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Relation of the States of the Carbon Atom to Its Valence in Methane

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An extended Heitler-London-Pauling-Slater calculation is given for methane. In addition to the usual quadrivalent configuration of the carbon atom, divalent and other configurations with which it may "resonate" are considered, in order to ascertain whether or not s^2p^2 carbon plays a more important part than usually is supposed. The mathematical formulation, an example of the use of the vector model, leads to a seventh degree secular equation, which is solved for empirical values of the integrals. The influence of resonance upon the energy is found to be small, but not negligible, and increases the stability of the molecule about 1.2 volts over the value for the usual Pauling-Slater configuration. The state of the carbon atom when it forms four electron-pair bonds is obtained explicitly in terms of the atomic states, and is found to comprise ^5S, ^3D and ^1D of sp^3, together with ^3P and ^1D of s^2p^2 and of p^4. This, the "valence state" of Van Vleck, is 7 volts above the ground state of the carbon atom; resonance lowers it about 2.5 volts. The resonance causes a greater modification in the wave function and in the valence state than it does in the energy. In the final section the relative energies of CH, CH_2, CH_3 and CH_4 are examined under the approximation of electron pairing, and are shown to have the regularly graded values of 4.0, 8.0, 12.1 and 17.0 volts when the experimental values for CH and CH_4 are used to determine the unknown integrals. There is no indication that CH_2 occupies a favored position, and the valence of four for carbon remains understandable in the light of the theory.

THE Heitler-London-Pauling-Slater theory of valence has been applied to a number of the problems arising for carbon compounds, and has proved fruitful in explaining observed properties. Van Vleck,[1] and Penney[2] have examined directional effects ; Serber[3] has calculated the energies of hydrocarbons, and many other applications have been made,[4] with in general, good results. If these results are to retain validity, it must be shown that the methods of calculation are not subject to serious modifications. Now the usual theory assumes that for a valence of four the central carbon atom is in a configuration with four different orbits ; that is to say, in an excited state. In no case has account been taken of the possible effect of other configurations, such as s^2p^2 for instance, which may "resonate" with the excited state and thereby enable the carbon atom to form more stable bonds. It is thus important to ascertain whether or not such low energy configurations alter appreciably the theoretical valence properties of carbon. A calculation designed to answer this question is given here. It should be noted that in any case the H-L-P-S method is far from perfect ; but besides offering a simple picture of valence phenomena, it has qualitative significance and is important for the degree of valence.

Configurations considered

For convenience the calculation is based upon the four hybridized sp^3 tetrahedral wave functions : $t_i = \frac{1}{2}\psi(2s) + (3/4)^{\frac{1}{2}}\psi(2p\sigma_i)$, where $i = a$, b, c or d is one of the four tetrahedral directions, and $\psi(2p\sigma_i)$ means a $2p\sigma$ carbon wave function referred to the direction i. This involves no loss of generality, for four such orthogonal functions are just as good a system of reference as the usual s and p states. Three configuration types are considered : **A** that in which each of the four orbits is occupied by one electron, $t_a t_b t_c t_d$; **B** those with one orbit occupied by two electrons, or filled, $t_a^2 t_b t_c$, etc. ; and **C** those with two filled orbits, $t_a^2 t_b^2$, etc. **A** is the configuration usually used for quadrivalent carbon. As will be shown below, inclusion of **B** and **C** is equivalent to consideration of the carbon atom configurations s^2p^2, sp^3 and p^4.

The simplest quadrivalent carbon compound is methane, and it is the molecule treated. Hereafter **A**, **B** and **C** will signify the configuration of the complete molecule, including the four hydrogen orbits.

ENERGY MATRIX FOR METHANE

Number of symmetric states

The tetrahedral symmetry of CH_4 (point group T_d) causes considerable breaking-up of

* National Research Fellow in Chemistry.
[1] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).
[2] W. G. Penney, Trans. Faraday Soc. **31**, 734 (1935).
[3] R. Serber, J. Chem. Phys. **3**, 81 (1935).
[4] See the monograph of J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935), for details and a review of the subject of quantum mechanical valence.

the energy matrix. Of chief interest is the segment of lowest energy, that involving the symmetric singlet states. The number of these states can be determined by general group theoretical methods.[5, 6, 7] For configuration **A**, with eight nonidentical orbits, the permutation degeneracy leads to 14 singlet states, as may readily be seen from the "branching diagram."[8] Eyring, Frost and Turkevich,[5] and Seitz and Sherman,[6] have solved the methane problem for this configuration, and have shown that only 3 of the 14 states transform according to the symmetric irreducible representation A_1 of T_d[9] and hence contribute to the lowest segment of the energy matrix. These authors have also given methods, based upon bond eigenfunctions, of finding the symmetric states. Perhaps the best way of determining the number of states of any symmetry is to use the permutation group characters, as formulated by Serber.[7] It leads to the results for CH_4 shown in Table I, from which it is seen that symmetry reduces a problem of the 86th degree to one of the 7th degree. To elucidate the table, it should be remarked that there are 12 configurations of the type **B**, and that each of these has 6 nonidentical orbits, and hence gives rise to 5 singlet states. From the total of 60 states only three independent symmetric states (representation A_1) can be formed, as is readily shown by group theoretical methods.[10] Similarly, the 6

TABLE I. *Characters and irreducible representations of T_d for configurations of the methane molecule.*

Config.	E	$3C_2$	$6S_4$	$6\sigma_d$	$8C_3$	Irreducible representations
A	14	6	2	2	2	$3A_1+A_2+2E+T_1+T_2$
B	60	0	0	2	0	$3A_1+2A_2+5E+7T_1$ $+8T_2$
C	12	4	0	0	0	$A_1+A_2+2E+T_1+T_2$

[5] H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. **1**, 777 (1933).

[6] F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934).

[7] R. Serber, J. Chem. Phys. **2**, 697 (1934).

[8] See diagram on p. 192 of reference 4; also reference 11.

[9] The notation of R. S. Mulliken, Phys. Rev. **43**, 279 (1933), is used for group theoretical quantities. Note that the representation A_1 is not to be confused with the configuration **A**.

[10] The only class operations of T_d which do not transform all configurations of the type **B** into different configurations are E and $6\sigma_d$. They are thus the only classes which can have characters different from zero. E gives the character 5 for each configuration (cf. reference 8), and hence $12 \times 5 = 60$ for the sum. A typical element of the class $6\sigma_d$ leaves un-

configurations of the type **C**, with 4 nonidentical orbits, have 2 singlets apiece, and it can be shown that only one symmetric state derives from the 12 states which thus arise. The lowest segment of the energy matrix for the configurations **A**, **B** and **C** is therefore seen to involve seven states.

