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On the Theory of the Structure of CH₄ and Related Molecules: Part III

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(1) Use of Johnson's formulas for sp^3 levels in conjunction with existing experimental data makes it doubtful whether the 4S state of the carbon atom is only 1.6 volts above the ground state, as often assumed in the literature. (2) A formula is derived for the energy of the "valence state" of the C atom, which is a linear combination of sp^3 levels wherein the spins are paired with those of attached atoms. This state is characteristic of tetravalent carbon compounds involving four electron pair bonds, and is shown to involve an increase of about 7 volts in the internal energy of the C atom over that in the ground state. (3) Because of this increment, the net or observed bonding energy is less

than the gross or true inter-atomic bonding energy. The gross energy per bond is probably greater in CH₃ than in CH₄ although the reverse is true of the net. (4) A critical comparison is given of the Slater-Pauling theory of directed valence and the nondirectional Heitler-Rumer theory based on a 5S state of the C atom. The former leads to much firmer bonds. (5) The assumption of electron pairing, made in Part II, is shown to be well warranted in CH₄, as it yields an energy value which is very nearly the same as the deepest root of Eyring and colleague's more exact cubic secular equation. (6) The energies of CH₄ and 4CH are compared in the light of theory.

1. ENERGY LEVELS OF THE FREE CARBON ATOM

IN order for the carbon atom to exert its usual valence 4, it must be in the sp^3 configuration rather than in its normal state $s^2p^2\ ^3P$. In Part II,¹ all states (*viz.*, $^1,^3P$, $^1,^3D$, $^3,^5S$) belonging to sp^3 were regarded as having the same energy, whereas we now wish to consider the influence of the L, S structure of this configuration, and in general to examine more carefully than previously the effect of the energy differences between s^2p^2 and sp^3 .

First it is well to study the energy levels of the free carbon atom. The energies of the various states belonging to sp^3 have been calculated in terms of the Slater-Condon^{2,3} F 's, G 's and I 's by M. H. Johnson.⁴ The results are given in Table I. We omit Johnson's spin-orbit terms, as they are very small for light atoms like carbon.

TABLE I.

State	Theoretical energy	Obs., C	Obs., N ⁺
$sp^3\ ^5S$	$W_0 - 3G_1 - 15F_2$		
$sp^3\ ^3S$	$W_0 + G_1 - 15F_2$		19.2 volts
$sp^3\ ^3D$	$W_0 - 2G_1 - 6F_2$	7.9	10.4
$sp^3\ ^1D$	$W_0 - 6F_2$	9.7	.
$sp^3\ ^3P$	$W_0 - 2G_1$	9.3	13.5
$sp^3\ ^1P$	W_0	9.7	

¹ Part I of the present series appeared in J. Chem. Phys. **1**, 177 (1933); Part II, *ibid.* **1**, 219 (1933). See Part I for references to the literature. We neglected to state there that the method of "molecular orbitals," which is the essence of the Hund-Mulliken procedure, was first introduced by J. E. Lennard-Jones, though only for diatomic molecules (Trans. Faraday Soc. **25**, 668 (1929)). The present article connects particularly with Section 5 of Part II, based on the Heitler-London method.

² J. C. Slater, Phys. Rev. **34**, 1293 (1929).

³ E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

⁴ M. H. Johnson, Jr., Phys. Rev. **39**, 209 (1932): These formulas for sp^3 may also be derived very simply by the Dirac vector model, as will be shown in a future paper by the writer in *Phys. Rev.* We have used this model to determine the additive constant in the energy, which was not specified in Johnson's paper since he took 3D as the origin.

Here
$$W_0 = I(2s) + 3I(2p) + 3F_0(2s; 2p) + 3F_0(2p; 2p) - W(s^2p^2\ ^3P). \quad (1)$$

To avoid fractions, we use the Condon-Shortley³ rather than Slater convention on the F 's and G 's, and $G_1(2s; 2p)$, $F_2(2p; 2p)$ are throughout abbreviated to G_1 , F_2 . The origin for the energy is always taken at the normal state $s^2p^2\ ^3P$. The entries in the last two columns are the excitation energies of the spectroscopically known sp^3 states of C and N⁺. Clearly the observed values are not compatible with the formulae, since different intervals yield discordant values of F_2 or G_1 . For instance, $^1D - ^3D$ of C demands $G_1 = 0.9$, while $^1P - ^3P$ demands $G = 0.2$. This is not surprising, for the Slater relations seldom work well for light atoms. The observed energy of the 3S term of N⁺ however, is so unduly high as to suggest a misclassification, and hence possibly this term should be attributed to some other configuration than $2s2p^3$. Turner⁵ indicates that such a misclassification is not unlikely.

The position of the 5S state of C is of considerable interest in connection with the theory of valence. It has been suggested in the literature⁵ that this state is 1.6 volts above the normal level. This estimate is based upon band spectra and cannot be considered reliable, as there is considerable doubt concerning the identification of the dissociation products, as well as in the extrapolation of the potential energy curves.

In our opinion the preceding table makes it probable, though not absolutely certain, that the 5S state is not nearly as deep as 1.6 volts above normal. For instance according to the Johnson formulas it falls at 4.9 volts if we use the most favorable choice of the constants, *viz.*, the values

$$W_0 = 11.1, \quad G_1 = 0.9, \quad F_2 = 0.23 \text{ volts}, \quad (2)$$

which fit the observed 3D , 3P and 1D levels. The choice (2) does not give the correct position for the 1P term, but conceivably this term might be abnormal because of a perturbation. If the constants are adjusted so as to fit 1P at the expense of one of the three other known states, then 5S is even higher than 4.9. Of course it is true that numerical values of the F 's and G 's do not mean a great deal as long as the Johnson formulas do not hold, but at the same time the fact remains that F_2 or G_1 would have to be of a different order of magnitude than required to fit other intervals if 5S is really as deep as 1.6 volts. There appears to be no reason why 5S should be unduly deep compared to the simple theoretical expectations. On the contrary, singlet and triplet states of the C atom belonging to other configurations than sp^3 are rather more abundant than the quintets and so perturbations by these other configurations will presumably tend to depress 5S less than the other states of sp^3 . If the 5S state were as deep as 1.6, one would expect the 4S state of C⁺ to be abnormally low, since 5S of C is based on a 4S state of C⁺, whereas $^1,^3P$ and $^1,^3D$ are based on 2P and 2D . Actually 4S of C⁺ is only 1.14 volts⁶ deeper than 2D , while 2P is unknown.

