ \ldots\ q_N)$ in the configuration space. However, since all physical results must be independent of the individuality of the particles, this $|\psi^2|$ must remain invariant when the co-ordinates of the particle exchange their places. If P is any arbitrary permutation of the co-ordinates, then

$$P\ |\ \psi(q_1,q_2,\ldots q_N)^2| = |\psi(q_1,q_2,\ldots q_N)^2| \qquad (8)$$

This implies that either the wave-function (ψ) is anti-symmetric (corresponding to P= -1) or symmetric (corresponding to P=1) under such a permutation. Dirac and Heisenberg have shown that for particles obeying Fermi-Dirac statistics (called Fermions) i.e., those with half-integral spins, the total wave function is anti-symmetric to such an exchange of co-ordinates. As the electrons are Fermions, they have anti-symmetric wave-functions obeying the relation,

$$P\left|\psi(q_1,..q_2 \;....\; q_N)\right| = (-1)^p\, \psi(q_1,q_2,...q_N) \qquad (9)$$

where p = parity of the permutation P.

A practical way of writing an anti-symmetric molecular wave-function for N electrons of a molecule, is to write it in determinantal form, i.e. as a Slater determinant, also called an anti-symmetrised product (ASMO or AP) of their M.S.O.'s.

This has the following normalised form when written fully for N electrons.

$$\Phi_u = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(q_1) & \psi_2(q_1) & \cdots\cdots & \psi_N(q_1) \\ \psi_1(q_2) & \psi_2(q_2) & & \vdots \\ \vdots & \vdots & & \vdots \\ \psi_1(q_N) & \psi_2(q_N) & & \psi_N(q_N) \end{vmatrix} \qquad (10)$$

and is written for brevity as

$$\Phi_u = (N!)^{-\frac{1}{2}} \left|\psi_1(q_1)\ \psi_2(q_2) \;.......\; \psi_N(q_N)\right|$$

where only the leading diagonal of the determinant (10), is written within the bars. This is the reason for writing the total N-electron molecular wave function as in (6).

The anti-symmetrized product Φ_u (AP) has the following properties which follow from the elementary properties of determinants.

1) No two rows or two columns of the determinant are identical in all respects, otherwise the determinant vanishes.

2) No two M.S.O.'s are the same; only two M.O.'s can be the same and they also only so, if the M.S.O.'s have different spins.

This means that no two electrons can have the same space as well as the same spin-co-ordinates, which is just the well known Pauli exclusion principle, stated in a different way.

So, the A.P. in (10) satisfies Pauli's principle automatically.

Moreover, if (4) is true, then it can be shown that the A.P. in (10) is normalised, i.e.

$$\int \phi_i^* \phi_k \, d\tau = \delta_{ik} \qquad (11)$$

Then a suitable linear combination of the AP's in (6) can be classed as eigen-functions of the squared spin angular momentum operator S^2, [32] i.e.

$$\Omega^s = \sum_{q,p} a_{q,p} \, \Phi_p^S \qquad (12)$$

where a's are coefficients.

Each Ω^S is of a definite multiplicity and is a member of an orthonormal set, i.e.

$$\int \overset{*}{\Omega}{}_i^S \, \Omega_j^S \, d\tau = \delta_{ij} \qquad (13)$$

The term "configuration wave-function"(CWF) is used hereafter for each Ω^S.

In general there will be a large number of independent Ω^S of the same multiplicity and symmetry, arising from many electronic configurations, and all these(Ω^S) need to be taken into consideration in a configuration interaction treatment.

Then the wave-function for an electronic state is represented as a linear combination of the Ω^S i.e. OWF's having the multiplicity and symmetry of that particular electronic state, i.e.

$$\Psi_k^s = \sum_m b_{km} \Omega_{km}^s \qquad (14)$$

The energy E_k^s of this electronic state as given by the variation method is

$$E_k^s = \frac{\int \Psi_k^{*s} \; H \Psi_k^s \, d\tau}{\int \Psi_k^{*s} \Psi_k^s \, d\tau} \qquad (15)$$

and as the Ω^S are normalized, then

$$\int \Psi_k^{*s} \Psi_k^s \, d\tau = 1$$ and hence

$$E_k^s = \int \Psi_k^{s*} H \Psi_k^s \, d\tau \qquad (16)$$

where H is the total Hamiltonian operator for the N-electron system, and in the fixed nucleus approximation may be written as

$$H = H^0 + \sum_{v \neq u}^{N} \frac{e^2}{r_{vu}} \text{, where} \qquad (17)$$

$$H^0 = \sum_{v=1}^{N} H_v^0 (r_v) \qquad (18)$$

$H_v^0(r_v)$ being the single-electron operator for the vth electron in a potential field due to the nuclei, i.e.

$$H_v^0 (r_v) = T^0(v) + U_v^0 (r_v) \qquad (19)$$

where $T^o(v\ )$ is the kinetic energy operator for the vth electron and U_v^o is the potential energy operator for its attraction for all the nuclei of the molecule, i.e.

$$U_v^o(r_v) = -\sum_a \frac{Z_a e^2}{r_{va}} \qquad (20)$$

where Z_a is the charge on the nucleus "a" in units of electronic charge e, and r_{va} is the distance of the vth electron from the ath nucleus. The second term in (17) represents the inter-electron repulsion.

Two methods are used for evaluating (16), one is called the Self-Consistent-Field method (SCF), the other the Configuration Interaction method (CI). The LCAO/ASMO/SCF method has been treated by Roothaan.[4]

In this method, the coefficients C_{in} in (2), and an effective Hamiltonian (H_{eff}) in (16) are varied to minimise the energy, retaining simultaneously the orthonormality of the M.O.'s (ϕ_i). This method has been applied by many investigators[27-30] to molecules, and is most useful when Ψ_K^S consists of a single ϕ_K^S; such as for a closed shell configuration.

The alternative LCAO/ASMO/CI method has been treated by Craig,[5a] Coulson et al,[5b] and others[5c] and has been applied to a few specific examples[5,32].

In this method approximate M.O.'s are constructed from analytical A.O.'s by equation (2), and the best Ψ_K^S of the type in (14) determined by the variation method. The standard variation method for obtaining the eigen-value E_K^S obeying (16).

is well known,[31] and for a particular electronic state leads to large secular equations of the type

$$\sum_{u} a_u(H_{ku}-ES_{ku}) = 0 \qquad (21)$$

where

$$H_{ij} = H^*_{ji} = \int \overset{*}{\Omega}{}^{S}_{i}\, H \cdot \Omega^{S}_{j}\, d\tau \qquad (22)$$

and

$$S_{ij} = S^*_{ji} = \int \overset{*}{\Omega}{}^{S}_{i}\, \Omega^{S}_{j}\, d\tau \qquad (23)$$

If this system of equations is to have a solution different from the trivial one: every $a_u=0$; then the determinant constructed from the coefficients of the a_u must vanish, i.e.

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots\cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots\cdots & \cdot \\ \vdots & \vdots & & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots\cdots & H_{nn}-ES_{nn} \end{vmatrix} = 0 \qquad (24)$$

From (23) and (13), it can be seen that S_{ij}'s in the off-diagonal elements of (24) are all zero, while the S_{ii}'s in the diagonal elements are all equal to unity. So (24) reduces to the form,

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots\cdots\cdots\cdots & H_{1n} \\ H_{21} & H_{22}-E & \cdots\cdots & H_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} & H_{n2} & \cdots\cdots & H_{nn}-E \end{vmatrix} = 0 \qquad (25)$$

This is an nth degree equation in E and therefore has n roots, the lowest of these roots gives the energy of the electronic state under consideration.

The matrix elements H_{ii} and H_{ij} are evaluated by standard methods.[20a,20c].

The term CI means here that the off-diagonal matrix elements H_{ij} between the various configuration wave-functions (e.g. $\Omega_k^{j,s}$ and $\Omega_k^{k,s}$) of the same multiplicity and symmetry were taken into consideration when finding the lowest root of (25).

Hence there are nth degree equations of the type (25), for each electronic state, and the energies of the various electronic states are found by finding the lowest root of such equations in each case. How the lowest root is found is explained in Appendix IV.

CHAPTER 3

APPLICATION OF THE LCAO/ASMO/CI METHOD TO THE LINEAR METHYLENE RADICAL

A linear centro-symmetric geometry for the methylene radical with C-H bond distance equal to 1.0295 Å is assumed in this thesis.

Co-ordinate System:- The origin of the three Cartesian axes was chosen to be at the carbon nucleus, with positive Z axis pointing in the direction of the C-H' bond as shown in Fig.I; the arrows show the +Ve direction of the three axes.

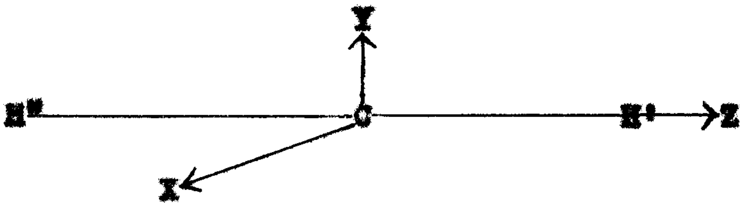

Fig.1.

Neglect of 1S Carbon Electrons:- CH_2 radical contains 8 electrons, six from the Carbon atom ($1S^2 2S^2 2p^2$), and one from each of the two hydrogen atoms H' and H". To treat this problem fully, all these 8 electrons should be considered. However, a reasonable assumption about the 1S carbon electrons greatly reduces the amount of labour without causing much loss of rigour in the calculations. It is assumed here that $(1S)^2$ electrons of carbon atom merely screen the carbon nucleus, so as to reduce the effective charge on carbon nucleus to +4e units.

This assumption has been made by many other investigators.[32,33]

This leaves six A.O.'s for the construction of M.O.'s, four from the carbon atom ($2S, 2p_x, 2p_y, 2p_z$) and two (h', h'') from the two hydrogen atoms, with six electrons to be placed in the M.O.'s.

