

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

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On the Theory of the Structure of CH_4 and Related Molecules: Part II

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Explicit calculations are made to examine whether the tetrahedral model of CH_4 is really the most stable in the Hund-Mulliken and Slater-Pauling theories. The secular determinant involved in the H-M procedure is too complicated (degree 8) to solve generally, but three methods of approximation are given applicable in three different limiting cases, in all of which the tetrahedral model proves to be that of least energy quite irrespective of repulsions between the H atoms. The fact that two of the methods do not assume the carbon s - p separation to be small shows that s - p hybridization is not a necessary condition for tetrahedral valence bonds. Calculations are also given which show that in the Heitler-London-Pauling-Slater method the regular tetrahedron is superior to other models of somewhat lower symmetry. It is further calculated according to both the H-M and H-L-P-S schemes that in compounds of the form CH_2X_2 , CHX_3 , and CH_3X , the most stable models are tetrahedra of less symmetry than the regular tetrahedron; i.e., models with the valence

angles somewhat distorted from 109.5° unless the C-H and C-X bonds are of equal intensity. The predicted directions of the deviations from 109.5° are in agreement with x-ray diffraction data for CH_2Cl_2 and CHCl_3 . The conclusion is rather prevalent in the literature that with s - p hybridization and electron pairing two bond axes tend to set themselves at 109.5° . This is shown incorrect; instead the angle can be anything between 90° and 180° depending on the relative intensities of the s and p bonds. If the s bonding power is not negligible, the angle between an NH axis and the pyramidal axis in NH_3 should be somewhat greater than the value 54.7° which is obtained if the three NH axes are orthogonal and which is characteristic of pure p -bonding. Actually Dennison and Uhlenbeck find 68° , and Lueg and Hedfeld 73° , from band spectra. It is shown that CH_4^+ should be a flattened rather than regular tetrahedron, conceivably even being plane. Also CH_3 should be a flatter pyramid than NH_3 .

IN Part I¹ a general comparison was given of the Hund-Mulliken and Slater-Pauling² theories of valence in carbon compounds. It was shown that the H-M procedure gives excessive accumulation of electrons on one atom, while the S-P viewpoint loses rather too much of the symmetry properties characteristic of an individual electron in fields of tetrahedral symmetry. We do not intend these remarks as disparaging criticisms, for insuperable mathematical difficulties prevent any really accurate solution, and both methods are to be admired for the headway they have made in the understanding of carbon valencies.

¹ J. H. Van Vleck, Part I, J. Chem. Phys. 1, 177 (1933).

² See Part I for references to the literature.

However, since none of the procedures are strictly correct, unless modified by exceedingly difficult higher approximations, it appears desirable as one aim of the present paper to prove that the tetrahedral model of CH_4 is the most stable by as many methods as possible, rather than to accept such a model solely because of the tetrahedral geometry of the sp^3 wave functions of Pauling and Slater. If, as it turns out, the tetrahedral configuration invariably has the least energy in the various feasible limiting cases represented in the different theories, we can feel reasonably sure that this configuration is also the best in the intractable intermediate case actually realized. Although we

shall give most of our space to the H-M scheme of attack (Sections 1-4), we do not wish to convey the impression that it is superior to the H-L-P-S one (Section 5). The H-M procedure is adaptable formally to a greater variety of models, but the H-L-P-S is probably more satisfactory if numerical success is desired. For numerical rather than formal results, everything in the H-M method would depend on a happy choice of a self-consistent field.

Before proceeding to the details of the calculations we shall state certain simplifications which we shall make throughout without further mention. We shall neglect all types of forces between H atoms, notably the Coulomb repulsions of the H nuclei in polar models, and terms due to mutual overlapping of the H wave functions. These H-H forces are doubtless repulsive,³ and so only accentuate the stability

of the tetrahedral model since in the tetrahedron the H atoms are evidently in the aggregate as far separated as possible. It is, however, of interest to show that the tetrahedral model evolves itself in virtue of the directional valence of the central C atom without invoking any H-H repulsions. To avoid excessive complexity, it will be supposed that all four H atoms are equidistant from the C atom. We shall always make the usual neglect of excited states of the C and H atoms. That is to say, we assume that in expanding the complete wave function in terms of unperturbed C and H wave functions, the coefficients of the 3,4..quantum states of C and 2,3..quantum states of H are comparatively small. Consideration of these higher states would be required if we were to include corrections for polarization. The very small bonding effect of the *K* shell of carbon will be disregarded.