An interesting calculation of the energy levels of the C atom has also been given by Beardsley.⁷ He calculates the various exchange and Coulomb integrals, and so obtains explicit numerical formulas rather than expressions involving undetermined parameters I , F_2 , G_1 such as we give. For our purposes, however, it appears better to use the formulas with parameters, as they bring out vividly the ratios between the various intervals, and do not require specialization of the wave functions except that they be of central character. The Beardsley paper naturally implicitly contains the Johnson formulas, for the ratios between the various intervals calculated by Beardsley are consistent with the simple theory. Beardsley's results correspond to the following choice of constants: $W_0 = 14.6$, $G_1 = 3.44$, $F_2 = 0.29$ volts. Such a choice locates 5S at less than a volt above the ground level, and the "valence state" to be discussed in the next section at 4.0 volts. However, it gives a spread between the observed levels of sp^3 which is of a much greater order of magnitude than is observed experimentally in C, but which is of almost exactly the order observed in N⁺. Of course

⁵ W. Heitler and G. Herzberg, *Zeits. f. Physik* **53**, 52 (1929); L. A. Turner, *Proc. Nat. Acad.* **15**, 526 (1929).

⁶ In their tables, Bacher and Goudsmit use different origins of energy for the doublets and quartets of C⁺,

but a common origin can immediately be secured by making use of the fact that absolute term values are known for both the triplets and singlets of C⁺⁺.

⁷ N. F. Beardsley, *Phys. Rev.* **39**, 913 (1932).

it could be that the observed levels in C are abnormally close because of perturbations and that N^+ represents more nearly the usual state of affairs. We prefer, however, to blame the anomaly on 3S of N^+ , and to dismiss attempts to compute the intervals directly from the wave functions as unreliable because the latter are not known sufficiently well. The question, however, must be regarded as still an open one.

In view of all the above, we conclude that 5S of C is probably 5 to 8 volts above the ground state, but 1.6 cannot be excluded with finality.

2. THE VALENCE STATE OF CARBON

The spread in energy among most of the states belonging to the configuration sp^3 is small compared to the energy difference between s^2p^2 and sp^3 , or in other words the effect of the quantum numbers L, S on the energy is small compared to that of the individual l 's. An exception is furnished by 5S , especially if really at 1.6 volts, but this is only one state out of many. Hence it seemed plausible that in our calculations in Part II no great harm was done by ignoring the L - S structure. This point may now be made more quantitative and definite if one uses calculations by the Heitler-London-Pauling-Slater method as in Section 5 of Part II. It will turn out that the influence of the L - S structure on the directional valence is even smaller than one would conjecture.

In our calculations by the H-L-P-S procedure in II, the spins of the four electrons belonging to sp^3 were assumed paired with those of the four atoms attached by the carbon. Such a condition of the carbon atom we may conveniently call its valence state. It is not identical with any one of the six atomic states tabulated in Section 1, and is instead to be regarded as a linear combination of these. Its internal energy may be calculated, as follows in terms of the Slater F 's and G 's.

Let K_{ij} and C_{ij} (Slater's J) be respectively the exchange and Coulomb integrals connecting electrons i and j of the carbon atom. Do not confuse the intra-atomic exchange integral K_{ij} with the inter-atomic exchange integrals J_{ij} used in Part II. Since the C atoms all have their spins paired with those of electrons in attached atoms, the intra-atomic energy of the carbon atom is

$$W = I(3s) + 3I(3p) + \sum_{i>j} (C_{ij} - \frac{1}{2}K_{ij}) - W(s^2p^2\ ^3P) \quad (3)$$

when referred to the ground state. As emphasized in Part II, the coefficient $-\frac{1}{2}$ is characteristic of exchange effects between electrons paired otherwise than with each other. The C electrons have wave functions of the form

$$\psi_i = \alpha_i \psi(2s) + \beta_i \psi(2p\sigma_i) \quad (4)$$

where, as in Part II, $\psi(2p\sigma_i)$ means a $2p\sigma$ wave function when referred to the axis C-H_{*i*}. In virtue of the well-known vectorial transformation properties of the p wave functions, given for instance in (6) of II, one finds that

$$C_{ij} = \alpha_i^2 \alpha_j^2 C(2s; 2s) + (\alpha_i^2 \beta_j^2 + \beta_i^2 \alpha_j^2) C(2s; 2p) + 4\alpha_i \alpha_j \beta_i \beta_j K(2s; 2p) \cos(i, j) \\ + \beta_i^2 \beta_j^2 [C(2p\sigma; 2p\sigma) \cos^2(i, j) + C(2p\sigma; 2p\pi) \sin^2(i, j)], \quad (5)$$

$$K_{ij} = \alpha_i^2 \alpha_j^2 K(2s; 2s) + \beta_i^2 \beta_j^2 [\cos^2(i, j) K(2p\sigma; 2p\sigma) + \sin^2(i, j) K(2p\sigma; 2p\pi)] \\ + 2\alpha_i \alpha_j \beta_i \beta_j \cos(i, j) C(2s; 2p) + [\alpha_i \beta_j \cos(i, j) + \alpha_i \beta_j] K(2s; 2p) + \alpha_i^2 \beta_j^2 \sin^2(i, j) K(2s; 2p). \quad (6)$$

Here $\cos(i, j)$ is the cosine of the angle between the axes C-H_{*i*} and C-H_{*j*}, and a common axis of quantization is to be understood in connection with all the Greek notation. Thus $C(2p\pi; 2p\sigma)$ is the same as $J(211; 210)$ in Slater's notation $J(nl m_i; n' l' m_i')$. The C 's and K 's on the right side of (5, 6) may immediately be expressed in terms of the F 's and G 's by means of Slater's tables (page 1312 of reference 2). We next sum over the various pairs of carbon electrons, as demanded by (3).