Construction of the symmetric states

A straightforward way to find the symmetric states is to employ the transformation matrices representing the permutations which correspond to operations of the point group in question. These matrices have been given for eight or fewer electrons by Serber.[7] However the symmetric states can also be found by other and more illuminating methods of the vector model without resorting to the matrices. Of course all variants of the vector model are very closely related; as methods of attack on the problem of permutation degeneracy they possess many advantages in elegance and simplicity. These advantages have been indicated by Van Vleck,[11] and by Serber.[7]

The various singlet states for an eight electron system are set up by taking all possible arrangements in the following scheme: The spins of the pairs of electrons 1 and 2, 3 and 4, 5 and 6, and 7 and 8 are coupled to 0 or 1. The resultants of the first and second pairs, and of the third and fourth, are then coupled to 2, 1 or 0; and finally the remaining two vectors are combined to give 0 resultant. The 14 states formed in such a fashion are the same as those used by Serber as a basis for the matrices representing the permutations, and are indicated schematically in Fig. 1. For configurations **B** and **C** the same states may be employed, but only those are allowed which have the spins of electrons in filled orbits coupled to zero. In all cases, the labels of the orbits and those of the electrons in them are taken to be the same.

With states constructed as outlined above, the simple rule[11] that states are antisymmetric for the

changed only 2 configurations out of the 12; the character for each is [2211] in the notation of reference 7. For $n=6$, $S=0$, [2211]=1, and thus the character for $6\sigma_d$ is 2. The characters for the reducible representation of the singlet states of configurations **B** are then 60, 0, 0, 2, 0, as given in Table I, and the number of times each irreducible representation occurs may be found by means of the usual formula.

[11] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

permutation of two orbits when the spins are coupled to 1, and symmetric when they are coupled to 0, together with judicious numbering of the electrons in the molecular array, suffices to determine all but one of the seven symmetric states for the three configuration types. By way of example, the construction of the three states for configuration **A** is sketched. Let the carbon orbits be denoted by 1, 3, 5, 7 and the hydrogen orbits bonded to them by 2, 4, 6, 8, respectively. Let the coupling scheme be as above, and consider the state where 1 and 2, and the three other pairs associated with the tetrahedral bonds, are coupled to zero. This is seen to be unchanged by any operation of T_d; it is a symmetric state, and in fact, that of electron pairing. By examination of Serber's matrices[7] it is found to be state number 14 in his notation and can be denoted by $I = A\{14\}$. Next consider the six states wherein the spins of the pairs forming two of the bonds are coupled to 1, and those for the other two bonds are coupled to zero. These states are transformed into each other by the operations of T_d, and their sum forms the symmetric state II. In terms of Serber's states it is, when normalized, $II = (1/\sqrt{6})(A\{6\}+A\{8\}+A\{9\}+A\{11\}+A\{12\}+A\{13\})$. The third state is built out of the three states which have all the bond pairs coupled to 1. Such a coupling leads to a four vector problem, and the transformations of the states cannot be obtained by simple rules. With the aid of the formulas for the coupling of four vectors, given by Johnson,[12] the transformations may be derived. However, the same information is contained in the matrices for the permutations. The generating elements of the group T_d, which are C_3 and a diagonal reflection, may be chosen as the permutations (135)(246) and (17)(28), with the orbits numbered as above. On multiplying the proper matrices to obtain the representations of these permutations, and noting that the states concerned are $\{1\}$, $\{2\}$ and $\{5\}$, it is found that $III = (1/3)(2A\{1\}+\sqrt{5}A\{5\})$.

For configurations **B** and **C**, where carbon orbits are paired, a different labelling scheme is imperative if the same spin-coupling states are to be used. Such a scheme is: 1, 2, 5, 6 for the carbon orbits, and 3, 4, 7, 8 for the corresponding

[12] M. H. Johnson, Jr., Phys. Rev. **38**, 1628 (1931).

hydrogen orbits. This scheme is used exclusively hereafter. With it, and the simple rule cited above, the symmetric states of **B** and **C** are readily found; they are shown in (1). For actual calculation of the interconfigurational elements of the matrix, the states of **A** are referred to the basis for the new labelling scheme. This is readily done by noting that the necessary permutation of the orbits is (23)(67), and computing the transformation matrix. The old symmetric states in terms of the new basis are then found from the inverse transformation. The seven symmetric states of the three configuration types are

$$I = (1/4)(3A\{5\}+\sqrt{3}A\{6\}$$
$$+\sqrt{3}A\{13\}+A\{14\}),$$

$$II = (1/2\sqrt{6})(4A\{2\}-\sqrt{3}A\{5\}$$
$$+A\{6\}+A\{13\}+\sqrt{3}A\{14\}),$$

$$III = (1/12)(8A\{1\}+\sqrt{5}A\{5\}-\sqrt{15}A\{6\}$$
$$-\sqrt{15}A\{13\}+3\sqrt{5}A\{14\}),$$

$$IV = (1/\sqrt{12})\sum_{i=1}^{12} B_i\{14\}, \qquad (1)$$

$$V = (1/\sqrt{12})(\sum_{i=1}^{6} B_i\{6\}+\sum_{i=7}^{12} B_i\{13\}),$$

$$VI = (1/\sqrt{12})(\sum_{i=1}^{6} B_i\{4\}+\sum_{i=7}^{12} B_i\{7\}),$$

$$VII = (1/\sqrt{6})\sum_{i=1}^{6} C_i\{14\}.$$

Here the orbital wave functions specifying the various configurations are, with the order of the electrons always 1 2 3 4 5 6 7 8,

$$
\begin{aligned}
A &= t_a t_b h_a h_b t_c t_d h_c h_d, & B_{10} &= t_c t_b h_c h_b t_d t_d h_d h_a, \\
B_1 &= t_a t_a h_a h_b t_c t_d h_c h_d, & B_{11} &= t_a t_c h_a h_c t_d t_d h_d h_b, \\
B_2 &= t_a t_a h_a h_c t_b t_d h_b h_d, & B_{12} &= t_a t_b h_a h_b t_d t_d h_d h_c, \\
B_3 &= t_a t_a h_a h_d t_c t_b h_c h_b, & C_1 &= t_a t_a h_a h_b t_b t_b h_c h_d, \\
B_4 &= t_b t_b h_b h_a t_c t_d h_c h_d, & C_2 &= t_a t_a h_a h_c t_c t_c h_b h_d, \\
B_5 &= t_b t_b h_b h_c t_a t_d h_a h_d, & C_3 &= t_a t_a h_a h_d t_d t_d h_c h_b, \\
B_6 &= t_b t_b h_b h_d t_a t_c h_a h_c, & C_4 &= t_b t_b h_c h_b t_c t_c h_a h_d, \\
B_7 &= t_d t_b h_d h_b t_c t_c h_c h_a, & C_5 &= t_b t_b h_a h_b t_d t_d h_c h_a, \\
B_8 &= t_a t_d h_a h_a t_c t_c h_c h_b, & C_6 &= t_c t_c h_a h_b t_d t_d h_c h_d. \\
B_9 &= t_a t_b h_a h_b t_c t_c h_c h_d, &
\end{aligned} \qquad (2)
$$