Starting with m M.S.O.'s which is twice the number of M.O.'s and n electrons, there arise $\frac{m!}{n!\,(m-n)!}$ possible electronic configurations.[2a]

Since this number increases rapidly with the increasing value of m and n, it can be seen that neglect of 1S electrons and 1S A.O. of carbon atom, reduces the number of configurations to be considered, and thus reduces the calculations to manageable proportions.

Moreover, higher A.O.'s, e.g. 3_s, 3_p, 3_d, etc. for the carbon atom and 2S A.O.'s for the hydrogen atoms, are also neglected when setting up M.O.'s as LCA.O's.

I. ATOMIC ORBITALS:- For a bibliography of various forms for A.O.'s and their merits and demerits for use in Molecular Orbital calculations, see Hall.[34]

In most M.O. calculations, Slater A.O.'s[35] have been used and are also employed here. They have the analytical form

$$(nlm) = (2\delta)^{n+\frac{1}{2}}\left[(2n)!^{-\frac{1}{2}} r^{n-1} e^{-\delta r} S_{l,m}(\theta,\varphi)\right]$$

where $S_{l,m}, (\theta, \varphi)$ are real, normalized spherical harmonics.[36] The quantum number m is defined by $-l \leq m \leq l$, the parameter δ is related to Z effective of Slater and the quantum number n, where $n \geq l + 1$, by the relation

$$\delta = \frac{\text{Zeffective}}{n} \qquad (36)$$

Slater A.O.'s were used here in the specific forms:

$$1S_{H'} = (h') = \left(\frac{\delta'}{\pi}\right)^{\frac{1}{2}} \exp\,(-\delta' r')$$

$$1S_{H''} = (h'') = \left(\frac{\delta''}{\pi}\right)^{\frac{1}{2}} \exp\,(-\delta'' r'')$$

with $\delta' = \delta'' = 1$

$$1S_c = (1S) = \left(\frac{\delta_c'^3}{\pi}\right)^{\frac{1}{2}} \exp.\,(-\delta'_c r_c)$$

with $\delta'_c = 5.70$.

$$2S_c = (S) = \left(\frac{\delta_c^5}{3\pi}\right)^{\frac{1}{2}} r_c \exp.\,(-\delta_c r_c)$$

$$\left.\begin{aligned} 2p_x &= (\pi) = \\ 2p_y &= (\bar{\pi}) = \\ 2p_z &= (\sigma) = \end{aligned}\right\} \left(\frac{\delta_c^5}{\pi}\right)^{\frac{1}{2}} r_c \exp.\,(-\delta_c r_c) \qquad \left\{\begin{aligned} &x_c \\ &y_c \\ &z_c \end{aligned}\right.$$

With $\delta_c = 1.57$

ORTHOGONALIZED 2S CARBON A.O.:- One drawback of Slater type $2S_c$ Atomic orbital is that it is nodeless, i.e., it is not orthogonal to 1S carbon A.O. This is taken care of by setting up the orthogonalized form

$$2S_c^{*} = S^{*}) = \frac{(S - 0.20848\ 1S)}{0.97803},$$

where now the 2S carbon A.O. (S^{*}) is orthogonal to the 1S A.O. of carbon.

II. GROUP THEORETICAL DETERMINATION OF MOLECULAR ORBITALS AS LINEAR COMBINATIONS OF ATOMIC ORBITALS.

A linear centrosymmetric molecule, such as linear CH_2 belongs to the $D_{\infty h}$ point group and has the following symmetry elements corresponding to the operations which when applied to a geometrical figure transform it into itself.

(i) E:- the identity operation which leaves the molecule unchange

(ii) C_ϕ:- A rotation by an angle of $\pm\phi$ around the symmetry axis, i.e. the axis on which the nuclei lie.

(iii) σ_v:- Reflection across any plane in the molecule containing the symmetry axis.

(iv) iE:- Inversion through the centre of symmetry.

(v) iC_ϕ:- A rotation by an angle of $\pm\phi$ around the symmetry axis followed by inversion at the centre of symmetry.

(iv) $i\,\sigma_v$:- Reflection in any plane containing the symmetry axis followed by inversion at the centre of symmetry. It is equivalent to a reflection across any plane perpendicular to the σ_v plane and is also denoted by σ_h.

The various symmetry elements and symmetry operations are denoted by the same symbols. The characteristics of such molecular electronic properties as molecular electronic wave functions (Ψ) and configuration wave functions (Ω^s) are determined directly from the character table of the irreducible representations (also called symmetry species) of the $D_{\infty h}$ point group, which is reproduced in Table 1, and is explained below. The symbols in the first column are those used to describe the electronic states of the molecules of the $D_{\infty h}$ point group.

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with $\delta'_c = 5.70.$

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With $\delta_c = 1.57$

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$$2S_c^{*} = S^{*}) = \left(\frac{S - 0.20848\ 1S}{0.97803}\right),$$

where now the 2S carbon A.O. (S^{*}) is orthogonal to the 1S A.O. of carbon.

The orthogonalized form for the 2S Carbon A.O. (S^*) was used in evaluating all the mononuclear one-centre kinetic energy and nuclear attraction integrals, involving this A.O.; this improved their values considerably.

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The various symmetry elements and symmetry operations are denoted by the same symbols. The characteristics of such molecular electronic properties as molecular electronic wave functions (Ψ) and configuration wave functions (Ω^s) are determined directly from the character table of the irreducible representations (also called symmetry species) of the $D_{\infty h}$ point group, which is reproduced in Table 1, and is explained below. The symbols in the first column are those used to describe the electronic states of the molecules of the $D_{\infty h}$ point group.

Σ electronic states are non-degenerate and have $\Lambda = 0$ where Λ is the electronic angular momentum about the molecular axis in units of $\hbar$. If only one electron is present, these are the states for which $\lambda = 0$; where λ is the component of angular momentum along the molecular axis associated with an electron in a molecular orbital; e.g. $\lambda = 0$ for a σ-type M.O., $\lambda = \pm 1$ for a Π type M.O.

However, if several electrons are present in the M.O.'s, then for these states $\Lambda = \sum_i \lambda_i = 0$. Π and Δ electronic states have $|\Lambda| = 1$ and $|\Lambda| = 2$ respectively and are both doubly degenerate.

In addition Σ states are characterized by the designation + or - according to whether they are symmetrical or antisymmetrical with respect to the σ_v operation. All the electronic states are further characterized by the g ("gerade") or u ("ungerade") subscripts according to whether their wave-function remains invariant or changes sign upon inversion at the centre of symmetry, i.e. the i operation.

An alternative labelling of the group representations often used employs A_{1g} for Σ_g^+, A_{2g} for Σ_g^-, and so on; here subscripts 1 and 2 have the same meaning as + and - respectively.

The third column indicates the symmetry properties of the induced electric dipole moment M that arises in an electric transition. Only when $\Psi'' \Psi'$ contains a term with the symmetry properties of M, does the intensity controlling integral $\int \Psi'' \Psi' d\tau$, have a finite value for the transition, the double and single primes represent the lower and the upper combining states respectively.

The symmetry properties of $\Psi'' \Psi'$ are determined from a table, which gives the so-called "Direct Products"[20a] of various representations. This table is reproduced in Table 2.

To illustrate the use of this table, let Ψ' be a state of Σ_u^- symmetry and Ψ'' be another state of Σ_g^- symmetry, then the direct product of the representation is Σ_u^+ which belongs to the same species as M_a; hence for a $\Sigma_g^- \leftrightarrow \Sigma_u^-$ transition the electric dipole moment is along the molecular axis 'a'.

By use of the direct products table, the following selection rules can be deduced[20a] for the various electronic transitions:

Parallel to a $\Delta\Lambda=0$, $g \leftrightarrow u$, $\pm \leftrightarrow \pm$

Perpendicular to a $\Delta\Lambda = \pm 1$, $g \leftrightarrow u$.

The next six columns list the characters of the irreducible representations of the $D_{\infty h}$ point group. For a detailed discussion of the various group theoretical terms introduced here, see Eyring et al[20a] and Wilson et al[20b].

In general any arbitrary set of M.O.'s, constructed as linear combinations of atomic orbitals can be used in M.O. calculations; however the calculations become easier if the M.O.'s are constructed so as to transform like the irreducible representations of the symmetry point group of the molecule under investigation (e.g. $D_{\infty h}$ for linear CH_2). This is due to the fact that M.O.'s thus constructed of different symmetry classes are orthogonal to each other, and hence many integrals involving such pairs of M.O.'s vanish automatically.

How the M.O.'s of proper symmetry are constructed is discussed below, with reference to the linear CH_2 radical. The M.O.'s are to be constructed as independent linear combinations of the six A.O.'s, given below:

$$h', h'', S, \sigma, p\underline{+} = 2^{-\frac{1}{2}} (\Pi \pm i \overline{\Pi}).$$

These A.O.'s must form the basis of a representation of the $D_{\infty h}$ point group.[20a]

The representation which in general will be a reducible one is found by applying the symmetry operations of the $D_{\infty h}$ point group to the set of six A.O.'s given above.

The results are given in Table 3.

Explanation of Q:- The application of the various symmetry operations to the set of A.O.'s generates a representation, which in general will be a reducible one. To reduce this to its irreducible components, as much as diagonalization of the transformation matrices for the representation is done as possible, by a similarity transformation.[20a] In this reduction, the characters remain unchanged, and in the row labelled Q are summed up the characters for each symmetry operation.

From the character table given above for the $D_{\infty h}$ point group, it can be shown that these sums are the same as those for the group of representation

$$\Gamma = 2\Sigma_g^+ + 2\Sigma_u^+ + 2\Pi_u$$

This means that there should be two molecular orbitals of each symmetry species given in the expression for Γ i.e. Σ_g^+, Σ_u^+ and Π_u.

To set up the two independent M.O.'s of each symmetry species, use is made of Equation 10.45 of Eyring et al[20a], and using the symbols given there, we have as follows:

Σ_g^+ representation occurs twice in Γ and is of dimension one, hence $S=2$, $l=1$.