We can utilize the fact that the four wave functions (4) satisfy the relations

$$\alpha_i^2 + \beta_i^2 = 1, \quad \Sigma \alpha_i^2 = 1, \quad \Sigma \beta_i^2 = 3, \quad \alpha_i \alpha_j + \beta_i \beta_j \cos(i, j) = 0,$$

because of the orthogonality and normalization to unity. These formulas materially simplify the final form of (3), which is found to be

$$W_v(C) = W_0 + \frac{1}{4}(1 - \mu)[F_0(2s; 2s) - 2F_0(2s; 2p) + F_0(2p; 2p)] - \frac{1}{2}(19 + 2\mu)F_2 + \frac{1}{2}(-5 + 2\mu)G_1 \quad (7)$$

with W_0 as in (1) and $\mu = \alpha_1^4 + \alpha_2^4 + \alpha_3^4 + \alpha_4^4$.

Since the hybridization ratios depend on the directions C-H_{*i*}, the expression μ is a function of the angles between the four valence directions of the C atom. It is rather remarkable that the only angular dependence is of the one type μ . The minimum value $\frac{1}{4}$ of μ is characteristic of the tetrahedral model, where all four electrons have the same hybridization ratio and hence $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \frac{1}{2}$. The maximum value of μ is unity, and is achieved in a model without hybridization, i.e., a model where three of the valence directions are mutually orthogonal, and represent pure p bonds, while the fourth has an arbitrary direction, and corresponds to a pure s bond.

To form a numerical estimate of (7), we adopt for the various constants the values (2) together with

$$F_0(2s; 2s) - 2F_0(2s; 2p) + F_0(2p; 2p) = 17.9 - 2 \times 16.1 + 14.8 = 0.5 \text{ volts.} \quad (8)$$

The result (8) is obtained theoretically from Beardsley's calculations,⁸ as empirical methods are not feasible for this particular expression. The numerical value of (7) then ranges from 7.0 volts at $\mu = \frac{1}{4}$ to 7.3 volts at $\mu = 1$. We thus conclude that:

(a) The effect of the L - S structure on the directional properties of valence is small, since the value of (7) varies but little with the choice of the valence directions as manifested in μ ;

(b) The "valence" state of C has about 7 or 8 more volts of intra-atomic energy than the normal state. This is the energy required to make the C atom acquire a chemically active condition, but should not be confused with an "energy of activation" in the usual chemical sense, since the latter is lower because it includes allowance for the offsetting effect of the inter-atomic bonding energy.

Conclusion (a) would not be altered if different numerical values than (2), (8) were adopted, while the estimate 7 volts in (b) would be changed at most by a volt or two. This insensitivity is because F_2 , G_1 , and (8) are in any case small compared with (1), and the main term W_0 is known with at least moderate precision. We have already mentioned that smaller values of the F 's and G 's than (2) are obtained if we fit three other known states rather than 1D , 3D , 3P as in (2). Hence our choice of the F 's and G 's tends, if anything, to overestimate the directional effect of the L - S structure and to underestimate somewhat the energy of the valence state. The individual terms in (8) are quite large, but the value of $F(2s; 2p)$ is intermediate between $F(2s; 2s)$ and $F(2p; 2p)$ and somewhat less than their mean, so that the expression (8) is small and positive. These statements are true for almost any reasonable choice of Beardsley's parameters α , x , y and are not peculiar to his optimum selection $\alpha = 5.7$, $x = 1.3$, $y = 0.6$ which we have used to obtain a numerical value in (8). Thus the order of magnitude of (8) seems fairly certain even though the particular value 1.5 may be considerably in error.

Analogous calculations on the effect of the L - S structure could also be made for other compounds, where the valence is 2 or 3 rather than 4, and where in consequence the state of the central atom is intermediate between s^2p^2 and sp^3 . These computations, however, do not seem worth while, as in Section 6 of Part II our theory included allowance for the individual l 's on the energy, and it seems reasonably clear from the above that the L - S refinement will be unimportant at the present state of accuracy of valence theories.

⁸ The expressions αK , $\alpha(O + \frac{3}{2}P)$, αP , αQ , on page 918 of Beardsley's paper are respectively the same as $F_0(2s; 2p)$, $F_0(2p; 2p)$, $3F_2$, $F_0(2s; 2s)$ in our notation.

3. RELATIVE ENERGY OF CH₃ AND CH₄

Mulliken⁹ emphasizes the fact that the apparent energy per bond has a larger value, 4.0 volts, in CH₄ than in CH₃, where he estimates the value to be 3.6 volts or less. In our opinion this is not because the true inter-atomic bond energy is greater in CH₄ than in CH₃, but simply because the C atom must be excited to the "valence state" before it can form either a trivalent or quadrivalent compound. Once it has been thus excited at the expense of unfavorable intra-atomic energy, it is clearly in the best interests of the atom to form as many bonds as possible. We must distinguish between net and gross energy per bond, the former being that observed experimentally, and the latter the true inter-atomic bond energy obtained by increasing the experimental value by the energy of excitation of the valence state prorated to the different bonds. The values quoted by Mulliken are net. If we assume that this excitation energy is 7.1 volts, the corresponding gross values are 5.8 volts for CH₄ and 6.1 volts, or less, for CH₃.