The t_i are the tetrahedral carbon wave functions defined above; the h_i are the hydrogen orbits. t_a and h_a (and other orbits with identical sub-
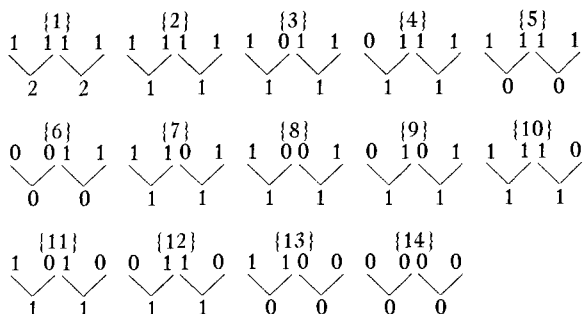
FIG. 1. The 14 spin coupling schemes for the singlets of eight electron systems. The four numbers forming the first rows are the resultants for the pairs 1 and 2, 3 and 4, 5 and 6, and 7 and 8 respectively, and are always kept in the same order in the figure. The final resultant (not shown) is of course 0.

scripts) always belong to the same tetrahedral direction a. Each of these configurations has singlet states, designated by $B_1\{14\}$, etc., according to the spin coupling scheme indicated in Fig. 1. Note that there are only two singlet states for the configurations **C**, but that they are numbered in accordance with the 14 states of **A**.

Calculation of matrix elements

The elegant matrix method of Dirac,[13] extended by Serber[14] to include several configurations, may be used to obtain the energy matrix. To secure the elements connecting the various states (1), formula (13) of reference 14 is used, together with the permutation matrices of reference 7. The fact that only symmetric states are involved facilitates determination of the elements. Thus for interactions between I and IV, only one configurational component of IV needs to be considered, since I is symmetric and would give the same result for any other component. If terms involving the squares of non-orthogonality integrals are neglected, only simple permutations need be included, except in those cases where identical orbits are interchanged. Under these conditions the energy matrix is found to be[15] as shown in Eq. (3).

Eq. (3). Energy matrix for methane. $H =$

	I	II	III	IV	V	VI	VII
I	$H_I^{AA} - 3\gamma - 3\beta + 4\alpha - 6\delta$	$(9/2)^{\frac12}(\beta + \gamma - 2\delta)$	0	$(3/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$(9/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$3(\theta - \kappa)$	$-(3/2)^{\frac12}\mu$
II	$(9/2)^{\frac12}(\beta + \gamma - 2\delta)$	$H_I^{AA} - 4\gamma - 4\beta$	$(5/2)^{\frac12}(\beta + \gamma - 2\delta)$	$(3)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$H_I^{BA} - \theta - \eta - \kappa$	$(2)^{\frac12}(\theta - 4\eta + 3\kappa)$	$-(3)^{\frac12}\mu$
III	0	$(5/2)^{\frac12}(\beta + \gamma - 2\delta)$	$H_I^{AA} - \gamma - \beta - 4\alpha - 2\delta$	$(15/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$-(5/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$-(5)^{\frac12}(\theta - \kappa)$	$-(15/2)^{\frac12}\mu$
IV	$(3/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$(3)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$(15/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$H_I^{BB} + 4\theta - 2\mu - 2\alpha - 6\delta$	$-(3)^{\frac12}(\delta - \alpha + 2\eta - 2\kappa)$	0	$-2(H_I^{BA} - \theta - \eta - \kappa)$
V	$(9/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$H_I^{BA} - \theta - \eta - \kappa$	$-(5/2)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$-(3)^{\frac12}(\delta - \alpha + 2\eta - 2\kappa)$	$H_I^{BB} - 2\gamma + 8\theta - 4\mu - 2\beta - 4\delta - 4\eta$	$(8)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	0
VI	$3(\theta - \kappa)$	$(2)^{\frac12}(\theta - 4\eta + 3\kappa)$	$-(5)^{\frac12}(\theta - \kappa)$	0	$(8)^{\frac12}(H_I^{BA} - \theta - \eta - \kappa)$	$H_I^{BB} - 4\gamma + 2\mu - 2\beta - \alpha - 3\delta - 4\eta + 4\kappa$	$2(6)^{\frac12}(\eta - \kappa)$
VII	$-(3/2)^{\frac12}\mu$	$-(3)^{\frac12}\mu$	$-(15/2)^{\frac12}\mu$	$-2(H_I^{BA} - \theta - \eta - \kappa)$	0	$2(6)^{\frac12}(\eta - \kappa)$	$H_I^{CC} - 4\gamma - 2\alpha - 6\delta$

[13] P. A. M. Dirac, *The Principles of Quantum Mechanics*, second edition, p. 222.

[14] R. Serber, Phys. Rev. **45**, 461 (1934).

[15] The actual calculation of the matrix elements is a little involved. The element I IV, for example, is not simply the interaction between states of two configurations **A** and **B**, but is the sum of the interactions of state I of **A** with certain states of the 12 configurations comprised in **B**. Furthermore, with the configurational wave functions as written in (2), higher permutations give rise to simple exchange integrals in some cases. To avoid the labor of computing the matrices for such higher permutations, the bases for the states of

these configurations may be changed; that is to say, a new arrangement of the orbits may be taken. The old states in terms of those for the new arrangement are then found from the proper transformation matrix. Even after this is done, triple exchanges yield single exchange integrals for some interactions (B_1 with B_8 for instance). In such cases great care must be taken with the signs of the coefficients. (For sign conventions in linear transformations see E. Wigner, *Gruppentheorie*, p. 113 ff.) Finally it should be mentioned that in the matrix (3) certain dependent exchange integrals for the carbon orbits, which appeared originally, have been eliminated.