Similarly for the Σ_u^+ representation, $S=2$ and $l=1$ and for the Πu representation $S=2$ and $l=2$, because Πu is of dimension two. For the meaning of 'dimension' implied here, see Eyring et al.[20a]

The application of Equation 10.45 for each irreducible representation gives the following relations:

1. For the Σ_g^+ representation:

$$\begin{array}{lrcl} \sum_R Q_{\Sigma_g^+}(R)\ R & h' & = & 4h' + 4h'' \\ '' & h'' & = & 4h' + 4h'' \\ '' & S & = & 8S \\ '' & p^+ & = & 0 \\ '' & p^- & = & 0 \\ '' & \sigma & = & 0 \end{array}$$

where

$Q_j(R) = \sum_{t=1}^{l_j} T_j(R)_{tt}$ and $T_j(R)$ is the matrix corresponding to the operation R of the jth irreducible representation and $T_j(R)_{tt}$ is the tt-th component of the above matrix.

From the above relations, two independent linear combinations given below are obtained:

(1) $S + (h' + h'')$

(2) $S - (h' + h'')$

These have the following normalized form and are denoted as the M.O.'s ϕ_0 and ϕ_4 respectively.

$\phi_0 = (2N_0)^{-\frac{1}{2}}(S+h^+)$

$\phi_4 = (2N_4)^{-\frac{1}{2}}(S-h^+)$

where $N_0 = 1+\int S^*(1)h^+(1)dv_1$ and $N_4 = 1-\int S^*(1)h^+(1)dv_1$ are the normalization factors;

$h^+ = (2N_s^+)^{-\frac{1}{2}}(h'+h'')$ with

$N_s^+ = 1+\int h'^*(1)h''(1)dv_1$.

$\int h'^*(1)h''(1)dv_1$ is the overlap integral between the atomic orbitals h' and h".

2\. For the Σ_u^+ representation:

$\sum_R Q_{\Sigma_u^+}(R)\ R \qquad h' = 4h' - 4h''$
$\qquad\qquad ''\qquad h'' = 4h' - 4h''$
$\qquad\qquad ''\qquad \sigma = 4\sigma$
$\qquad\qquad ''\qquad S, p^+, p^- = 0.$

From these relations, two independent linear combinations properly normalised, denoted by the M.O.'s ϕ_1 and ϕ_5, of the form given below are obtained:

$\phi_1 = (2N_1)^{-\frac{1}{2}}(\sigma+h^-)$

$\phi_5 = (2N_5)^{-\frac{1}{2}}(\sigma-h^-)$ where

$N_1 = 1 + \int \sigma^*(1)h^-(1)dv_1$

$N_5 = 1 - \int \sigma^*(1)h^-(1)dv_1$ are the normalization factors and

$h^- = (2N_s^-)^{-\frac{1}{2}}(h'-h'')$ with

$N_s^- = 1- \int h'^*(1)h''(1)dv_1$.

3\. For the Π_u representation:

$$\sum_R Q_{\Pi u}(R)\ R \quad \left.\begin{matrix} h' \\ h'' \\ S \\ \sigma \end{matrix}\right\} = 0$$ due to the orthogonality theorems[20a], and

$$\begin{array}{lll} \sum_R Q_{\Pi u}(R) & R & p^+ = (8+8\cos\phi)p^+ \\ & // & p^- = (8+8\cos\phi)p^- \end{array}$$

Thus the only two linearly independent combinations from the above relations are p^+ and p^- themselves; these are already normalized and are designated by the M.O.'s ϕ_2 and ϕ_3 respectivel where

$$\phi_2 = p^+ = 2^{-\frac{1}{2}}(\Pi + i\bar{\Pi})$$

$$\phi_3 = p^- = 2^{-\frac{1}{2}}(\Pi - i\bar{\Pi})$$

$\phi_2^* = \phi_3$, $\phi_3^* = \phi_2$ and ϕ_2 and ϕ_3 are thus degenerate.

The above discussion illustrates the use of Group Theoretical methods in constructing molecular orbitals of proper symmetry species as linear combinations of atomic orbitals.

III. MOLECULAR ORBITALS:-

To summarize, by using Group Theoretical methods, the following orthonormal set of Molecular Orbitals is obtained, when all the N_i are calculated:

M.O.	Symmetry Species	Analytical Expression
ϕ_0	σ_g^+	$0.5280\,S+0.3400(h'+h'')$
ϕ_1	σ_u^+	$0.5300\sigma+0.4200(h'-h'')$
$\phi_2=\phi_3^*$	Πu	$2^{-\frac{1}{2}}(\Pi+i\bar{\Pi})$
$\phi_3=\phi_2^*$	Πu	$2^{-\frac{1}{2}}(\Pi-+i\bar{\Pi})$
ϕ_4	σ_g^+	$1.5500S-0.9995(h'+h'')$
ϕ_5	σ_u^+	$1.4990\sigma-1.1875(h'-h'')$

The above orthonormal set of M.O.'s spans the irreducible representations of the $D_{\infty h}$ point group, and alternatively could be built up starting from symmetry orbitals, following Roothaan's procedure; where M.O.'s are expressed as linear combinations of symmetry orbitals of the same symmetry species, e.g. h^+ and S (σ_g^+), σ and h^- (σ_u^+) given in this thesis. Both the methods give the same results.

IV. AP CONFIGURATION WAVE FUNCTIONS.

There is a total of 924 ways in which six electrons can be distributed among the six M.O.'s, ϕ_0 to ϕ_5, in accordance with the Pauli Principle to give all possible configurations. Many of these represent highly improbable situations in which only the highest energy M.O.'s are occupied and so have negligibl effect on the energies of the lower electronic states in a Configuration Interaction treatment.

In order to reduce the calculations of the energies of these states to manageable proportions, only those configurations which differed from the ground state configuration by promotion of from one to four electrons were included in the CI treatment. However, one particular triply excited configuration, having one electron in each of the six M.O.'s, ϕ_0 to ϕ_5 was neglected, because of the great complexity of the spin degeneracy problem for six non-equivalent electrons.

Classifications of the resultant electronic states are obtained by either (a) taking the direct products of the representations of the symmetry species for all the singly occupied M.O.'s, doubly occupied M.O.'s being totally symmetrical or (b) determining the resultant component of electronic angular momentum Λ, along the molecular axis as a vector sum of the components λ_i for the individual electrons, such that

$$\Lambda = \sum_i \lambda_i$$

$\Lambda = 0, \pm 1, \pm 2, \ldots$ correspond to Σ, Π, Δ, ... states respectively. The multiplicity of a state is determined in a similar manner as a vector sum, S, of individual electron spin angular momentum vectors S_i, where

$$S = \sum_i S_i.$$

The various λ_i values associated with an electron in the molecular orbital are given below:

M.O.	λ_i
ϕ_0, ϕ_4	0
ϕ_1, ϕ_5	0
ϕ_2, ϕ_3^*	1
ϕ_3, ϕ_2^*	-1

A. AP CWF's for closed shell configurations, not involving the degenerate pair of Πu M.O.'s:

These configurations give rise to only ${}^1\Sigma_g^+$ states; the symmetry is + because for non-degenerate M.O.'s the resulting AP CWF is always symmetrical to the σ_v operation, and the subscript is g because there are an even number of electrons in M.O.'s of the u character.

Some examples are:

(i) $\phi_0^2 \phi_1^2 \phi_4^2$ ${}^1\Sigma_g^+$

(ii) $\phi_0^2 \phi_1^2 \phi_5^2$ ${}^1\Sigma_g^+$

The AP CWF for such a configuration is formed by permutating the six electrons among the occupied M.O.'s, and for the configuration in (i), it is written as a Slater determinant of the form

$$\Phi_1 = (6!)^{-\frac{1}{2}} \begin{vmatrix} \phi_0\alpha(1) & \phi_0\beta(1) & \phi_1\alpha(1) & \cdots & \phi_4\beta(1) \\ \phi_0\alpha(2) & \phi_0\beta(2) & & & \vdots \\ \vdots & \vdots & \phi_1\alpha(3) & & \vdots \\ \vdots & \vdots & \vdots & & \vdots \\ \phi_0\alpha(6) & \phi_0\beta(6) & \phi_1\alpha(6) & \cdots & \phi_4\beta(6) \end{vmatrix}$$

where α and β represent the spin functions and 1 to 6 are the electrons. The above Φ_1 is written in the abbreviated form, explained in Chapter 2 as

$$\Phi_1 = \Omega_1 = 0\ \bar{0}\ 1\ \bar{1}\ 4\ \bar{4}$$

Similarly the AP CWF Φ_2, for the configuration in (ii) is

$$\Phi_2 = \Omega_2 = 0\ \bar{0}\ 1\ \bar{1}\ 5\ \bar{5}$$

B. AP CWF's for a configuration with two singly occupied M.O.'s:-

An example of such a configuration is $\phi_0^2\ \phi_1^2\ \phi_4\ \phi_5$, the over all symmetry is Σ_u^+, the direct product of the species of the M.O.'s ϕ_4 (σ_g^+) and ϕ_5 (σ_u^+).

A singlet and a triplet CWF arises from such a configuration and following Roothaan,[4] they are written as follows:

$$\Omega_1 = \Phi_{1\Sigma_u^+} = 2^{-\frac{1}{2}} (\Phi_1 - \Phi_2)$$

$$\Omega_3 = \Phi_{3\Sigma_u^+} = 2^{-\frac{1}{2}} (\Phi_1 + \Phi_2) \text{ where}$$

$\Phi_1 = 0\ \bar{0}\ 1\ \bar{1}\ 4\ \bar{5}$ and $\Phi_2 = 0\ \bar{0}\ 1\ \bar{1}\ \bar{4}\ 5$

C. AP CWF's for a configuration involving one electron only in each Π_u M.O.:-

$\phi_0^2\ \phi_1^2\ \phi_2\ \phi_3$ is such a configuration, for which $\Lambda = \Sigma_i \lambda_i = 0$, and so only Σ CWF's arise from it. As discussed in B, Φ_1 and Φ_2 AP functions are given below. The singlet and triplet CWF's are written as follows:

$$\Phi_1 = 0\ \bar{0}\ \ 1\ \bar{1}\ \ 2\ \bar{3}$$

$$\Phi_2 = 0\ \bar{0}\ \ 1\ \bar{1}\ \ \bar{2}\ 3$$

$$\Omega_1 = 2^{-\frac{1}{2}}\ (\Phi_1 - \Phi_2)$$

$$\Omega_3 = 2^{-\frac{1}{2}}\ (\Phi_1 + \Phi_2)$$

However, Ω_1 is invariant to the σ_v operation and thus has the $^1\Sigma_g^+$ symmetry; Ω_3 transforms into its negative by the σ_v operation and so corresponds to the $^3\Sigma_g^-$ symmetry. The underlying principle is that the ϕ_2 M.O. goes into the ϕ_3 M.O. and vice versa by the σ_v operation, which gives the following relations:

$\phi_2 \xleftrightarrow{\sigma_v} \phi_3$ (underlying principle).

$$0\ \bar{0}\ \ 1\ \bar{1}\ \ 2\ \bar{3} \xleftrightarrow{\sigma_v} (0\ \bar{0}\ \ 1\ \bar{1}\ \ 3\ \bar{2})$$

$$= -(0\ \bar{0}\ \ 1\ \bar{1}\ \ \bar{2}\ 3)$$

i.e. $\Phi_1 \xleftrightarrow{\sigma_v} -\Phi_2$

$\therefore\ \Omega_1 \xleftrightarrow{\sigma_v} \Omega_1$, thus Ω_1 has the $^1\Sigma_g^+$ symmetry.