Theoretically, the gross energy per bond should be somewhat higher in CH₃ than in CH₄ for two reasons. In the first place the repulsive energy between the H atoms should be less in CH₃ than in CH₄, due to a removal of an H atom. In the following section we shall estimate the H-H repulsive energy to be 2.5 volts in CH₄. The corresponding value in CH₃ is 1.2, as there are here 3 rather than 6 repulsive H pairs. This is on the assumption that the tetrahedral angles are preserved in CH₃. With a plane model, the repulsive energy is further reduced from 1.2 to 1.0 volts. In the second place, quite irrespective of H-H repulsions, the true C-H valence energy per bond should, if anything, theoretically be somewhat greater in CH₃ than in CH₄. With the Heitler-London-Pauling-Slater method, one can see this most readily by noting that the energy per bond is identical in CH₃ and CH₄ if the tetrahedral angles are preserved in CH₄ (*viz.*, when $\theta = 109.5^\circ$, the expression (37) of Part II is exactly 3/4 as large when $\mathfrak{N} = 0$ as when $\mathfrak{N} = N$). Now in Part II we saw that, even without H-H repulsions, the tetrahedral angles were not the best, and that a somewhat flatter model gave

lower total energy for the CH₃ molecule, or in other words higher bonding energy. Hence when the most favorable angles are used, the energy per bond will be increased over the tetrahedral or CH₄ value. The increase, however, is not large, as the variation of (37) of II with θ is not great. In fact the difference in the value of (37) for the tetrahedral and plane models of CH₃ is

$$W_t - W_p = 0.375(N_{ss} - N_{\sigma\sigma}) + 0.345N_{ss}.$$

We shall see in the next section that $N_{ss} - N_{\sigma\sigma}$ and N_{ss} are probably not more than a volt or so in magnitude, and possibly of opposite sign. So the decrease in energy occasioned by departures from the tetrahedral angles probably does not amount to more than a fraction of a volt. With any given values of $N_{\sigma\sigma}$, N_{ss} , N_{ss} the best value of the angles could be determined by means of (44) of Part II, but the N 's are not known with sufficient precision to make this repaying. With the Hund-Lennard-Jones-Mulliken method, it is not possible to reach as definite conclusions on the relative magnitudes of the energies per bond in CH₃ and CH₄. With forms (i) and (ii) of this method given on page 237 of Part II, the energy per bond appears to be greater in CH₃ than in CH₄, but with (iii) the reverse is apparently sometimes true.

Instead of comparing the energies per bond in CH₃ and CH₄, it is often convenient to examine instead the energy of the reaction $\text{CH}_4 = \text{CH}_3 + \text{H}$, since Mulliken's estimates of the energy per bond in CH₃ are simply deduced from an assumed energy for this reaction along with a known heat of formation of CH₄ from $\text{C} + 4\text{H}$. His net value 3.6 volts per bond in CH₃ is under the assumption that removal of an H atom from CH₄ requires 5 volts. Mulliken concludes from ionization potential data, etc., that the energy connected with this removal is between 5 and 7 volts, and is probably much nearer 5 than 7. Any increase above 5 is reflected in a decrease of the net CH₃ value below 3.6. We may attempt an estimate of the heat of the reaction $\text{CH}_4 = \text{CH}_3 + \text{H}$ from our theory. The gross energy per bond in CH₄ is increased from 5.8 to 6.4 volts when we correct for the H-H repulsions so as to have the pure C-H energy rather than the resultant of C-H and H-H actions. With the

⁹ R. S. Mulliken, J. Chem. Phys. 1, 500 (1933).

H-L-P-S method one should expect the energy of the process $\text{CH}_4 = \text{CH}_3 + \text{H}$ to be about $1\frac{1}{2}$ to 2 volts less than the corrected gross energy per bond in CH_4 , the difference arising because of the two effects noted in the preceding paragraph. Thus by an entirely different method we roughly confirm Mulliken's estimate that this process requires about 5 volts.

4. COMPARISON WITH THE HEITLER-RUMER THEORY

Besides the Hund-Lennard-Jones-Mulliken and Slater-Pauling theories which we have discussed in detail in Parts I and II, still another and somewhat earlier theory of valence in carbon and nitrogen compounds has been given by Heitler and Rumer.¹⁰ The H-R theory, like the S-P one, is based on the Heitler-London method, but, unlike S-P, does not introduce electron pairing. Instead the valence electrons of the central atom have their maximum possible resultant spin, so that in carbon and in nitrogen compounds the C and N atoms are respectively in 5S and 4S states. In the S-P theory, on the other hand, the spin of the central atom is not a good quantum number, and the spin of each C or N electron is compounded with the spin of an electron of an attached atom to give zero resultant spin for the two, which thus constitute an electron pair. In the S-P form all the private properties of the central atom are sacrificed in order to give "maximum overlapping" between the two wave functions involved in an electron pair. As a result the L and S of the central atom cease to be good quantum numbers, while the hybridization spoils even the l 's of the individual electrons. In the H-R theory, L , S , and the l 's are all good quantum number, but at the expense of having less overlapping. Whether the S-P or H-L method is the better approximation depends upon whether the total energy of the chemical bonds is large or small compared to the separation between the various terms belonging to the electron configuration of the central atom (configuration sp^3 in C; s^2p^3 in N), or, in other words, upon whether it is more important to diagonalize the intra-atomic or inter-atomic part of the Hamiltonian function. We shall examine this question somewhat quantitatively in the next few paragraphs, and we shall see that usually the S-P approximation is the better one.