Here the integrals are

$$H_I{}^{AA} = (A \mid \boldsymbol{H} \mid A), \quad H_1{}^{CC} = (C_1 \mid \boldsymbol{H} \mid C_1),$$
$$II_I{}^{BB} = (B_1 \mid \boldsymbol{H} \mid B_1), \quad H_1{}^{BA} = (B_1 \mid \boldsymbol{H} \mid A). \quad (4)$$

Also

$$\alpha = (t_a h_a ; h_a t_a), \quad \theta = (t_a t_b ; t_c t_a),$$
$$\beta = (h_a h_b ; h_b h_a), \quad \kappa = (t_a h_c ; h_c t_b),$$
$$\gamma = (t_a t_b ; t_b t_a), \quad \lambda = (t_a t_b ; t_a t_c), \quad (5)$$
$$\delta = (t_a h_b ; h_b t_a), \quad \mu = (t_a t_b ; t_c t_a),$$
$$\eta = (t_a h_a ; h_a t_b),$$

where abbreviations of the type $(t_a h_a ; h_a t_a)$ $= (t_a(1)h_a(2) \mid \boldsymbol{H} \mid h_a(1)t_a(2))$ have been used.

The element $I\,I$ represents the approximation of electron pairing. The section involving the first three states (configuration **A**) yields the cubic secular equation given by Seitz and Sherman,[6] and, in a somewhat different form, by Eyring, Frost and Turkevich.[5] The numerical value of the complete matrix will be discussed in a later section.

RELATION OF ENERGY MATRIX TO THE STATES OF THE CARBON ATOM

Identification of the states contained

When the $C-H$ and $H-H$ integrals are set equal to zero, the matrix (3) depends only on the properties of the carbon atom, and yields seven atomic states. Symmetry considerations permit these states to be identified beforehand. It is only necessary to find what states of the C atom give rise to the symmetric representation A_1 of T_d when combined with four hydrogen orbits in a tetrahedral array.

The seven states for CH_4 were constructed so as to be symmetric (under the operations of T_d) in the orbital factor of the wave function. But they must also be symmetric in the spins, since the spin characters are the same as the orbit characters for even permutations,[16] and all the permutations of T_d for CH_4 are even (two electrons in each tetrahedral bond). By forming direct products of the representations of orbits for the carbon atom states and of those for four hydrogen orbits, and reducing the direct products, the possible representations of T_d for the orbital function of CH_4 are found. The same may be done with the spin functions. The carbon atom

configurations which must be considered are those that can be used to construct sp^3 hybridized configurations; they are sp^3, and s^2p^2 and p^4 in equal amounts.

The orbital functions for the s^2p^2 and p^4 carbon states (which are *gerade*) of $L=0$ and 1 belong to the representations A_1 and T_1, respectively; and those for the sp^3 states (which are *ungerade*) of $L=0$, 1 and 2 to A_2, T_2 and $E+T_1$.[17] The representations for the transformations of the four hydrogen orbits are found by means of the characters for the symmetric permutation group,[18] and are A_2, T_1 and E when the spins are coupled to 2, 1 and 0, respectively. On reducing the direct products for combinations that can give rise to singlets for CH_4, it is found that the states ^3P and ^1D of s^2p^2 and p^4, and the states ^5S, ^3D and ^1D of sp^3 can each yield the representation A_1 once. With s^2p^2 and p^4 of equal rank, it is seen that there are just seven states in all. To clinch the identification, the spin functions must also be proven symmetric.

The representations of the spin functions for four electrons in a tetrahedral array are A_1, T_2 and E for $S=2$, 1 and 0, and are the same for both the carbon atom and the totality of the hydrogen orbits.[19] Reduction of the proper direct products (squares in this case) shows that any quintet, triplet or singlet state of the carbon atom can give rise to A_1 once and only once. Thus the seven states of the carbon atom which should be contained in the matrix (3) when interatomic terms are omitted are $s^2p^2\,{}^3P$, $s^2p^2\,{}^1D$, $sp^3\,{}^5S$, $sp^3\,{}^3D$, $sp^3\,{}^1D$, $p^4\,{}^3P$ and $p^4\,{}^1D$. The states which cannot participate in the carbon valences in CH_4 are $s^2p^2\,{}^1S$, $sp^3\,{}^3P$, $sp^3\,{}^3S$, $sp^3\,{}^1P$ and $p^4\,{}^1S$.

Transformation of matrix to form based on states of the carbon atom

By applying a canonical transformation to the energy matrix, it may be reduced to a form indexed by the seven carbon atom states listed above. The atomic states of interest are shown

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[16] See for instance B. L. van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik*, p. 135.

[17] R. S. Mulliken, Phys. Rev. **43**, 293 (1933), Table II.
[18] See R. Serber, reference 7. Also E. Wigner, *Gruppentheorie*, p. 149.
[19] The spin representations are readily found from those of the orbits by noting that the spin character is the same as that for the orbits for even permutations, and is of opposite sign for odd permutations, cf. reference 16.

in Table II in terms of the Slater parameters.[20, 21] The carbon integrals in terms of the same parameters are

$$\gamma = (1/16)[F_0(2s, 2s) - 2F_0(2s, 2p) \\ + F_0(2p, 2p) + 4G_1 + 28F_2],$$
$$\theta = (1/16)[F_0(2s, 2s) - 2F_0(2s, 2p) \\ + F_0(2p, 2p) - 8F_2],$$
$$\lambda = (1/16)[F_0(2s, 2s) + 2F_0(2s, 2p) \\ - 3F_0(2p, 2p) - 4G_1 + 12F_2], \quad (6)$$
$$\mu = (1/16)[F_0(2s, 2s) - 2F_0(2s, 2p) \\ + F_0(2p, 2p) - 4G_1 + 4F_2],$$
$$\chi = (1/16)[F_0(2s, 2s) + 6F_0(2s, 2p) \\ + 9F_0(2p, 2p) - 4G_1 - 12F_2].$$

Further, the coulomb integrals for the carbon atom only are[22]

$$H_I{}^{AA}(C) = I(2s) + 3I(2p) + 6\chi,$$
$$H_I{}^{BB}(C) = I(2s) + 3I(2p) + 6\chi + 2\gamma - 2\mu,$$
$$H_I{}^{CC}(C) = I(2s) + 3I(2p) + 6\chi + 4\gamma - 4\mu, \quad (7)$$
$$H_I{}^{BA}(C) = \tfrac{1}{4}I(2s) - \tfrac{1}{4}I(2p) + 3\lambda + 2\theta - 2\mu.$$

When these quantities are substituted in (3), and interatomic terms are neglected, $H(C)$, the matrix for the carbon atom, is obtained. A transformation R may then be found, such that $R^{-1}H(C)R = H'(C)$ has for diagonal terms the quantities listed in Table II, and only has non-diagonal elements (of magnitude G_1) connecting the interacting levels; i.e. connecting $s^2p^2\ {}^3P$ with $p^4\ {}^3P$, and $s^2p^2\ {}^1D$ with $p^4\ {}^1D$. In obtaining the transformation it is first convenient to note that $sp^3\ {}^5S$ is a root of the cubic equation for configuration A, as Van Vleck[23] has shown. After this term has been placed on the diagonal, the remaining sixth degree segment can be separated into parts corresponding to the triplets and singlets,[24] and these parts can be reduced individually. In this manner the complete transformation R is constructed.