$\Omega_3 \xleftrightarrow{\sigma_v} -\Omega_3$ thus Ω_3 has the $^3\Sigma_g^-$ symmetry.

D. AP CWF's for doubly excited configurations:-

A doubly excited configuration is one with four singly occupied M.O.'s. Such a configuration leads to one quintet, three triplets and two singlet Ω functions.[37]

In general, if there are N non-equivalent M.O.'s, a,b,c,... N, each singly occupied by an electron of either spin, then there arise 2^N determinantal antisymmetrised product (ASMO or Slater determinant) wave functions,[32] each satisfying the Pauli principle.

As mentioned in Chapter 2, suitable linear combinations of these (ASMO) wave functions can be classed as eigen functions of the squared spin angular momentum operator S^2, which has the general form[20a]

$$S^2 = (S_x - iS_y)(S_x + iS_y) + \hbar S_z + S_z^2 \qquad (A)$$

where $\hbar = \frac{h}{2\pi}$

$S_x = \sum_n S_{xn}$, $S_y = \sum_n S_{yn}$, $S_z = \sum_n S_{zn}$, the summation is over all the electrons n, in singly occupied M.O.'s.

S_{xj}, S_{yj} and S_{zj} are the operators for the x, y and z components of the spin respectively of the jth electron.

Also define

$$S_+ = \sum_n (S_{xn} + i\,S_{yn}) = S_x + i\,S_y$$

$$S_- = \sum_n (S_{xn} - i\,S_{yn}) = S_x - i\,S_y,$$

then $S^2 = S_-\,S_+ + \hbar\,S_z + S_z^2 \;\ldots\ldots \quad (B)$

In the case under consideration, there are four singly occupied M.O.'s, i.e. $N=4$ which are denoted by a, b, c and d; thus the number of ASMO functions is $2^N=2^4=16$.

Hence all the multiplet CWF's arising from the above configuration, can be represented as suitable linear combinations of the sixteen ASMO functions which arise from this configuration.

However, each of the multiplets will have one net Z component of spin of all electrons, measured in units of $\hbar$, which is called here M_s, equal to zero,[2] and information about all the eigen functions of S^2, can be obtained by considering only this component.[2]

In order to get $M_s=0$, there must be an equal number of electrons associated with α spin and β spin, which have eigen values of $\frac{1}{2}$ and $-\frac{1}{2}$ (in units of h) respectively for the z-component of the spin operator, i.e.

$$S_z\alpha(i) = +\tfrac{1}{2}\hbar\,\alpha(i)$$
$$S_z\beta(i) = -\tfrac{1}{2}\hbar\,\beta(i)$$

There are six ($^4C_2=6$) such possible combinations which yield $M_s=0$, starting with four electrons. These six combinations are given below, where a, b, c, d are the M.O.'s which house the four electrons; + or - denotes that the electron is associated with α spin or β spin respectively.

Combinations for $M_s=0$, spin degeneracy of 4 electrons.

No. of Combination	a	b	c	d	Symbol
1	+	+	-	-	D_1
2	+	-	+	-	D_2
3	+	-	-	+	D_3
4	-	+	+	-	D_4
5	-	+	-	+	D_5
6	-	-	+	+	D_6

The D_i's are the Slater determinants, e.g.

$D_1 = a(1)\ b(2)\ \bar{c}(3)\ \bar{d}(4)$ in the notation of Craig.[5a]
In the approximation that the Hamiltonian operator for many electron system is not a function of spin co-ordinates of the electrons, i.e. when spin-spin interactions and also spin-orbital interactions are neglected, the spin operators S^2 and S_z commute with the Hamiltonian,[20a] and so can be used to find the eigen value of the S^2 operator for the various AP CWF's; the latter being written as the linear combinations of D-function given above.

The eigen value for S_z, of any D_i given above is found from the following equation,[20a]

$$S_z\, D_i = (n_\alpha - n_\beta)\, \frac{\hbar}{2}\, D_i$$

where n_α = number of columns with spin α in D_i.

n_β = number of columns with spin β in D_i.

As for all the D_i's given above, $n_\alpha = n_\beta$, the eigen value of every D_i for S_z operator is zero, i.e.

$$S_z D_1 = (0)\ D_1 \quad \ldots\ldots\ldots \quad (C)$$
$$S_z^2 D_1 = (0)\ D_1 \quad \ldots\ldots\ldots \quad (D)$$

Now from (B),

$$S^2 D_1 = S_- S_+ D_1 + \hbar S_z D_1 + S_z^2 D_1$$

and using (C) and (D), we have

$$S^2 D_1 = S_- S_+ D_1 \quad \ldots\ldots\ldots \quad (E)$$

Moreover the following relations[20a] hold good for $\alpha(j)$ and $\beta(j)$ the spin functions of the jth electron.

$$(S_{xj} + i\, S_{yj})\ \alpha(j) = 0$$
$$(S_{xj} + i\, S_{yj})\ \beta(j) = \hbar\ \alpha(j)$$
$$(S_{xj} - i\, S_{yj})\ \alpha(j) = \hbar\ \beta(j)$$
$$(S_{xj} - i\, S_{yj})\ \beta(j) = 0$$

If the various Di's are denoted by an abbreviated notation, in which the electron's spins α and β are written, we have:

$D_1 = (\alpha\alpha\beta\beta)$ $\qquad$ $D_4 = (\beta\alpha\alpha\beta)$

$D_2 = (\alpha\beta\alpha\beta)$ $\qquad$ $D_5 = (\beta\alpha\beta\alpha)$

$D_3 = (\alpha\beta\beta\alpha)$ $\qquad$ $D_6 = (\beta\beta\alpha\alpha)$

When S+ and S₋ operate on the various D's, the relations given on p.236 by Eyring et al[20a] are obtained and by using these, the following relations are obtained when S^2 operates on the various D_i's.

$$S^2 D_1 = \hbar^2\ (2D_1+D_2+D_3+D_4+D_5) \quad \ldots\ldots \quad (I)$$
$$S^2 D_2 = \hbar^2\ (2D_2+D_1+D_3+D_4+D_6) \quad \ldots\ldots \quad (III)$$

$S^2 D_3 = \hbar^2 (2D_3+D_1+D_2+D_5+D_6)$ ...... (V)
$S^2 D_4 = \hbar^2 (2D_4+D_1+D_2+D_5+D_6)$ ...... (VI)
$S^2 D_5 = \hbar^2 (2D_5+D_1+D_3+D_4+D_6)$ ...... (IV)
$S^2 D_6 = \hbar^2 (2D_6+D_2+D_3+D_4+D_5)$ ...... (II)

Hence none of these D's is an eigen function of the S^2 operator. But if suitable linear combinations of these D's are taken, they do become eigen functions of S^2 as shown below.

For example, consider the following linear combinations:

(1) $\Omega^{1}_{3} = 2^{-\frac{1}{2}} (D_1 - D_6)$

Then using (I) and (II), it can be shown that

$S^2 \Omega^{1}_{3} = 2\hbar^2 (\Omega_3^{1})$ i.e. the eigen value of the operator S^2 is 2. But the eigen value of $S^2 = S(S+1)$, from this S=1 and so the multiplicity of Ω^{1}_{3} is $(2S+1)=3$. Thus Ω^{1}_{3} is a triplet wave function.

Similarly it can be shown that the following two CWF's are also triplet:

(2) $\Omega^{11}_{3} = 2^{-\frac{1}{2}} (D_2-D_5)$

(3) $\Omega^{111}_{3} = 2^{-\frac{1}{2}} (D_3-D_4)$

Further, it can be shown, using (I) to (VI), that the following two CWF's are singlet with S=0.

(4) $\Omega^{'}_{1} = \frac{1}{2} \left\{ (D_1+D_6) - (D_2+D_5) \right\}$

(5) $\Omega^{''}_{1} = 12^{-\frac{1}{2}} \left\{ (D_1+D_6)+(D_2+D_5)-2\,(D_3+D_4) \right\}$

and that Ω_5 is a quintet CWF with S=2 where

(6) $\Omega_5 = 6^{-\frac{1}{2}} \left\{ (D_1+D_6)+(D_2+D_5)+(D_3+D_4) \right\}$

Furthermore, it can be shown that except the triplet CWF's given above, all others are orthogonal to each other, and starting with the triplet CWF's (1) to (3), the following three orthonormal triplet CWF's can be set up by taking fresh linear combinations of triplet CWF's given in (1) to (3) above:

$$(7) \quad {}^3\Omega_1 = 6^{-\frac{1}{2}} \left\{(D_1-D_6)+(D_2-D_5)+(D_3-D_4)\right\}$$

$$(8) \quad {}^3\Omega_2 = 12^{-\frac{1}{2}} \left\{(D_1-D_6)+(D_2-D_5)-2(D_3-D_4)\right\}$$

$$(9) \quad {}^3\Omega_3 = 2^{-1} \left\{(D_1-D_6)-(D_2-D_5)\right\}$$

Thus three triplets, two singlets and one quintet orthonormal CWF's have been constructed which are the only ones arising from a doubly excited configuration.[2a]

In addition we have to classify the above CWF's with respect to the σ_v operation, i.e. reflection in the plane of the molecule. To do so, the four M.O.'s a, b, c and d may be identified with the M.O.'s of the linear CH_2 radical, and allowed to transform under the σ_v operation. For example, if a, b, c and d are the M.O.'s ϕ_1, ϕ_2, ϕ_3 and ϕ_4 respectively (which shall be denoted in the various D_i functions involving these M.O.'s by the numeral of their subscripts) then the behaviour of the various D_i functions under the σ_v operation is shown below.