Before doing this we must caution that when we speak of the S-P and H-R theories, we always mean them in their most restricted forms, as this usage furnishes a terminology for different simple methods of approximation. Extended forms of the theories cease to be so sharply delineated. The original H-R paper did, indeed, treat all valence orbits of the central atom as identical and as effectively s -states, thus abnegating all directional valence effects, but Heitler and Rumer doubtless did not mean to imply that directional properties should not ultimately be considered in a more refined theory. Similarly, the S-P wave functions lend themselves particularly aptly to electron pairing, but both Slater and Pauling have abandoned the restriction to unique pairs or bond structures in certain of their calculations, *viz.*, those of Slater¹¹ on the water molecule and especially those of Pauling on "resonance" in complicated organic molecules.¹²

Under the assumption of electron pairing, the expression for the energy of formation of the CH_4 molecule is

$$W(\text{CH}_4) - W(\text{C} + 4\text{H}) = W_V(\text{C}) + 0.5N_{ss} - 2.5N_{\sigma\sigma} + 4N_{\pi\pi} - 5.196N_{\sigma s} + W_{\text{ion}}(\text{CH}_4) + W_{\text{coul.}}(\text{CH}_4) + 6 \times (-0.35)M(\text{H}_2) \quad (9)$$

if one utilizes the Slater-Pauling hybridized wave functions. Here, as in Part II, the N 's have the significance

$$N_{kl} = - \int \int \int \int \int \int \psi_H(1) \psi_k(2) \mathbf{H} \psi_l(1) \psi_H(2) dv_1 dv_2 \quad (k, l = 2s, 2p\sigma, \text{ or } 2p\pi \text{ of C}), \quad (10)$$

¹⁰ W. Heitler and G. Rumer, *Zeits. f. Physik* **68**, 12 (1931).

¹¹ J. C. Slater, *Phys. Rev.* **38**, 1109 (1931).

¹² L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 362 (1933); L. Pauling and I. Sherman, *ibid.* **1**, 679 (1933).

and, except for N_{ss} , are the negative of ordinary exchange integrals. The portion of (9) involving the N 's, i.e., the C-H exchange contributions, was derived in Eq. (37) or (38) of Part II, when the angles in (37) or (38) are specialized to tetrahedral values. As compared with Part II, we now use a more complete expression for the energy of formation, as we now include the internal energy of excitation $W_V(C)$ of the valence state of the C atom, given by (7) with $\mu = \frac{1}{4}$, the Coulomb energy between the C and H atoms, an ionic term, and the energy due to forces between the hydrogen atoms, which is the last term in (9). The Coulomb portion was not explicitly included in (37) or (38) of Part II partly because it is somewhat subordinate to exchange terms, and especially because we were interested in II primarily in the dependence of the energy on the arrangement of the attached atoms. One can easily show that in compounds of the structure $CWXYZ$, wherein the C atom attaches any four univalent atoms W, X, Y, Z , and in which the C atom is in the configuration sp^3 either with or without hybridization, the Coulomb energy connecting the C atom with the attached atoms is independent of how these atoms are arranged in space as long as their distances from the C atom are not varied. Hence the considerations in Section 5 of Part II are not affected. In the present discussion the Coulomb energy must be included since we are considering absolute energy of formation rather than just directional dependence.

The ionic term is included in order to allow for the fact that in CH_4 the C atom doubtless acquires some negative charge at the expense of the four hydrogens. This term, again, is important for absolute bonding energies, but probably does not vary greatly with the orientation of the valence axes, so that it was sufficiently allowable to omit the ionic effect in Part II.

In the last, or H-H term of (9), the symbol $M(H_2)$ denotes a Morse function for the normal state of the H_2 molecule. Following Eyring and Polanyi,¹³ we have assumed that H-H bonding can be represented by a Morse function, and that this bonding is ten percent Coulomb and ninety percent exchange. The factor $-0.35 = 0.1 - \frac{1}{2} \times 0.9$ owes its origin to the fact that the exchange coefficient between members of different pairs is $-\frac{1}{2}$. The factor 6 is, of course, simply because there are six H-H pairs in all. According to the Raman data of Dickinson, Dillon and Rasetti on the moment of inertia of CH_4 , the C-H and H-H separations are respectively 1.08 and 1.77 Angstroms. With $r = 1.77 \times 10^{-8}$, one finds $M(H_2) = -1.18$ volts.

With the Heitler-Rumer theory, where the carbon atom is in a 5S state, the expression corresponding to (9) is

$$W(CH_4) - W(C + 4H) = W(^5S) - N_{ss} - N_{\sigma\sigma} - 2N_{\pi\pi} + W_{ion}(CH_4) + W_{coul.}(CH_4) + 6 \times (-0.8)M(H_2). \quad (11)$$

Here $W(^5S)$ is the excess of energy of sp^3 5S over the ground state s^2p^2 3P of C. The H-H term now has a factor $-0.8 = -1 \times 0.9 + 0.1$ rather than -0.35 because the spins of all the H atoms must be mutually parallel in order to be able to neutralize the spin $S=2$ of the C atom, and this requires that the exchange coefficient for each H-H pair be -1 . Heitler and Rumer give $+4(CH)$ for the C-H exchange term, where (CH) denotes the C-H exchange integral. However, they regard all four two-quantum orbits of the C atom as identical. When we allow for difference in sign convention, and distinguish between the various types ($2s, 2p\sigma, 2p\pi$) of C orbits, their $+4(CH)$ becomes replaced by $-(N_{\sigma\sigma} + N_{ss} + 2N_{\pi\pi})$, in our notation. This is fairly obvious from the fact that the 5S state of C has the structure $2s2p\sigma 2p\pi^2$ when referred to any set of Cartesian axes x, y, z .¹⁴ Another derivation of the N terms will also be given in Section 5.