1. FIRST STAGES OF CALCULATION ACCORDING TO GENERALIZED HUND METHOD

Following Hund, we shall assume that the molecular wave functions of CH₄ can be expressed to a sufficient approximation as linear combinations of the eight wave functions

$$\psi(1s; H_i), (i=a, b, c, d); \quad \psi(2s; C), \quad \psi(2p\sigma_x; C), \quad \psi(2p\sigma_y; C), \quad \psi(2p\sigma_z; C). \quad (1)$$

Here $\psi(2p\sigma_x; C)$ means a carbon $2p$ state which has $m_l=0$ when viewed along the x axis. The functions (1) are to be taken as solutions of the equations

$$[\nabla^2 + (8\pi^2m/h^2)(W_k^C - V_C)]\psi(2k; C) = 0 \quad (k=s \text{ or } p), \quad [\nabla^2 + (8\pi^2m/h^2)(W^H - V_{H_i})]\psi(1s; H_i) = 0, \quad (2)$$

where V_H and V_C are the potential energies of an electron in the field of an H and C atom, respectively. These potential energies need not be considered those due to a bare H nucleus and a C nucleus surrounded by $-6e$, but rather these nuclei surrounded by an appropriately chosen centro-symmetric electron density clouds, so that $\psi(1s; H)$ is not necessarily an ordinary hydrogenic wave function. The question of the best choice of the cloud need not concern us, as our aim is a proof of the tetrahedron's stability rather than numerical calculation of the binding energy. The cloud screening the C nucleus will be greater than $-6e$ if it attracts much charge from the H atoms, making the molecule appreciably polar. The choice of the screening cloud must, for tractability, be taken independent of the spatial arrangement of the H atoms. It may be urged that the "best cloud" does actually depend on the arrangement; but this does not vitiate our proof, since with any given cloud we will prove the tetrahedral model that of least energy. The embodiment of electron repulsions through a statistical charge density or cloud is essentially the Hartree method of the self-consistent field except that, as noted to the writer by Professor Kramers, our procedure does not represent the Hartree method in its full generality. Hartree uses different clouds for obtaining different solutions corresponding to various classes of electron orbits, whereas we must use the same screening cloud for all eight solutions of our forthcoming secular problem.

We shall use the following notation for integrals which will enter in the construction of the secular determinant:

³ Cf. Heitler and Rumer, *Zeits. f. Physik* **68**, 12 (1931) and discussion to be given in Part III.

$$\left. \begin{aligned} B &= \int \int \int \psi(1s; H_i)^2 V_C dv, & C_k &= - \int \int \int \psi(2k_i; C)^2 V_{H_i} dv, \\ D &= - \int \int \int \psi(2s; C) \psi(2\sigma_i; C) V_{H_i} dv, & Q_k &= - \int \int \int \psi(1s; H_i) \psi(2k_i; C) V_{H_i} dv, \\ R_k &= - \int \int \int \psi(1s; H_i) \psi(2k_i; C) V_C dv, & T_k &= \int \int \int \psi(1s; H_i) \psi(2k_i; C) dv, \end{aligned} \right\} \quad (3)$$

with $k = \pi, \sigma$, or s . Note that $Q_\pi = R_\pi = T_\pi = 0$.

The notation π_i, σ_i means that the spatial quantization is relative to the axis $C-H_i$, and the indices $p\pi, p\sigma$ are here and henceforth abbreviated to π, σ . A π state has $m_l^2 = 1$; a σ state $m_l = 0$. The vanishing of Q_π and R_π follows from the axial symmetry of V_{H_i}, V_C on integrating over the azimuthal coordinate φ involved in $dv = r^2 \sin \theta dr d\theta d\varphi$. The integrals are independent of i because all four H atoms are equidistant from C.