Note that ϕ_2 goes into ϕ_3 by σ_v and vice versa, i.e.

$$\phi_2 \xleftrightarrow{\sigma_v} \phi_3$$

$$D_1 = 1\ 2\ \bar{3}\ \bar{4} \xleftrightarrow{\sigma_v} 1\ 3\ \bar{2}\ \bar{4} = -1\ \bar{2}\ 3\ \bar{4} = -D_2$$

and similarly

$$D_2 = 1\ \bar{2}\ 3\ \bar{4} \xleftrightarrow{\sigma_v} -1\ 2\ \bar{3}\ \bar{4} = -D_1$$

$$D_3 = 1\ \bar{2}\ \bar{3}\ 4 \xleftrightarrow{\sigma_v} -1\ \bar{2}\ \bar{3}\ 4 = -D_3$$

$$D_4 = \bar{1}\ 2\ 3\ \bar{4} \xleftrightarrow{\sigma_v} -\bar{1}\ 2\ 3\ \bar{4} = -D_4$$

$$D_5 = \bar{1}\ 2\ \bar{3}\ 4 \xleftrightarrow{\sigma_v} -\bar{1}\ \bar{2}\ 3\ 4 = -D_6$$

$$D_6 = \bar{1}\ \bar{2}\ 3\ 4 \xleftrightarrow{\sigma_v} -\bar{1}\ 2\ \bar{3}\ 4 = -\ D_5$$

Using these relations, it can be shown that when σ_v operate on the various CWF's previously given, the following relations are obtained.

$$\sigma_v \Omega_1' = \sigma_v \tfrac{1}{2} \left\{ (D_1+D_6) - (D_2+D_5) \right\}$$

$$= \tfrac{1}{2} \left\{ -(D_2+D_5)+(D_1+D_6) \right\} = \Omega_1'$$

i.e. Ω_1' is symmetrical with respect to the σ_v operation.

Moreover, for the above configuration $\sum_i \lambda_i = \Lambda = 0$, and so this leads only to Σ CWF's. The g or u character of these CWF's is determined from the symmetries of the occupied M.O.' of the configuration giving rise to these CWF's and is u for the configuration considered above.

Thus the Ω_1' CWF is classified as the ${}^1\Sigma_u^+$ CWF.

Similarly it can be shown that $\sigma_v \Omega_1'' = -\Omega_1''$, i.e. Ω_1'' is antisymmetrical to σ_v, and so is classified as the ${}^1\Sigma_u^-$ CWF.

Further, when σ_v operates on the orthonormal triplets and the quintet CWF's, the results are as follows:

$^3\Omega_1 \overset{\sigma_v}{\longleftrightarrow} -{}^3\Omega_1$ and is classified as the $^3\Sigma_u^-$ CWF.

$^3\Omega_2 \overset{\sigma_v}{\longleftrightarrow} -{}^3\Omega_2$ and is classified as the $^3\Sigma_u^-$ CWF.

$^3\Omega_3 \overset{\sigma_v}{\longleftrightarrow} {}^3\Omega_3$ and is classified as the $^3\Sigma_u^+$ CWF

$\Omega_5 \overset{\sigma_v}{\longleftrightarrow} -\Omega_5$ and is classified as the $^5\Sigma_u^-$ CWF

To sum up, the following orthonormal set of CWF's is obtained from the doubly excited configuration considered above.

Singlet CWF's	**Symmetry**
$\Omega_1' = 2^{-\frac{1}{2}}\left\{(D_1+D_6)-(D_2+D_5)\right\}$	$^1\Sigma_u^+$
$\Omega_1'' = 12^{-\frac{1}{2}}\left\{(D_1+D_6)+(D_2+D_5)-2(D_3+D_4)\right\}$	$^1\Sigma_u^-$
Triplet CWF's	
$^3\Omega_1 = 6^{-\frac{1}{2}}\left\{(D_1-D_6)+(D_2-D_5)+(D_3-D_4)\right\}$	$^3\Sigma_u^-$
$^3\Omega_2 = 12^{-\frac{1}{2}}\left\{(D_1-D_6)+(D_2-D_5)-2(D_3-D_4)\right\}$	$^3\Sigma_u^-$
$^3\Omega_3 = 2^{-1}\left\{(D_1-D_6)-(D_2-D_5)\right\}$	$^3\Sigma_u^+$
Quintet Configuration Wave Function:	
$\Omega_5 = 6^{-\frac{1}{2}}\left\{(D_1+D_6)+(D_2+D_5)+(D_3+D_4)\right\}$	$^5\Sigma_u^-$

The general technique described above can be applied to any configuration to obtain Configuration Wave Functions of proper multiplicity and symmetry.

It was necessary to use this procedure to set up CWF's for the ${}^1\Sigma_g^-$, ${}^5\Sigma_g^-$ and ${}^1\Sigma_u^-$ symmetry classes, since these arise only from doubly excited configurations.

CHAPTER 4.

1. RESULTS AND DISCUSSION

The calculated electronic energy levels are given in Table 4. "Before CI" energies refer to the lowest energy single configuration of each state, the energy values being relative to the lowest energy configuration of the $^3\Sigma_g^-$ symmetry, with the value of -306.15 e.v. "After CI" energies refer to the energies of the states when CI is included; the energy values are again relative to the energy of the lowest state ($^3\Sigma_g^-$) with the value -307.59 e.v.

The column "Depression" gives the lowering of energy caused by including CI for each state. These energies are also plotted on an energy level diagram, given in Fig.2.

The depression of the energy levels on including CI ranges from 0.33 e.v. for the $^1\Pi_u$ state to 4.49 e.v. for the $^1\Sigma_u^-$ state. Also, it can be seen that the order of the electronic states is the same before and after CI treatments, while in many CI calculations[5,32] a reversal in sequence of the electronic states has been reported.

Experimentally, the only spectroscopic transition observed in absorption for the CH_2 radical is that reported by Herzberg and Shoosmith[6] at 1415 Å; very recently some other transitions

ENERGY LEVEL DIAGRAM FOR THE LINEAR CH_2 RADICAL

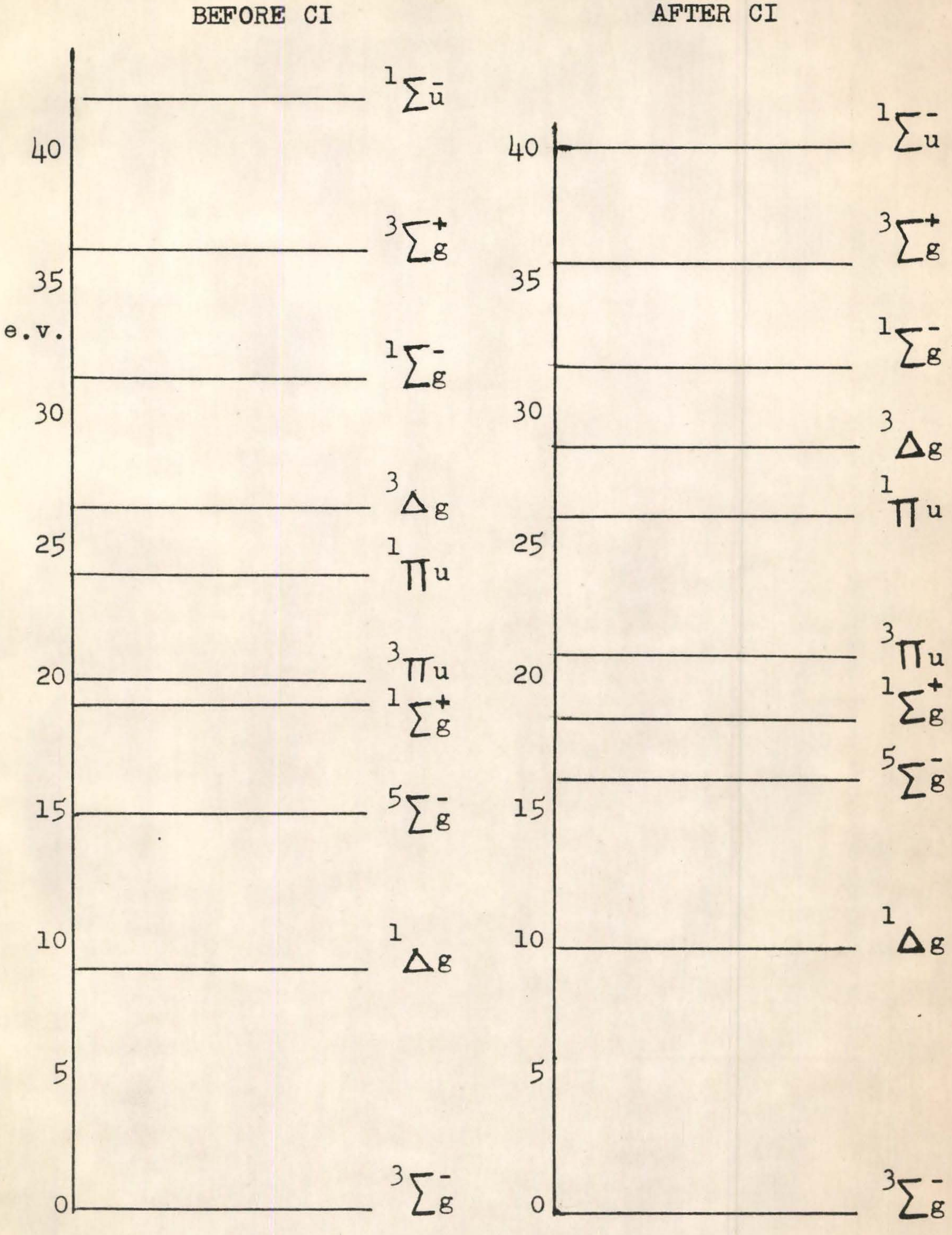

FIGURE 2.

have also been observed in the visible and near infra-red region by Herzberg[17]. The experimental energy of the 1415Å transition is 8.6 e.v.