¹³ H. Eyring and M. Polanyi, *Zeits. f. physik. Chemie* **12**, 279 (1931); H. Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931). Dr. A. Sherman informs the writer that it is better to take the exchange part as 86 rather than 90 percent of the Morse function, at least in calculations of activation energies. This modification is too small to be of consequence

for our work, and so we use the round value 90.

¹⁴ For a quintet state involving four electrons, the Pauli principle allows only one electron to each orbital state. There are two kinds of $2p\pi$ states, viz., the left- and right-handed varieties, or orthogonal linear combinations thereof.

The expressions $N_{\sigma\sigma}$, N_{ss} , N_{ss} are all positive, while $N_{\pi\pi}$ and $M(\text{H}_2)$ are negative. Hence all the N terms except that involving N_{ss} have lower values in (9) than in (11), meaning that the C-H exchange effects tend to make the S-P structure more stable than the H-R one. The forces between the attached H atoms also favor S-P, as can be seen by comparing the last terms of (9) and (11). The first or internal carbon term is deeper in (11) than in (9), but not enough so to offset the influence of the other terms. To examine this point more quantitatively, let us assume that the first terms of (9) and (11) can be calculated respectively by (7) and Johnson's formula with the constants (2), and that the constants involved in the other terms of (9, 11) have the following magnitudes

$$N_{\sigma\sigma} = +2.3, \quad N_{ss} = +2.0, \quad N_{\pi\pi} = -0.6, \quad N_{ss} = +1.0, \quad M(\text{H}_2) = -1.18 \text{ volts.} \quad (12)$$

This choice for $N_{\sigma\sigma}$ and $N_{\pi\pi}$ is suggested by an analysis of C-H potential energy curves to be published by J. R. Stehn and the writer, as well as by Coolidge's calculations on the H₂O molecule.¹⁵ The basis for the choice of N_{ss} will be given below. Coolidge's work indicates a somewhat larger value of N_{ss} than $N_{\sigma\sigma}$, but this does not allow for the fact that the 2s wave functions are screened less from the C nucleus than the 2p, so that they are drawn in more and tend to overlap the hydrogen atoms less. Hence we take for N_{ss} the round value two volts.

With the choice of constants discussed in the preceding paragraph, the value of (9) is 10.2 volts lower than that of (11). The corresponding value of $W(^5S)$ is 4.9 volts (cf. Section 1). However, even if instead of using this theoretical estimate based on Johnson's formula we take $W(^5S) = 1.6$ volts, the doubtful spectroscopic value sometimes quoted, the expression (9) is still 6.9 volts below (11).

It is not surprising that the S-P approximation gives a firmer binding than the H-R one, for the latter lacks the favorable overlapping which is the essence of directional valence, and which is reflected particularly in the low value of the $N_{\sigma\sigma}$, N_{ss} terms in (9). The importance of directional valence is shown particularly clearly by the actual pyramidal structure of the ammonia molecule. If one makes a H-R calculation based on a 4S state of the nitrogen molecule, one predicts a plane model for the molecule, as the only directional effects are the H-H repulsions. This difficulty is avoided when one makes a calculation based on electron pairing and directed valence, as in Part II.

5. COMPARISON WITH MORE ACCURATE SOLUTION, NOT REQUIRING ELECTRON PAIRING

Eyring, Frost and Turkevich¹⁶ have ingeniously demonstrated that the secular problem connected with the permutation degeneracy in the Slater-Pauling sp^3 model of methane can be solved without the necessity of assuming electron pairing. This is feasible, as they show, because the tetrahedral symmetry permits extensive factorization of the secular equation, which otherwise would be of degree 14 for the states of zero spin. The factor in which we are interested corresponds to the Bethe representation Γ_1 , and leads to an algebraic equation for W of degree 3. This cubic is given in convenient form by F. Seitz and A. Sherman in Eq. (19) of their paper,¹⁷ which immediately precedes our own in the present issue, and so need not be repeated here. Their constants α , β , γ , δ , Q have the following significance in terms of the more rudimentary and fundamental constants which we have used

$$-4\alpha = N_{ss} + 3N_{\sigma\sigma} + 2\sqrt{3}N_{ss}, \quad \beta = 0.9M(\text{H}_2), \quad (13)$$

$$16\gamma = F_0(2s; 2s) - 2F_0(2s; 2p) + F_0(2p; 2p) + 28F_2 + 4G_1, \quad (14)$$

$$-12\delta = 3N_{ss} + N_{\sigma\sigma} + 8N_{\pi\pi} - 2\sqrt{3}N_{ss}, \quad (15)$$

¹⁵ A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

¹⁶ Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

¹⁷ F. Seitz and A. Sherman, J. Chem. Phys. **1**, 11 (1934). The appropriate cubic secular determinant is given in this paper in a form in which W appears only down the principal

diagonal and which hence facilitates the application of perturbation theory. In reference 16, a less convenient, non-orthogonal form is given. The writer is indebted to the various authors mentioned in notes 16 and 17 for the opportunity of seeing their manuscripts in advance of publication.

$$Q = \frac{3}{8}[F_0(2s; 2s) + 6F_0(2s; 2p) + 9F_0(2p; 2p) - 12F_2 - 4G_1] + I(2s) + 3I(2p) - W(s^2p^2 {}^3P) + W_{\text{ion}}(\text{CH}_4) + W_{\text{coul.}}(\text{CH}_4) + 0.6M(\text{H}_2). \quad (16)$$

Formula (14) is an immediate consequence of (6) specialized to tetrahedral angles. The term Q consists of six times the expression (5), so specialized, plus $I(2s) + 3I(2p) - W({}^3P)$ and the proper inter-atomic terms, thus yielding (16). The formula for β is merely a statement of our apportionment of the Morse function for H_2 between exchange and Coulomb effects. The values of α and δ follow from the rotational transformation properties of sp^3 wave functions (cf. page 232 and Eq. (6) of Part II.)