The expressions C, D, Q, T , defined in (3) may all be considered positive. Here and elsewhere we omit subscripts when our remarks apply collectively to the π, σ , and s types. It is true that some of the integrals are really arbitrary in sign because of arbitrary phase factors in the wave functions, but the final formulas which we shall obtain for the energy will naturally involve these expressions only through products (e.g., $Q_\sigma T_\sigma$) which are invariant of the choice of phases. It is convenient, however, to take these expressions individually positive. To see that this is possible, one notes that $\psi(1s; H_i)$ is nodeless and so may be taken everywhere positive, while $\psi(2s; C), \psi(2\sigma_i; C)$ can be taken positive where they overlap the atom H_i , which will be well beyond the node of $\psi(2s; C)$. The potential energy V_{H_i} is, of course, everywhere negative, since the charge screening the H nucleus is surely less than that of a proton. The signs of B, R are immaterial for our purposes.

The model will not be assumed tetrahedral. Instead it will be supposed that an axis $C-H_i$ ($i = a, b, c, d$) has arbitrary direction cosines l_i, m_i, n_i . The secular equation is then

$$\begin{vmatrix} E & s_l & s_m & s_n & q & q & q & q \\ s_l & F_l & r_{lm} & r_{ln} & a_l & b_l & c_l & d_l \\ s_m & r_{lm} & F_m & r_{mn} & a_m & b_m & c_m & d_m \\ s_n & r_{ln} & r_{mn} & F_n & a_n & b_n & c_n & d_n \\ q & a_l & a_m & a_n & G & 0 & 0 & 0 \\ q & b_l & b_m & b_n & 0 & G & 0 & 0 \\ q & c_l & c_m & c_n & 0 & 0 & G & 0 \\ q & d_l & d_m & d_n & 0 & 0 & 0 & G \end{vmatrix} = 0, \quad (4)$$

with the abbreviations

$$\left. \begin{aligned} a_l &= l_a [-Q_\sigma + (W_p^c - W) T_\sigma], & q &= -Q_s + (W_s^c - W) T_s, \\ E &= W_s^c - 4C_s - W, & F_l &= W_p^c - 4C_\pi + (C_\pi - C_\sigma) \sum_i l_i^2 - W, \\ G &= W^H + B - W, & r_{lm} &= -(C_\sigma - C_\pi) \sum_i l_i m_i, & s_l &= -D \sum_i l_i. \end{aligned} \right\} \quad (5)$$

It is to be understood that b_m, \dots, d_n denote expressions similar to that in (5) for a_l except that m_b, \dots, n_d replace l_i . Analogous remarks apply to the rest of the notation (5).

That the direction cosines enter in the way that they do in (4) follows from the fact $\psi(2s; C)$ is centro-symmetric, and that the wave functions $\psi(2\sigma_x; C), \psi(2\sigma_y; C), \psi(2\sigma_z; C)$ are of the form $xf(r), yf(r), zf(r)$, and hence transform from one coordinate system to another like the components

of a vector.⁴ For instance

$$\psi(2\sigma_x; C) = l_i \psi(2\sigma_i; C) + (1 - l_i^2)^{1/2} \psi(2\pi_i; C). \quad (6)$$

Eqs. (5) show that terms $-WT_s$, $-WT_\sigma$ involving W appear off the diagonal in (4). Such terms have arisen because the C and H wave functions are not orthogonal. In place of the formula for q in (5) we could equally well have set $q = -R_s + (W_i^H - W)T_s$, as Eqs. (2) and the self-adjoint property of the Hamiltonian operator \mathbf{H} give us the relation

$$W_s^C T_s - Q_s = \int \int \int \psi(1s; H_i) \mathbf{H} \psi(2s; C) dv = \int \int \int \psi(2s; C) \mathbf{H} \psi(1s; H_i) dv = W^H T_s - R_s. \quad (7)$$

Analogous remarks apply to the definitions of a , b , c , d . We are using only real wave functions, which involves no loss of generality in the absence of magnetic forces. Hence (4) is symmetric as well as Hermitean.

Eq. (4) differs from Eq. (2) of Part I only in the system of representation, as (2) of I was based on sp^3 functions for carbon instead of the usual nonhybridized functions (1). The zero elements occurring in (4) are due to our agreement to neglect H-H forces.