With the aid of R the state of the carbon atom for electron pairing may be found in terms of the atomic states. Now the approximation of electron pairing is tantamount to the assumption that the element $I I$ of (3) is a factor of the entire matrix, and thus the state of the carbon atom in I is that for electron pairing. The inverse transformation R^{-1} gives the old states in terms of the new, and from it one finds that the state of the carbon atom when it forms four equivalent electron-pair bonds is

$$I(C) = \tfrac{1}{8}[-2\sqrt{5}(sp^3\ {}^5S) - 3(p^4\ {}^3P) \\ - 3\sqrt{2}(sp^3\ {}^3D) + 3(s^2p^2\ {}^3P) + \sqrt{3}(p^4\ {}^1D) \\ + \sqrt{2}(sp^3\ {}^1D) - \sqrt{3}(s^2p^2\ {}^1D)]. \quad (8)$$

This is the "valence state" of the carbon atom, defined by Van Vleck.[4, 23]

If the transformation R is applied to the complete matrix (3) a form is secured which displays the carbon atom energy levels. It is $H' = R^{-1}HR$, and is given in Eq. (9) (see next page).[24a] Here

$$X = H_I{}^{AA} + \tfrac{1}{8}[5F_0(2s, 2s) + 14F_0(2s, 2p) \\ - 19F_0(2p, 2p) - 4G_1 - 4F_2] + I(2s) - I(2p) \quad (10)$$

and

$$Z = M_{ss} - \tfrac{1}{3}M_{\sigma\sigma} - \tfrac{2}{3}M_{\pi\pi}. \quad (11)$$

The integrals M_{kk} are defined by

$$M_{kk} = \int\int \psi_k(1)h(2)\left[\frac{e^2}{r_{12}} - \frac{e^2}{r_{H1}}\right]\psi_k(1)h(2)dv_1dv_2, \quad (12)$$

where $k = 2s,\ 2p\sigma$ or $2p\pi$ of C and the direction of reference for m_l is the $C-H$ axis. $W(sp^3\ {}^5S)$ denotes the energy of the carbon level $sp^3\ {}^5S$ above the ground level $s^2p^2\ {}^3P$, etc. Hence $W(s^2p^2\ {}^3P) = 0$.

Solution of the Secular Equation

Values of integrals

Instead of attempting to evaluate the integrals in (3) or (9), the procedure of assuming plausible values, and of treating certain integrals as adjustable parameters, is followed. This method probably exploits all the real information contained in a Heitler-London calculation; at any rate it is sufficient to give an unambiguous answer in the present case. The relative roots of

[20] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[21] To avoid fractional coefficients, the conventions of E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931) are used for the F's and G's.

[22] Here, and in Table II, $I(2s)$ and $I(2p)$ are not the I's defined by Slater (reference 20), but include the constant terms $W(C2s)$ and $W(C2p)$ respectively.

[23] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[24] The multiplicities can be determined readily from the spin coupling scheme used in setting up the symmetric states.

[24a] The complete connections between (3) and (9) may be of value. Numerically $X = H_I{}^{AA} - 9.75$ volts. $H_I{}^{BB}$ and $H_I{}^{CC}$ are the same as $H_I{}^{AA}$ except for the carbon atom terms given in (7). $H_I{}^{BA} = H_I{}^{BA}(C) + Z$. $H_I{}^{AA}$ is given explicitly in (18).

Eq. (9). **H'** =

	I'	II'	III'	IV'	V'	VI'	VII'
I'	$X+W(sp^3\,{}^5S)$ $+\alpha+3\delta-6\beta$	$-(5/4)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$-(5/2)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$	$(5/4)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	0	0	0
II'	$-(5/4)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(p^4\,{}^3P)$ $-4Z-4\delta+4\kappa$ -2β	$-(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	G_1	$(3)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$	$(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	0
III'	$-(5/2)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$	$-(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(sp^3\,{}^3D)$ $-4\delta+4\kappa-2\beta$	$(1/2)^{\frac12}(\delta-\alpha$ $-2\delta+2\kappa)$	$(3/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$\delta-\alpha$ $+2\eta-2\kappa$	$-(3/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$
IV'	$(5/4)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	G_1	$(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$X+W(s^2p^2\,{}^3P)$ $+4Z-4\delta-8\eta$ $-4\kappa-2\beta$	0 •	$-(1/2)^{\frac12}(\delta$ $-\alpha-2\eta$ $+2\kappa)$	$(3)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$
V'	0	$(3)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$	$(3/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	0	$X+W(p^4\,{}^1D)$ $-4Z-2\alpha-6\delta$ $+4\eta+4\kappa$	0	G_1
VI'	0	$(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$\delta-\alpha+2\eta-2\kappa$	$-(1/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	0	X $+W(sp^3\,{}^1D)$ $-2\alpha-6\delta$	0
VII'	0	0	$-(3/2)^{\frac12}(\delta-\alpha$ $-2\eta+2\kappa)$	$(3)^{\frac12}(\delta-\alpha$ $+2\eta-2\kappa)$	G_1	0	$X+W(s^2p^2\,{}^1D)$ $+4Z-2\alpha-6\delta$ $-4\eta-4\kappa$

the secular equation depend only on the parameters describing the carbon atom, the quantity Z, β, and the C$-$H exchange integrals. The parameters for the carbon atom may be determined by empirical fitting of the energy levels, and from the theoretical calculations of Beardsley.[25] The values used are

$$F_0(2s, 2s) = 17.82 \text{ volts}, \quad F_0(2s, 2p) = 16.07, \quad F_0(2p, 2p) = 14.75 \tag{13}$$

from Beardsley's formulas, and

$$G_1 = 2.18 \text{ volts}, \quad F_2 = 0.188, \quad I(2p) - I(2s) = 12.79 \tag{14}$$

from Van Vleck's[26] fitting of the sp^3 levels, together with the above values of the F_0's. Such values, when used in the formulas of Table II,