The calculated energies for various spectroscopic transitions using CI results are given below.

Transition	Energy in e.v.
$^1\Sigma_g^- \longleftrightarrow {}^1\Sigma_u^-$	7.19
$^1\Sigma_g^+ \longleftrightarrow {}^1\Pi_u$	8.30
$^1\Pi_u \longleftrightarrow {}^1\Sigma_g^-$	6.33
$^3\Sigma_g^- \longleftrightarrow {}^3\Pi_u$	20.19
$^3\Pi_u \longleftrightarrow {}^3\Sigma_g^+$	15.25
$^1\Delta_g \longleftrightarrow {}^1\Pi_u$	16.43
$^3\Pi_u \longleftrightarrow {}^3\Delta_g$	6.81

From above, possible transitions observed by Herzberg et al[6,17] are

$^1\Sigma_g^- \longleftrightarrow {}^1\Sigma_u^-$

$^1\Sigma_g^+ \longleftrightarrow {}^1\Pi_u$

$^1\Pi_u \longleftrightarrow {}^1\Sigma_g^-$

$^3\Pi_u \longleftrightarrow {}^3\Delta_g$

Possible low energy singlet-triplet transitions which although formally forbidden might appear with low intensity are

Transition	Energy in e.v.
${}^1\Sigma_g^+ \longleftrightarrow {}^3\Pi_u$	2.88
${}^1\Pi_u \longleftrightarrow {}^3\Sigma_g^+$	9.83
${}^1\Pi_u \longleftrightarrow {}^3\Delta_g$	1.39

In the near infra-red region, the transition may be ${}^1\Sigma_g^+ \longleftrightarrow {}^3\Pi_u$, and if the same lower ground state $({}^1\Sigma_g^+)$ is also responsible for the transition in the Vacuum UV, then this transition could be either

$${}^1\Sigma_g^+ \longleftrightarrow {}^1\Pi_u \quad \text{or} \quad {}^1\Sigma_g^- \longleftrightarrow {}^1\Sigma_u^-.$$

As for the actual states involved in the transitions, the final answer must await till all the rest of the electronic states are calculated, and the observed spectra are analysed, giving clues to the states involved in the transitions.

From the results of the calculated energies of the electronic states treated in this thesis, the lowest energy allowed transition from the ground state $({}^3\Sigma_g^-)$ is ${}^3\Sigma_g^- \longleftrightarrow {}^3\Pi_u$; the energy for this transition is 20.19 e.v. and so this transition will lie in the far Vacuum UV region; this may explain why the ground state of the CH_2 radical has not been observed so far spectroscopically.

Moreover, these results and the inferences drawn therefrom, should be accepted with reserve till a full 8-electron CI treatment for the CH_2 radical is completed, incorporating accurately evaluated all the three-centre integrals.

II. ROLE OF CONFIGURATION INTERACTION:

The results show that the inclusion of Configuration Interaction lowers the calculated energy of the ground state $(^3\Sigma_g^-)$ of the linear CH_2 radical by 1.44 e.v. and the lowering of the calculated energies of the excited states by including CI varies from state to state.

The $^1\Sigma_g^-$ and $^5\Sigma_g^-$ CWF's arise from doubly excited configurations as do the $^1\Sigma_u^-$ CWF's, and while by including CI the calculaged energy of the $^1\Sigma_u^-$ state is lowered by 4.49 e.v., the calculated energies of the $^1\Sigma_g^-$ and $^5\Sigma_g^-$ states are lowered by 0.76 e.v. and 0.39 e.v. respectively.

This might be explained as due to the neglect of the $^1\Sigma_g^-$ and $^5\Sigma_g^-$ CWF's arising from the triply excited configuration $(\phi_0, \phi_1, \phi_2, \phi_3, \phi_4, \phi_5)$, which if included in the CI treatment for these states might cause a greater lowering in the energies of the states.

Moreover, for the carbon atom 3_s, 3_p A.O.'s and for the hydrogen atoms 2_s, 2_p .. A.O.'s are neglected in these calculations, and the CWF's involving these A.O.'s, if included in the CI treatment of the electronic states of the appropriate symmetry, might cause greater depression in energy for these states than reported here.

In conclusion, it appears undoubtedly that configuration interaction plays an extremely vital role in calculating the energies of not only the ground but also the excited electronic states of even very simple molecules, and must be included in all Molecular Orbital calculations.

TABLE 1

CHARACTER TABLE FOR THE $D_{\infty h}$ POINT GROUP

Symmetry Species	Λ	M	E	$2\,C_\phi$	σ_v	1E	$21C_\phi$	$1\sigma_v$
$A_{1g}(\Sigma_g^+)$	0		1	1	1	1	1	1
$A_{2g}(\Sigma_g^-)$	0		1	1	-1	1	1	-1
$A_{1u}(\Sigma_u^+)$	0		1	1	1	-1	-1	-1
$A_{2u}(\Sigma_u^-)$	0	M_a	1	1	-1	-1	-1	1
$E_{1g}(\Pi_g)$	1		2	$2\cos\phi$	0	2	$2\cos\phi$	0
$E_{1u}(\Pi_u)$	1	$M_{b,c}$	2	$2\cos\phi$	0	-2	$2\cos\phi$	0
$E_{2g}(\Delta_g)$	2		2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
$E_{2u}(\Delta_u)$	2		2	$2\cos 2\phi$	0	-2	$2\cos 2\phi$	0

TABLE 2

"DIRECT PRODUCTS" TABLE FOR THE $D_{\infty h}$ POINT GROUP

	Σ_g^+	Σ_g^-	Σ_u^+	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u
Σ_g^+	Σ_g^+	Σ_g^-	(Σ_u^+)	Σ_u^-	Π_g	(Π_u)	Δ_g	Δ_u
Σ_g^-		Σ_g^+	Σ_u^-	(Σ_u^+)	Π_g	(Π_u)	Δ_g	Δ_u
Σ_u^+			Σ_g^+	Σ_g^-	(Π_u)	Π_g	Δ_u	Δ_g
Σ_u^-				Σ_g^+	(Π_u)	Π_g	Δ_u	Δ_g
Π_g					$\Sigma_g^+\Sigma_g^-$ Δ_g	$(\Sigma_u^+)\Sigma_u^-$ Δ_u	$\Pi_g\Phi_g$	$(\Pi_u)\Phi_u$
Π_u						$\Sigma_g^+\Sigma_g^-$ Δ_g	$(\Pi_u)\Phi_u$	$\Pi_g\Phi_g$
Δ_g							$\Sigma_g^+\Sigma_g^-$ Γ_g	$(\Sigma_u^+)\Sigma_u^-$ Γ_u
Δ_u								$\Sigma_g^+\Sigma_g^-$ Γ_g

TABLE 3

A.O.	E	$2C_\phi$	σ_v	1E	$21C_\phi$	$1\sigma_v$
h'	1	1	1	0	0	0
h"	1	1	1	0	0	0
S	1	1	1	1	1	1
pz(σ)	1	1	1	-1	-1	-1
p^+	2	2 cos ϕ	0	-2	-2 cos ϕ	0
p^-	2	2 cos ϕ	0	-2	-2 cos ϕ	0
Q	8	4+4 cos ϕ	4	-4	-4 cos ϕ	0

TABLE 4

CALCULATED ENERGY LEVELS OF THE LINEAR CH_2 RADICAL

State	No. of Configurations	Energy levels in e.v.		Depression in e.v.
		Before CI	After CI	
$^3\Sigma_g^-$	14	-306.15 =0	-307.59 =0	1.44
$^1\Sigma_g^+$	20	17.62	17.31	1.75
$^3\Sigma_g^+$	8	35.57	35.44	1.57
$^1\Sigma_g^-$	4	31.26	31.94	0.76
$^1\Sigma_u^-$	8	42.18	39.13	4.49
$^5\Sigma_g^-$	4	14.89	15.94	0.39
$^1\Pi_u$	8	24.50	25.61	0.33
$^3\Pi_u$	8	19.76	20.19	1.01
$^1\Delta_g$	10	8.81	9.18	1.07
$^3\Delta_g$	4	26.76	27.00	1.20

TABLE 5

ONE CENTRE INTEGRALS

Integral	Value	Integral	Value
(1S:2S)	0.208485	(h'h':h'h')	0.625000
(h'Th')	0.500000	$(S^*S^*:S^*S^*)$	0.557258
(1ST1S)	16.245000	$(S^*S^*:\sigma\sigma)$ $(S^*S^*:\pi\pi)$ $(S^*S^*:\bar{\pi}\bar{\pi})$	0.563044
(STS)	0.410817		
(S^*TS^*)	1.38865		
$(\sigma T\sigma)$	1.23245	$(S^*\sigma:S^*\sigma)$ $(S^*\pi:S^*\pi)$ $(S^*\bar{\pi}:S^*\bar{\pi})$	0.117918
$(\pi T\pi)$	1.23245		
(1STS)	-0.507042		
(H':h'h')	1.000000	$(\sigma\sigma:\sigma\sigma)$ $(\pi\pi:\pi\pi)$ $(\bar{\pi}\bar{\pi}:\bar{\pi}\bar{\pi})$	0.614508
(C:1S1S)	5.700000		
(C:SS)	0.785000	$(\sigma\pi:\sigma\pi)$ $(\sigma\bar{\pi}:\sigma\bar{\pi})$ $(\pi\bar{\pi}:\pi\bar{\pi})$	0.0331172
$(C:\sigma\sigma)$	0.785000		
$(C:\pi\pi)$	0.785000	$(\sigma\sigma:\pi\pi)$ $(\sigma\sigma:\bar{\pi}\bar{\pi})$ $(\pi\pi:\bar{\pi}\bar{\pi})$	0.548273
$(C:S^*S^*)$	0.859415		