If α is negative and large in absolute magnitude compared to β , γ , δ the deepest root of the cubic equation mentioned above is approximately

$$W = Q + 4\alpha - 3\beta - 3\gamma - 6\delta - [9(\beta - 2\delta + \gamma)^2/2(-4\alpha - \beta - \gamma + 6\delta)]. \quad (17)$$

Here the terms outside the brackets embody the result of first order perturbation theory (retention of only diagonal elements in Eq. (19) of Seitz and Sherman) and give exactly the same expression as that (9) characteristic of electron pairing. The bracketed part of (17) is yielded by second order perturbation theory, applied to the cubic under the assumption that α is much larger in absolute magnitude than the other constants. Use of (2), (8) and (12) in (13-16) gives

$$\alpha = -3.09, \quad \beta = -1.06, \quad \gamma = +0.67, \\ \delta = -0.01 \text{ volt.} \quad (18)$$

With these numerical values, the bracketed portion of (17) amounts to less than a tenth of a volt. Thus electron pairing is an exceedingly good approximation for a H-L-P-S calculation in methane. The particular numerical estimate of an error less than 0.1 volt which we have given is perhaps a little optimistic, since the particular choice (12) happens to make the constant δ , which appears prominently off the diagonal in the Seitz-Sherman Eq. (19), almost vanish. However, one finds that one can vary any of the constants (except $N_{\pi\pi}$, which is fortunately probably the best known) a volt or so from the values (12) and still the bracketed part of (17) usually remains less than a volt. Instead of using second order perturbation theory to gauge the error involved in electron pairing, one could, of course, solve the cubic numerically, and compare with (9), but this is clearly unnecessary.

In the previous paragraph we examined the absolute error involved in electron pairing. It is

also instructive to study the relative error in the sense of how large the bracketed term of (17) is compared to the separation of the roots of the cubic. One finds that with (18) and either first or second order perturbation theory, the other two roots are respectively 12 and 24 volts above (17), which alone represents favorable pairing. Thus the relative error is also small. The other roots are clearly not adapted to chemical bonding.

It is clearly to be understood that although electron pairing is a good approximation for solving the cubic, this does not at all imply that the underlying Heitler-London procedure is satisfactory. Also electron pairing is not always feasible for other problems than methane. For instance, there is no natural scheme of pairing for Seitz and Sherman's other cubic Eq. (17) which applies to eight atoms at the corners of a cube.

If γ is positive and large in magnitude compared with α , β and δ , the deepest root of the cubic Eq. (19) of Seitz and Sherman is

$$Q - 6\gamma + 3\delta + \alpha - 6\beta.$$

With the aid of (13-16) and Johnson's formula for $W({}^5S)$ one finds that this is the same expression as (11). We thus have an additional proof of (11) in the Heitler-Rumer theory. This does not, however, mean that use of (11) is legitimate, for (18) shows that γ is not large in magnitude compared to the other constants. Consequently the spin of the central atom is not a good quantum number, and we again conclude that the H-R assumption of a central 5S state is not warranted. In short, Eqs. (9) and (11) are

asymptotic solutions of the cubic under different limiting conditions, which actually are nearly fulfilled only in the case of (9).

When inter-atomic terms are omitted, one of the roots of the cubic reduces, as we have seen, to the energy $W(^5S)$ of the quintet state of the carbon atom. We must not expect the other roots to reduce similarly to other of the Johnson levels given in Section 1, for in order to obtain the cubic, it was necessary for Eyring and his school to assume hybridized sp^3 wave functions. Now the states of the free C atom cannot be represented by hybridized, rather than pure s and pure p , wave functions except in the special case of quintets. With the latter, the orbital portion of the wave function is antisymmetric, and hence when it is written out explicitly in the form

$$\sum_{ijkl} a_{ijkl} \psi_i(x_1) \psi_j(x_2) \psi_k(x_3) \psi_l(x_4)$$

where i, j, k, l can be chosen from $2s, 2p\sigma_z, 2p\sigma_y, 2p\sigma_x$, the coefficients will vanish unless i, j, k, l all refer to different orbital states. The hybridization of the central atom is thus only "apparent" when the spin of the central atom has its maximum value. Except when the Heitler-Rumer hypotheses are literally valid, there is always a certain amount of error committed in assuming that the complete molecular wave function can be constructed out of sp^3 wave functions. Hence even the cubic given by Eyring, Frost and Turkevich, or by Seitz and Sherman, does not represent a complete first order Heitler-London calculation. (As here used, the term "first order" means neglect of polarization, and has nothing to do with the orders involved in the two parts of Eq. (17).) In other words, the L - S structure of the carbon atom is not rigorously treated by the inclusion of the γ terms in their cubic determinant. Section 2 shows that this structure is not of dominating importance, and so the resultant error is not serious, probably of about the same size as the terms of order γ^2 in (17).

6. RELATIVE ENERGY OF CH₄ AND 4CH

It is interesting to compare the expression (9), based on electron pairing, with the observed energy of formation of CH₄ from C and H

atoms. Not much in the way of numerical agreement is to be expected, since the N constants are not known accurately, and especially since (9) neglects triple and higher permutations and the lack of orthogonality of the various H and C wave functions. Because but little is known about the magnitudes of $W_{\text{coul.}}$ and especially $W_{\text{ion.}}$, it is instructive to compare the energy of CH₄ with that of 4CH rather than of C+4H. These magnitudes then do not enter if one assumes as a rough approximation that the Coulomb and ionic terms are four times as large for CH₄ as for the diatomic molecule CH. One can show¹⁸ that under the assumption of electron pairing, the energy of CH is

$$W(\text{CH}) - W(\text{C} + \text{H}) = k - N_{\sigma\sigma} + N_{ss} + \frac{1}{2}N_{\pi\pi} + W_{\text{ion}}(\text{CH}) + W_{\text{coul.}}(\text{CH}), \quad (19)$$

where $k=0.315$ volt is one-fourth the separation of the 3P and 1D terms of the C configuration s^2p^2 . Hence if as usual we take the ground state of C as the origin of energy

$$\begin{aligned} W(\text{CH}_4) - 4W(\text{CH}) &= W_V(\text{C}) - 4k \\ &- (7/2)N_{ss} + (3/2)N_{\sigma\sigma} + 2N_{\pi\pi} \\ &- 5.196N_{ss} - 2.10M(\text{H}_2). \quad (20) \end{aligned}$$