TABLE II. *States of the carbon atom contained in the energy matrix for methane, in terms of the Slater parameters.*

State	Coefficient of:						
	$F_0(2s,2s)$	$F_0(2s,2p)$	$F_0(2p,2p)$	G_1	F_2	$I(2s)$	$I(2p)$
$p^4\,{}^1D$			6		-9		4
$p^4\,{}^3P$			6		-15		4
$sp^3\,{}^1D$		3	3		-6	1	3
$sp^3\,{}^3D$		3	3	-2	-6	1	3
$sp^3\,{}^5S$		3	3	-3	-15	1	3
$s^2p^2\,{}^1D$	1	4	1	-2	1	2	2
$s^2p^2\,{}^3P$	1	4	1	-2	-5	2	2

reproduce the observed s^2p^2 and sp^3 levels quite well, as Van Vleck has shown; for the p^4 levels they give values about 1.4 volts above the energies computed by the Bacher-Goudsmit extrapolation method.[27]

It is easy to show that Z vanishes identically if Slater's nodeless wave functions[28] are used, and if the same effective nuclear charges are used for the carbon $2s$ and $2p$ orbits. In any case Z should be small, and the value $Z=0$ may be assumed.

β is the same as the exchange integral for the hydrogen molecule, except for terms of the order of squares of nonorthogonality integrals, and is taken to be 0.9 of the Morse function for H_2. For CH_4, with C$-$H distance 1.09A, $\beta = -1.06$ volts.

The C$-$H integrals are related to the N_{kl} defined by Van Vleck[1, 23] as follows:

$$\alpha = -\tfrac14[N_{ss} + 3N_{\sigma\sigma} + 2\sqrt{3}N_{s\sigma}],$$
$$\delta = -\tfrac14[N_{ss} + \tfrac13 N_{\sigma\sigma} - (4/3)^{\frac12}N_{s\sigma} + (8/3)N_{\pi\pi}], \tag{15}$$
$$\eta = -\tfrac14[N_{ss} - N_{\sigma\sigma} + (4/3)^{\frac12}N_{s\sigma}],$$
$$\kappa = -\tfrac14[N_{ss} + \tfrac13 N_{\sigma\sigma} - (4/3)^{\frac12}N_{s\sigma} - (4/3)N_{\pi\pi}].$$

The N's have been discussed in some detail by Van Vleck, and by Penney.[29, 30] Two sets of

[25] N. F. Beardsley, Phys. Rev. **39**, 913 (1932).
[26] J. H. Van Vleck, J. Chem. Phys. **2**, 297 (1934); also reference 23.

[27] R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).
[28] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[29] W. G. Penney, Trans. Faraday Soc. **31**, 734 (1935).
[30] W. G. Penney, Proc. Roy. Soc. **A146**, 223 (1934).

values are considered in particular here :

$$N_{ss} = 2, \quad N_{\sigma\sigma} = 2.3, \quad N_{s\sigma} = 1.0, \quad N_{\pi\pi} = -0.6, \quad (16)$$

from Van Vleck's illuminating treatment of CH_4;[23] and

$$N_{ss} = 2.0, \quad N_{\sigma\sigma} = 2.2, \quad N_{s\sigma} = 2.1, \quad N_{\pi\pi} = -0.6, \quad (17)$$

taken from Penney,[29] who determined the most uncertain integral, $N_{s\sigma}$, by fitting the bending vibration frequency of methane.

Roots of the secular equation

With the values of the integrals defined above, the energy of the molecule for electron pairing (diagonal term $I\,I$ of (3)) is $X = 2.12$ volts for choice (16), and $X - 7.59$ for choice (17) of the N's. The lowest roots of the complete secular equation are[31] $X - 3.50$ and $X - 8.77$ volts for the two choices, and it is seen that the total energy of the molecule is lowered only 1.38 or 1.18 volts, respectively, by the influence of the other six states. The effect of states II and III in the cubic secular equation for configuration A was shown to be unimportant by Van Vleck.[23] Thus the small lowering of the energy is due principally to the configurations B and C, and there is a certain amount of resonance.

Other reasonable values of the N's lead to roots which are not much lower. Since electron pairing is a fairly good approximation, the secular equation in the form (3) may be solved by applying second order perturbation theory. This is readily done for a variety of cases. With the limits 1 volt and 2.5 volts for N_{ss} and $N_{s\sigma}$, and 1.5 and 2.5 for $N_{\sigma\sigma}$, no combination can be found which lowers the total energy more than two volts. The same approximation gives lowerings of 1.11 and 0.87 volts (instead of the accurate values 1.38 and 1.18) for the two particular cases (16) and (17). It therefore is apparent that the low energy configurations B and C of the central carbon atom are not very effective in increasing the binding energy in methane, and that the formula for electron pairing remains a moderately good approximation. However, although the energy is not greatly changed by the resonance, the wave functions and the pro-

[31] A convenient method of solving secular equations is that given by James and Coolidge, J. Chem. Phys. **1**, 834 (1933).

motional energy of the valence state are altered considerably.

Modification of the valence state by resonance

The wave functions for the lowest roots of the secular equation in the form (9) are shown for the choices (16) and (17) in Table III. The wave

TABLE III. *Wave functions for the valence state of the carbon atom.*

State in (9)	Atomic state	Coefficients for:		
		Electron pairing	(16)	(17)
I'	$sp^3\ {}^5S$	−0.559	−0.460	−0.445
II'	$p^4\ {}^3P$	−.375	−.189	−.251
III'	$sp^3\ {}^3D$	−.531	−.527	−.541
IV'	$s^2p^2\ {}^3P$	.375	.539	.509
V'	$p^4\ {}^1D$	.216	.132	.174
VI'	$sp^3\ {}^1D$	.177	.145	.169
VII'	$s^2p^2\ {}^1D$	−.216	−.382	−.358

function for the state of electron pairing, (8), is also shown. The changes produced in the coefficients by the influence of the configurations B and C are quite appreciable and may be expected to modify the energy of the valence state. The energy of the carbon atom for electron pairing is known to be about 7 volts above $s^2p^2\ {}^3P$ from Van Vleck's[23] analysis. It may of course also be found from (8) and the numerical values of the carbon atom energy levels (the interaction terms G_1 must be taken into account). The corresponding energies of the carbon atom in methane for choices (16) and (17) are found from the respective wave functions, and are 4.02 and 4.80 volts. The exact value for electron-pair bonds is 7.03 volts. Nevertheless, in spite of the 2.2 to 3 volts decrease in promotional energy, resonance increases the stability of the molecule by only 1.4 volts. Poorer bonding in the "divalent" configuration B, and in the "zerovalent" configuration C causes the compensation. However. the considerable change in the energy of the valence state indicates that too great a significance should not be attached to this quantity.