TABLE 6

TWO CENTRE INTEGRALS

Integral	Value	Integral	Value
$(h':h'')$	0.202972	$(H':h'h'')$	0.099900
$(h':S)$	0.614233	$(C:h'h')$	0.483083
$(h':\sigma)$	0.490869	$(C:h'S)$	0.402198
$(h'Th'')$	-0.001590	$(C:h'\sigma)$	0.279643
$(h'TS)$	0.120600	$(h'h':SS)$	0.430557
$(h'T\sigma)$	0.273105	$(h'h':h''h'')$	0.254053
$(H':SS)$	0.486114	$(h'h':\sigma\sigma)$	0.469588
$(H':h''h'')$	0.256479	$(h'h':\pi\pi)$ $(h'h':\bar{\pi}\bar{\pi})$	0.411037
$(H':\pi\pi)$ $(H':\bar{\pi}\bar{\pi})$	0.436635	$(h'h':\sigma S)$	0.118546
$(H':1S1S)$	0.514000	$(h'S:h'S)$	0.206844
$(H':\sigma\sigma)$	0.584685	$(h'h'':h'h'')$	0.0181574
$(H':h'S)$	0.444378		
$(H':h'\sigma)$	0.518539	$(h'S:h'\sigma)$	0.187869

Table 6 (continued)

TABLE 7

THREE-CENTRE INTEGRALS

Integral	Value	Integral	Value
$(h'\sigma : h'\sigma)$	0.199223	$(h'S : h''S)$	0.1573
$(h'\pi : h'\pi)$	0.0329917	$(h'h'' : SS)$	0.08739
$(h'h' : h'h'')$	0.0889858	$(h'h'' : h'S)$	0.05424
$(h'h' : h'S))$	0.330494	$(h'h' : h''S)$	0.1294
$(h'h' : h'\sigma)$	0.338975	$(h'\sigma : h''\sigma)$	-0.1089
$(h'S : SS)$	0.315697	$(h'h'' : h''\sigma)$	-0.04529
$(h'\sigma : SS)$	0.237793	$(h'\sigma : h''h'')$	0.1776
$(h'S : S\sigma)$	0.0519302	$(h'h'' : \sigma\sigma)$	0.09531
$(h'\sigma : \sigma S)$	0.094072	$(h'h'' : \pi\pi)$ $(h'h'' : \bar{\pi}\bar{\pi})$	0.08342
$(h'S : \sigma\sigma)$	0.326165	$(h'\pi : h''\pi)$ $(h'\bar{\pi} : h''\bar{\pi})$	0.02706
$(h'S : \pi\pi)$	0.310214	$(H'' : h'S)$	0.2281 0.211363 (Accurate)
$(h'\sigma : \sigma\sigma)$	0.260976		
$(h'\sigma : \pi\pi)$	0.226201		
$(h'\pi : \sigma\pi)$	0.0109814	$(C : h'h'')$	0.1271
$(h'\pi : S\pi)$ $(h'\bar{\pi} : S\bar{\pi})$	0.0561670	$(H'' : h'\sigma)$	0.1273 0.10309 (Accurate)

TABLE 8

INTEGRALS IN A.U. OVER THE M.O.'s

(only four figures are given here)

$J_{00} = 0.4221$

$J_{01} = 0.4557$

$J_{02} = J_{03} = 0.4940$

$J_{04} = 0.4328$

$J_{05} = 0.3718$

$J_{11} = 0.5092$

$J_{12} = J_{13} = 0.4710$

$J_{14} = 0.3578$

$J_{15} = 0.2827$

$\left.\begin{array}{l}J_{22}\\J_{23}\\J_{33}\end{array}\right\} = 0.5786$

$J_{24} = J_{34} = 0.4182$

$J_{25} = J_{35} = 0.5453$

$J_{44} = 0.2796$

$J_{45} = 0.5700$

$J_{55} = 0.9762$

$K_{01} = 0.1271$

$K_{02} = K_{03} = 0.08709$

$K_{04} = 0.09056$

$K_{05} = 0.09212$

$K_{12} = K_{13} = 0.02117$

$K_{14} = 0.01833$

$K_{15} = 0.07297$

$K_{23} = 0.3238$

$K_{24} = K_{34} = 0.05523$

$K_{25} = K_{35} = 0.09116$

$K_{45} = -0.02154$

$(0004) = 0.05394$

$(0114) = 0.01741$

$(0150) = -0.003118$

$(0145) = 0.1806$

$(1104) = 0.008742$

$(1115) = 0.03428$

$(1405) = 0.07246$

$(1225) = 0.02038$

$(1522) = 0.1089$

$(1504) = 0.06652$

$(0224) = 0.05560$

$(0422) = 0.1243$

$(0455) = 0.2597$

$(0444) = 0.0007526$

$(1500) = 0.06722$

$(1544) = 0.03952$

$(1555) = 0.2974$

$(1445) = -0.2115$

$(4550) = -0.0742$

APPENDICES

I. INTEGRALS OVER ATOMIC ORBITALS

A. One and Two-Centre Integrals:[36,38]- The atomic units (A.U.) used in these calculations are the same as those used by Scherr[28] in his excellent work on N_2, and are as follows:

Length: $a_o = 0.529171$ Å = Bohr radius of hydrogen

Energy: $e^2/a_o = 27.206$ e.v. = twice the ionization energy of hydrogen.

Integrals over Atomic Orbitals are defined and designated as follows and are in A.U. defined above; except the overlap integrals which are dimensionless.

In what follows, x_a, x'_a, x''_a, ... and x_b, x'_b, x''_b .... are the atomic orbitals on atoms a and b respectively, dv_1 and dv_2 are the volume elements of the electron 1 and 2 respectively, and $dv = dv_1\, dv_2$.

1. **Overlap Integrals:**

$(x_a:x_b) = \int X_a^*(1)x_b(1)dv_1$. This integral is also denoted as S_{ab}.

2. **Kinetic energy integrals:**

$$(x_aTx_b) = (x_a|-\tfrac{1}{2}\Delta|\, x_b = -\tfrac{1}{2}\int x_a^*(1)\Delta x_b(1)dv_1$$

$$(x_aTx'_a) = (x_a|-\tfrac{1}{2}\Delta|x'_a) = -\tfrac{1}{2}\int x_a^*(1)\Delta x'_a(1)dv_1$$

3. **Nuclear attraction integrals:**

$$(A:x_ax_b) = (x_a\, |\frac{z_a}{r_a}|\, x_b)$$

$$= z_a\int x_a^*(1)\frac{1}{r_a}x_b(1)dv_1$$

$$(B:x_a x'_a) = (x_a|\frac{z_b}{r_b}|\, x'_a)$$

$$= z_b \int x_a^*(1)\frac{-1}{r_b}x'_a(1)\,dv_1$$

$$(A:x_a x'_a) = (x_a|\frac{z_a}{r_a}|x'_a)$$

$$= z_a \int x_a^*(1)\frac{1}{r_a}\, x'_a(1)\,dv_1$$

4. <u>Coulomb integrals</u>

$$(x_a x'_a : x_b x_b) = \iint x_a^*(1)x'_a(1)\frac{1}{r_{12}}x_b^*(2)x'_b(2)\,dv$$

5. **Mononuclear integrals:**

$$(x_a x'_a : x''_a x'''_a) = \iint x_a^*(1)x'_a(1)\frac{1}{r_{12}}x_a^{*''}(2)x'''_a(2)\,dv$$

All the above type integrals were calculated from the analytical expressions given by Roothaan[36], Kotani et al[38] and Barnett and Coulson[39]; the different methods gave values in excellent agreement. Moreover, the magnitudes of the integrals were compared with the values obtained by Mulligan[27], Ellison and Shull[40] and Boyd[30] wherever appropriate, and were found to be as expected.

6. <u>Hybrid integrals:</u>- They have the form:

$$(x_a x'_a : x''_a x_b) = \iint x_a^*(1)x'_a(1)\frac{1}{r_{12}}x_a^{*''}(2)x_b(2)\,dv$$

and since in the linear CH_2 radical, one of the nuclei of the C-H bond is hydrogen, the tables of Kotani et al[38] were used to evaluate these integrals by five-point Lagrangian interpolation. The magnitudes of the integrals were as expected by comparison with the values of other workers.[30,40] Similarly the hybrid integral (h'h":h"h") was interpolated from the tables of Hirschfelder and Linnett.[42]

6. Exchange integrals:

$$(x_a x_b : x'_a x'_b) = \iint x_a^*(1) x_b(1) \frac{1}{r_{12}} x_a^{*\prime}(2) x_b'(2) dv$$

The exchange integrals were all obtained from the tables of Kotani et al[38] by five-point Lagrangian interpolation except for the integral (h'h":h'h") which was similarly interpolated from the tables of Hirschfelder and Linnett[42].

All the above integrals are given in Tables 5 and 6.

The A.O.'s used in evaluating these integrals are those given in Chapter 3, except that the non-orthogonalized 2S Carbon A.O. given there was used in evaluating the two and three-centre integrals (to be described later), while the orthogonalize 2S* carbon A.O. was used for the mononuclear , one-centre Kinetic energy and nuclear attraction integrals involving the 2S carbon atomic orbital.

B. Three-centre integrals:- In almost all recent molecular orbital calculations, multi-centre integrals have either been approximated or in a few simple cases have been evaluated exactly. Some groups are concentrating their efforts concurrentl in evaluating accurately certain three-centre integrals. Thus Prof. Roothaan and his co-workers at Chicago have coded a progra for three-centre nuclear attraction integrals and the author is indebted to Dr. Huzinaga who with the kind permission of Prof. Roothaan, evaluated for him a few three-centre integrals. However they were not used in the calculations.

There exist many approximations for multi-centre integrals; for their merits and demerits see Ellison and Shull.[40] In this thesis, the Ruedenberg-Mulliken (R-M) approximation[43] was used for all the three-centre integrals except for the integrals (C:h'h"), (H":h'σ) and (h'π:h"π); their evaluation is described later.