The actual bonding energy of CH₄ is 17.3 volts according to thermochemical data,¹⁹ while that of CH is 4.0 according to a rather uncertain

¹⁸ Eq. (19) is proved by the same methods as given in Section 5 of Part II or in fine print in J. H. Van Vleck and P. C. Cross, J. Chem. Phys. 1, 357 (1933). Concerning the need of the k term see note 13 of the latter reference.

¹⁹ This numerical value is taken from L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933). Mulliken bases his calculations on a lower value 15.8 volts. To facilitate comparison with Mulliken's article, we have utilized 15.8 rather than 17.3 volts as the heat of formation of CH₄ in all our estimates of the relative energies of CH₃ and CH₄ in Section 3. Use of 17.3 instead of 15.8 would not affect our conclusions in Section 3 that the gross energy per bond is greater in CH₃ than CH₄, and that our theory leads to an energy for the reaction CH₄=CH₃+H of approximately the proper magnitude 5 volts. This is all, of course, provided the promotional energy to the valence state of carbon is 7 volts or more. If it is only about 4 volts, as is the case provided there is really a 5S state only 1.5 volts above normal, or provided we accept Beardsley's numerical estimates of the F 's and G 's, the gross energies per bond are nearly equal in CH₃ and CH₄. In this case $W_V(\text{C}) \sim 4$ volts, Eq. (20) demands $N_{ss}=0.4$ rather than 1 volt.

estimate by Mulliken²⁰ from band spectra. The empirical value of the left side of (20) is thus roughly -1.3 volts. This value is also obtained for the right side if one assumes that the various constants have the values (2), (6) and (12). These values were all obtained from semi-empirical, semi-theoretical considerations except that the value of N_{ss} is then regarded as unknown and is arbitrarily adjusted to give (20) the observed value. One may also form a rough estimate of N_{ss} from theoretical calculations involving the evaluation of inter-atomic integrals. Such calculations of Ireland²¹ on BeH suggest that N_{ss} should be somewhat larger than N_{ss} or N_{ss} , although exact comparison is difficult because the N 's are not uniquely defined unless the various wave functions are orthogonal, which actually they are not. Thus one would guess that N_{ss} is at least as large as 2 volts. Some reasons why our estimate 1 volt by means of (20) may be too low are the following: (a) N_{ss} , which gives an important term in (20) may be less than 2 volts, (b) the values of $W_V(C)$ may be a volt or so more than 7.0 volts for reasons explained in Section 2, (c) we have not considered the corrections for the "zero point" or residual half-quantum vibrational energy, (d) the Coulomb terms of CH_4 may not be 4 times as great as those of CH. Use of a factor 4 seems warranted in the ionic part, but the Coulomb energy of CH_4 is only $8/3$ that of CH if one assumes for instance, that the Coulomb integrals involving $2p\sigma$ and $2s$ are equal, while those for $2p\pi$ are negligible. The residual vibrational terms will cancel to a large extent in a comparison of CH_4 with 4CH , but not entirely so, since CH_4 has more than four times as many vibrational degrees of freedom as CH. It is doubtful, however, whether all these effects (a)-(d) alter the right side of (20) by more than a few volts, so that according to (20) it is hard to see how N_{ss} could in any case be more than 1.5 or possibly 2 volts. This still seems somewhat small, but one yet has the errors due to non-orthogonality

and higher permutations, and even when these errors are eliminated, Heitler-London calculations seldom agree quantitatively with experiment. In any case one qualitative conclusion is clear. It is purely accidental that the bonding energy in CH_4 is almost exactly four times that in CH. The exchange and hybridization effects are such that the *gross* energy per CH bond is greater in CH_4 than in CH. However, the CH_4 molecule involves excitation of the C atom to the sp^3 state, and H-H repulsive energy, both of which do not enter in CH, and this is why the *net* energies per bond can fortuitously be nearly equal in CH_4 and CH.

Before closing, we must by all means mention that a calculation of the heat of formation of CH_4 has also been made by H. J. Woods.²² He endeavors to compute the absolute bonding energy, or in other words compares CH_4 with $\text{C}+4\text{H}$ rather than 4CH . Like us, he assumes electron pairing, although he does not list the contribution of the various elementary integrals in quite the explicit form (9). He does not include any ionic term or examine at all closely the internal energy of the C atom, and we are inclined to believe that the good agreement which he obtains with experiment is in part accidental.²³ In many respects Woods's calculations represent considerably more refinement than ours. In particular, he considers the corrections arising from want of orthogonality, and to a certain extent the higher permutations. Also he proceeds to his answer by really evaluating the inter-atomic integrals such as (10), etc., a task which we have eschewed throughout the present series. Since the numerical success of the Heitler-London method is now known to be rather limited, we have concentrated primarily on the study of the semi-quantitative results, notably the directional effects, which can be deduced from the general structure of the formulae without the need of too accurate numerical knowledge of exchange integrals and the like.

²² H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).

²³ If the promotional energy to the valence state of C is 7 volts, the gross energy per bond in CH_4 is 6 volts, rather than 5 as stated by Woods.

²⁰ R. S. Mulliken, Rev. Mod. Phys. **4**, 80 (1932).

²¹ C. Ireland, Phys. Rev. **43**, 329 (1933).