RELATIVE ENERGIES OF CH_4, CH_3, CH_2 AND CH

The energy for CH_4 given by the single configuration which includes the state for four electron-pair bonds has proved to be roughly valid

with respect to the possible interaction of other configurations. Corresponding approximations for single configurations may be used to determine the energies of CH_3, CH_2 and CH in terms of the same integrals defined for CH_4, and in this way relative energies for the four molecules may be secured. These quantities are of great importance in chemical kinetics, and are not known at all well experimentally, so that even rough estimates should be of value. Furthermore, such a comparison may be expected to shed light on the reasons for the quadrivalence of carbon.

In securing relative energies, the unknown integrals are treated as arbitrary parameters, and are used to fit the observed energies of CH_4 and CH. The integrals, and the $C-H$ distances, are assumed to be the same for all four molecules.

CH_4

The electron pairing energy is, from (3),

$$W(CH_4) = H_I{}^{AA} - 3\gamma - 3\beta + 4\alpha - 6\delta$$
$$= I(2s) + 3I(2p) + 6\chi + 4W(H)$$
$$+ 4K(CH_4) + 6K(H_2) - 3\gamma - 3\beta + 4\alpha - 6\delta. \quad (18)$$

Here $K(CH_4) + (3/2)K(H_2)$ is one-fourth of the interatomic coulomb energy for CH_4, and

$$K(CH_4) = M_{ss} + M_{\sigma\sigma} + 2M_{\pi\pi} + V_{CH}$$
$$+ \int h(1)V_C(1)h(1)dv_1, \quad (19)$$

where the M's are as in (12), V_{CH} is the potential energy between carbon and hydrogen centers, and V_C is the potential of the carbon center. $K(H_2)$ is the same as the coulomb energy for the hydrogen molecule, and is taken as $1/10$ of the Morse function for H_2, $M(H_2)$. Thus $K(H_2) - (1/2)\beta = -0.35M(H_2) = 0.41$ for CH_4.

On combining (6) and (15) with (18), it is found that the energy of formation of methane is[32]

$$W(CH_4) - W(C) - 4W(H) = W_V(C)$$
$$+ 4K(CH_4) + 6(0.41) + \tfrac{1}{2}N_{ss}$$
$$- (5/2)N_{\sigma\sigma} - 3\sqrt{3}N_{s\sigma} + 4N_{\pi\pi}. \quad (20)$$

Here

$$W_V(C) = I(2p) - I(2s) + (1/16)[-13F_0(2s, 2s)$$
$$- 22F_0(2s, 2p) + 35F_0(2p, 2p) - 4G_1 - 76F_2]$$
$$= 7.03 \text{ volts} \quad (21)$$

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[32] Eq. (20) is the same as Van Vleck's (9) (cf. reference 23), except that W_{ion} has been omitted.

is the energy of the valence state of carbon, the value of which follows from (13) and (14); and $W(C)$ is $s^2p^2\,{}^3P$ as given in Table II, i.e., the energy of the normal carbon atom. $K(CH_4)$ may be estimated from Woods'[33] numerical calculation for CH_4. Subtraction of $(3/2)K(H_2)$ from his coulomb energy gives $K(CH_4) = -2.64$ volts. N_{ss}, $N_{\sigma\sigma}$ and $N_{\pi\pi}$ are fairly well known, and are assumed to be 2.0, 2.3 and -0.6 volts, respectively. $N_{s\sigma}$ is then used to reproduce the observed energy of formation of methane. If the value $W(CH_4) - W(C) - 4W(H) = -17.0$ volts[34] is adopted, then $N_{s\sigma} = 1.69$, a figure which is between the value 1.0 determined by Van Vleck[23] on the assumption that the coulomb energy in CH_4 is four times that in CH, and the value 2.1 secured by Penney[29] from the vibration frequencies of CH_4. The new value of $N_{s\sigma}$, together with $K(CH_4)$, will be used to estimate the energies of formation of CH_3 and CH_2.

CH_3

This molecule is a seven electron problem, and ordinarily would involve 14 states for a Heitler-London treatment, but with the symmetry of the point group C_{3v}, the secular equation for the symmetric doublets is only of the fourth degree. The secular equation may be obtained for a carbon atom configuration with four different orbits, and conveniently be evaluated in two cases; (a) a right-angled model with the three hydrogens bound to three $p\sigma$ carbon orbits, and a free s orbit; and (b) a plane model, as formulated by Penney,[29] with three equivalent sp^2 hybridized wave functions at angles of 120° for the bonds, and a free p_π orbit. Electron pairing is found to be a good approximation in (b), but rather poor in (a). However the total binding is about 3 volts greater in (b) than in (a), so that Penney's conclusion that CH_3 is plane is substantiated, and the electron pairing formula may be employed. The energy of formation for plane CH_3 is

$$W(CH_3) - W(C) - 3W(H)$$
$$= 7.20 + 3K(CH_4) + 3K(H_2) - (3/2)\beta$$
$$- (3/2)N_{\sigma\sigma} - 3\sqrt{2}N_{s\sigma} + 3N_{\pi\pi}. \quad (22)$$

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[33] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).
[34] This includes 1 volt of zero-point energy. It may be in error by as much as a volt because of the uncertainty of the heat of sublimation of carbon. See, V. Deitz, J. Chem. Phys. **3**, 58 (1935); R. Schmid, Zeits. f. Physik **99**, 274 (1936); G. Herzberg, Nature **137**, 620 (1936).

Here it is to be noted that the valence state, 7.20 volts above the ground state, is slightly different from that for CH_4. Using the values derived for CH_4, and noting that in this case $K(H_2) - (1/2)\beta = 0.34$, it is found that $W(CH_3) - W(C) - 3W(H) = -12.12$ volts. This gives an energy of 4.88 volts for the reaction $CH_4 = CH_3 + H$, in agreement with the estimates of Mulliken[35] and Van Vleck.[23] The latter author has discussed the reasons for a difference of this order of magnitude, and little has been added here beyond an explicit formulation of the energy.