1. The R-M approximation for a three-centre nuclear attraction integral $K_{a,bc}$ is of the form:

$$K_{a,bc} = \int x_b^*(1)\frac{1}{r_a}x_c(1)\,dv_1$$

$$\doteq \tfrac{1}{2}S_{bc}\left(G_{a,b}{}^2 + G_{a,c}{}^2\right).$$

where $S_{bc} = (x_b : x_c)$ is the overlap integral $\int x_b^*(1)x_c(1)\,dv_1$

and $G_{a,b}{}^2 = \int x_b^*(1)\frac{1}{r_a}x_b(1)\,dv_1$

$$G_{a,c}{}^2 = \int x_c^*(1)\frac{1}{r_a}x_c(1)\,dv_1$$

are two-centre nuclear attraction integrals. Thus the original three-centre integral is expressed in terms of one and two-centre integrals which can be easily evaluated exactly.

2. The R-M approximation for a four-centre integral in general has the form:

$$L_{ab,cd} = \iint x_a^*(1)x_b(1)\frac{1}{r_{12}}\,x_c^*(2)x_d(2)\,dv$$

where x_a, x_b, x_c and x_d are the atomic orbitals of the atoms a, b, c and d respectively.

$$L_{ab,cd} \doteq \tfrac{1}{4}S_{ab}S_{cd}\left(L_{aa,cc}+L_{aa,dd}+L_{bb,cc}+L_{bb,dd}\right).$$

where S_{ab} and S_{cd} are the overlap integrals:

$$S_{ab} = (x_a : x_b)$$

$$S_{cd} = (x_c : x_d)$$

and

$L_{aa,cc} = (x_a x_a : x_c x_c)$, in the notation of Appendix A, with similar expressions for other integrals inside the curly brackets.

From this general expression, explicit expressions for the appropriate three-centre integrals were derived by putting two of the four centres equal. To illustrate this, the following are some examples:

(1) $L_{ab,bc} \doteq \frac{1}{4} S_{ab} S_{bc} \left(L_{aa,bb} + L_{aa,cc} + L_{bb,bb} + L_{bb,cc} \right)$

(2) $L_{ac,bb} \doteq \frac{1}{4} S_{ac} S_{bb} \left(L_{aa,bb} + L_{aa,bb} + L_{cc,bb} + L_{cc,bb} \right)$

$\doteq \frac{1}{2} S_{ac} \left(L_{aa,bb} + L_{bb,cc} \right)$

(3) $L_{ab,ac} \doteq \frac{1}{4} S_{ab} S_{ac} \left(L_{aa,aa} + L_{aa,cc} + L_{bb,aa} + L_{bb,cc} \right)$

Hence three-centre integrals are expressed in terms of one and two centre integrals, which can be easily evaluated exactly.

(b) The integral $(\sigma : h'h'')$ was evaluated by the method of Barker and Eyring.[44a] Required values for the exponential integral were obtained from the Tables published by the Federal Works Agency.[45]

(c) The integral $(H'' : h'\sigma) = \int h'^{*}(1) \frac{1}{r''} \sigma(1) \, dv_1$ was evaluated by the method of Barker and Eyring[44b], which involves the use of the functions $E_n(x) \int_1^{\infty} e^{-xu} u^{-n} \, du$ and $B_m(x) = \int_{-1}^{1} e^{-xv} v^m \, dv$; these were obtained from the tables of

Placzek[46] and Kotani et al[38] respectively. Well-known recursion formulae[38,44] were also used for evaluating $B_m(x)$ with large m values. A series expansion is employed in this method for the exponential terms occurring in a three-centre integral, and only the first four terms of the MacLaurin series expansion were used here; because the higher terms became relatively insignificant and so can be neglected.

(d) The R-M approximation for the integral

$$(h'\pi : h''\pi) = \iint h'(1)\,\pi(1)\frac{1}{r_{12}}\,h''(2)\,\pi(2)\,dv$$

gives the value zero, and so evidently fails here. Gray et al[47] have given an expression for the R-M approximation for the cases where it fails; from their expression, after a little algebra, the following expression was derived for this integral, which gave 0.02706 A.U. as the value for this integral.

$$(h'\pi : h''\pi) = (h'\bar{\pi} : h''\bar{\pi})$$

$$\doteq \frac{(h'\pi : h'\pi)\left[2(h'h' : \pi\pi)+(\pi\pi : \pi\pi)+(h'h' : h''h'')\right]}{\left[(h'h' : h'h')+(\pi\pi : \pi\pi)+2(h'h' : \pi\pi)\right]}$$

All the one and two-centre integrals required here are known and so this expression could be evaluated.

All the three-centre integrals are given in Table 7.

APPENDIX II

EQUIVALENT RELATIONS AND SIGNS OF INTEGRALS OVER ATOMIC ORBITALS

As stated in Chapter 3, the positive direction of the $2p_z(\sigma)$ carbon atomic orbital was taken to be along the C-H' bond; the origin of the Cartesian axes being at the carbon nucleus, the centre of symmetry for linear CH_2. This makes some integrals involving the h" and σ A.O.'s numerically equal but with opposite sign to those involving the h' and σ A.O.'s. To avoid ambiguity and ensure clarity, this appendix is added.

1. Overlap integrals

$(h':\sigma) = +Ve$

$(h'':\sigma) = -Ve = -(h':\sigma)$.

2. Nuclear Attraction integrals

$(C:h'\sigma) = +Ve$

$(C:h''\sigma) = -(C:h'\sigma)$

$(H':h'\sigma) = +Ve$

$(H'':h''\sigma) = -Ve = -(H':h'\sigma)$

$(H':\sigma\sigma) = (H'':\sigma\sigma)$

3. Kinetic energy integrals

$(h'T\sigma) = +Ve$

$(h''T\sigma) = -(h'T\sigma)$

4. Coulomb integrals:

$(\sigma\sigma:h'h') = (\sigma\sigma:h''h'')$

$(\sigma S:h'h') = -(\sigma S:h''h'')$

But $(\sigma\Pi:h'h') = +Ve$

$(\sigma\Pi:h''h'') = -(\sigma\Pi:h'h')$.

5. Exchange integrals

$(h'S:h'\sigma) = +Ve$

$(h''S:h''\sigma) = -(h'S:h'\sigma)$

$(\sigma h':\sigma h') = (\sigma h'':\sigma h'')$

6. Hybrid integrals

$(\sigma\sigma:\sigma h') = +Ve$

$(\sigma\sigma:\sigma h'') = -(\sigma\sigma:\sigma h')$

Also $(\sigma S:Sh') = -(\sigma S:Sh'')$

but $(\sigma S:\sigma h') = (\sigma S:\sigma h'')$

It can be seen that for all those integrals involving an even number of the σ A.O.'s, there is no change in sign where the h' A.O. is replaced by the h" A.O., but for those involving an odd number of the σ A.O.'s, there is a change in sign. This becomes comprehensible when it is realized that the σ A.O. has a component equal to +1 σ in the C-H' direction, but in the C-H" direction, equal to -1 σ, since $\cos.0^{\circ}=1$ and $\cos 180^{\circ}= -1$. This becomes clear when the σ A.O. is regarded as a vector which has components mentioned above in the directions of C-H' and C-H" bonds.

APPENDIX III

INTEGRALS OVER MOLECULAR ORBITALS

The integrals over the Molecular Orbitals are evaluated by expanding them into sums of the one, two, and three-centre integrals over the Atomic Orbitals already evaluated. The following notation for the Coulombic, exchange and hybrid integrals over M.O.'s is used. In what follows $dv = dv_1, dv_2$.

Coulombic integral

$$J_{ij} = \iint \phi_i^*(1)\phi_i(1)\left(\frac{e^2}{r_{12}}\right) \phi_j^*(2)\phi_j(2)dv$$

Exchange integrals

$$K_{ij} = \iint \phi_i^*(1)\phi_j(1)\left(\frac{e^2}{r_{12}}\right) \phi_i(2)\phi_j^*(2)dv$$

Hybrid integrals

$$(klmn) = G_{mn}^{kl} = \iint \phi_k(1)\phi_l(1)\left(\frac{e^2}{r_{12}}\right)\phi_m(2)\phi_n dv$$

The super and subscripts refer to the M.O.'s cleared of complex conjugates by using the relation,

$\phi_2^* = \phi_3$ and vice versa.

In general

$J_{ii} = K_{ii}$, $J_{ij} = J_{ji}$, $K_{ij} = K_{ji}$ and

$$G_{mn}^{kl} = G_{nm}^{kl} = G_{kl}^{mn} = G_{nm}^{lk} = G_{mn}^{lk} = G_{kl}^{nm}.$$

The various integrals over the M.O.'s are given in Table 8.

APPENDIX IV

COMPUTER TECHNIQUE FOR SOLVING THE SECULAR DETERMINANT

According to the variational principle, if we have a linear combination $\sum_m b_m \Omega_m$, of an orthonormal set of Ω functions for states of a given symmetry class, then the best approximation to the lowest energy state of this symmetry is given by the lowest root of the secular determinant:

$$(H_{ij} - S_{ij}E) = 0$$

where E occurs only in the diagonal elements, since $S_{ii}=1$ and $S_{ij} = 0$. The H_{ij} and S_{ij} are the matrix elements defined in Chapter 2. The above determinant is symmetrical as well as Hermitian.

A special sub-routine for evaluating determinants up to $N \leqslant 20$, where N is the order of the determinant, was available for the "Intercoms 103" Interpretive sub-routine of a Bendix D15G Computer. This was modified to find the lowest root of a determinant of the type given above up to $N \leqslant 22$, in the following way:

(i) The elements H_{ij} of the determinant below the main diagonal were fed into the computer memory as a traingular matrix, and the computer was programmed to set up from these elements the square determinant.

(ii) After this, a quantity λ approximately 40 e.v. lower than the first diagonal element of the determinant was automatically subtracted from all the diagonal elements and the determinant was evaluated.

(iii) λ was increased by an amount $d\lambda$, and procedure (ii) was repeated.

The determinant would vanish if λ is one of the roots of the determinant; the lowest of which would be lower in value than the lowest value diagonal element, i.e. H_{11}.

(iv) Thus procedure (iii) was repeated till the value of the determinant had opposite signs for two values of λ differing by 0.01 e.v. Then one of these two values of λ , nearer to zero, was taken as the lowest root of the determinant.

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