CH₂

For this molecule the carbon s^2p^2 configuration may be used. The resulting 4 electron problem gives rise to a quadratic equation; electron pairing is found to be a fair approximation to the accurate solution, the correction amounting to 0.4 volt. For right-angled CH_2 the energy formula is

$$W(CH_2) - W(C) - 2W(H) = (3/2)F_2 + 2K(CH)$$
$$+ K(H_2) - (1/2)\beta + 2N_{ss} - 2N_{\sigma\sigma} + N_{\pi\pi}. \quad (23)$$

$$K(CH) = 2M_{ss} + M_{\sigma\sigma} + M_{\pi\pi} + V_{CH}$$

$$+ \int h(1) V_C(1) h(1) dv_1 \quad (24)$$

is the interatomic coulomb energy for CH. For the right-angled model assumed here, $K(H_2) - (1/2)\beta = +0.63$. Because M_{ss} is greater in absolute value (more negative) than $M_{\pi\pi}$, $K(CH)$ may be expected to be somewhat larger than $K(CH_4)$; the limiting value is obtained by setting $M_{\pi\pi} = 0$, and is -4.0 if $K(CH_4) = -2.64$. $K(CH)$ is readily determined from the dissociation energy of CH. If the latter quantity is 3.7 volts,[36] $K(CH) = -3.38$; if it is 4.0 volts,[37] $K(CH) = -3.68$. The two cases give -7.45 and -8.05 volts for the energy of formation of CH_2 from the atoms, after the correction to the approximation of electron pairing has been applied.

CH

A quadratic equation gives the energy for CH; but electron pairing is found to be more than

sufficiently accurate. The energy formula has been given by Van Vleck;[23] in the present notation it is

$$W(CH) - W(C) - W(H) = (3/2)F_2 + K(CH)$$
$$+ N_{ss} - N_{\sigma\sigma} + \tfrac{1}{2}N_{\pi\pi}. \quad (25)$$

From this equation, and the dissociation energies, 3.7 or 4.0 volts, the values of $K(CH)$ used for CH_2 are obtained.

Discussion of relative energies

The estimated values 17.0, 12.1, 8.0 and 4.0 volts[38] for the energies of formation of CH_4, CH_3, CH_2 and CH form a well-graded series, and do not imply any special stability for the intermediate members. There is no indication that CH_2 occupies a favored position and that $W(CH_3) - W(CH_2)$ is only one or two volts, as has been supposed previously[39] from the fact that in CH_2 the carbon atom need not be promoted from the s^2p^2 state. The error in that supposition has been failure to recognize the fact that much stronger bonds can be formed once the central atom has been promoted, and that the promotion energy may well be offset by the greater bonding energy, as is seen to be the case for CH_3 and CH_4. Indeed, the bonding for hybridized orbits is so much more favorable than that for pure p orbits that CH_2 may perhaps be stabilized somewhat further by resonance involving excited configurations, an effect the very opposite of that invoked hitherto.

The relative energies are in accord with the experiments of Rice and co-workers[40] on the thermal decomposition of simple hydrocarbons. From a great wealth of experimental material, Rice concludes that the activation energies (which probably do not differ greatly from the dissociation energies) required to remove suc-

[35] R. S. Mulliken, J. Chem. Phys. **1**, 500 (1933).
[36] 3.5 volts given by H. Sponer (*Molekulspektren, I Tabellen* (1935)) plus $\frac{1}{2}$ quantum of vibration.
[37] R. S. Mulliken, Rev. Mod. Phys. **4**, 80 (1932).

[38] In a paper which appeared after the work reported here had been completed, G. Nordheim-Pöschl (Ann. d. Physik **26**, 258, 281 (1936)) also gives estimates, likewise based on the Heitler-London theory, of the relative energies of CH_4, CH_3, CH_2 and CH. Her results are in good agreement with the above, although the method of approach is considerably different. Nordheim-Pöschl bases her calculations on the $s^2p^2\ ^3P$ and $sp^3\ ^5S$ states of the carbon atom, and does not take into account the other states that enter in (8) or Table III.
[39] R. Mecke, Zeits. f. Electrochemie **36**, 589 (1930); R. G. Norrish, Trans. Faraday Soc. **30**, 103 (1934).
[40] See F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (The Johns Hopkins Press, 1935).

cessive hydrogen atoms from methane are all 4 volts or more. This is in agreement with the energies given here; there are, however, conflicting bits of evidence[41] and the matter cannot be considered settled on the experimental side.

Errors involved

It may not be out of place to discuss briefly some of the possible errors and their implications. First of all, the N's have been assumed to be the same for all the molecules. Actually they are not, and the N's for molecules with many positive centers should be slightly greater than those for CH. This would increase the relative stability of CH_4 still further; however, the added terms are small, and probably do not play an important part. The assumption of constant $C-H$ distances is borne out fairly well by the experimental data for CH_4 and CH.

The error involved in using the formula for electron pairing is known from the exact solutions of the secular equations. Only in the case of CH_2, where a correction has been applied, does the error exceed 0.1 volt.

Resonance, or the influence of other configurations, has been shown in the earlier sections to be of some importance in CH_4, where it contributes an additional 1.2 volts to the energy. It might be somewhat larger in CH_3, and strangely enough, perhaps still greater in CH_2. An electron pairing calculation for 120° CH_2 based on the same carbon configuration used for CH_3 yields

an energy of 6.0 volts, which compares favorably with 7.4 or 8.0 volts for the molecule based on s^2p^2 carbon. A complication that would diminish the possible resonance arises from the fact that the most stable CH_2 based on an sp^3 configuration is linear (sp hybridized functions), whereas the most stable CH_2 based on s^2p^2 is right-angled (except for the small $H-H$ repulsion). If resonance were taken into account, CH_2 would probably be found to have an angle intermediate between 90° and 180°, and a stability somewhat greater than that given above. Nevertheless, it is not likely that the relative energies would be modified to a very great extent by the inclusion of other configurations.

Finally, it must be admitted that the Heitler-London theory, when used for numerical calculations, has to a large extent the status of an empirical method. If nonorthogonality, higher exchanges and inner shells are included, the results obtained by direct evaluation of the integrals are worse than those yielded by the simple theory.[42] And furthermore, in that case so many integrals are introduced that they cannot effectively be treated as adjustable parameters. Use of the simple theory has led to a surprising number of valid results. As employed here it can at least be regarded as a powerful interpolation method.

In conclusion I should like to express my gratitude to Professor J. H. Van Vleck for suggesting this problem, and for many stimulating discussions.

[41] For instance, L. S. Kassel, J. Am. Chem. Soc. **57**, 833 (1935), and L. Belchetz, Trans. Faraday. Soc. **30**, 170 (1934), cite evidence supporting relatively greater stability for CH_2.

[42] Reference 4, pg. 192; A. S. Coolidge, Phys. Rev. **42**, 189 (1932); A. S. Coolidge and H. M. James, J. Chem. Phys. **2**, 811 (1934).