Twice the sum of the four lowest roots of (4) is the energy of the CH_4 molecule. The sum is to be doubled because the Pauli principle allows two electrons to each solution of the orbital wave equation, so that only four roots in all are needed to absorb the eight electrons available from the H atoms and the L shell of C.

Eq. (4) is still too complicated to solve except with simplifying assumptions.

2. THE "NEAR-IONIC" CASE $W^H - W^C \gg Q$

This case would be realized if CH_4 were nearly of the ionic structure $\text{C}^{4-}(\text{H}_4)^{4+}$, for it requires that the difference between the electron affinities of the C and H attracting centers (appropriately screened) be large compared to the various integrals (3), notably the resonance terms Q, R which are the main cause of the molecular binding. It further requires $W^H - W^C \gg Q$ so that electrons are in the mean attracted from H to C rather than *vice versa*. Actually this case will be a rather poor approximation in CH_4 , for the ionization potentials of C and H are nearly equal, and their electron affinities small. Nevertheless it is instructive to carry through a calculation for this case, because it is desirable to solve the secular determinant (4) for as many different limiting cases as possible, and especially because it here proves possible to obtain simple and illuminating formulas for the energy with arbitrary arrangement of the H atoms.

The mathematical simplicity of the present case rests in our ability to use a series development in the ratios of the integrals (3) to $W^H - W^C$. It is convenient to introduce a parameter λ into Eq. (4) by the following scheme: *multiply each Q or T term in (5) by λ , and each C or D term by λ^2* . The series development may then be regarded as a power series in λ . The convergence of the development is, of course, due to the smallness of the expressions (3) rather than of λ , since finally one must set $\lambda = 1$. The rôle of λ is thus only a formal one, and is primarily to describe the degree of approximation which first yields the tetrahedral model. The calculation will yield the following interesting result: the molecule's energy is a series in even powers of λ and is independent of the way the H atoms are arranged if the development is carried only to terms in λ^2 inclusive, but is a minimum for the tetrahedral model when terms of order λ^4 are included. These λ^4 terms are of two types. One kind arises from fourth powers of Q, T ; the other involves the product of a first power of C, D

⁴ In using (6) it must be mentioned that to specify a real π wave function completely, it is necessary to specify the phase ϵ in its azimuthal factor $\cos(\varphi - \epsilon)$. In (6) the value of ϵ is zero if the apse line for measuring φ is taken in the plane $x-C-z$. In calculating the values of the

elements r in (4), use must be made of the fact that if $\psi_\pi, \psi_{\pi'}$ denote π wave functions of C with different phases,

$$\int \int \psi_\pi \psi_{\pi'} V_{H_i} dv = -C_\pi \cos(\epsilon - \epsilon').$$

and a squared term in Q, T . (Squared terms in C, D prove to be absent.) Both types need not be of coordinate importance, but fortunately both yield the same dependence of energy on angular arrangement, favoring the tetrahedron. It appears impossible to say which type is the more important, as an answer to this question would require knowledge of the magnitude of C, D compared to Q . One knows, to be sure, that Q is large compared to C, D , but this is insufficient.

We now proceed with the details of the calculation. The first step is to apply a transformation which will for our purposes reduce the eighth order secular determinant to a fourth order one. The transformation in question is

$$S(ij) = -S(ji) = -K(ij)/h\nu(ij), \quad S(ii') = \delta_{i'i}, \quad S(jj') = \delta_{j'j} \quad (8)$$

where δ is the usual Kronecker symbol and the $K(mn)$ are defined by writing the matrix elements of (4) as $K(mn) - W\delta_n^m$. Note that because of the T terms in (5) the $K(mn)$ involve W . The indices i, i' refer to any of the C levels and j, j' to any of the H ones (i.e., the ground states of any of the four H atoms). One can verify that in the transformed matrix $S^{-1}KS$ the elements ij (which replace a, b, c, d, q in (4)) are of the order λ^3 and so affect the four lowest, i.e., perturbed carbon, roots of (4) only in the approximation λ^6 . As we shall stop with λ^4 , we therefore need retain in this transformed matrix only the fourth order piece (ii') which embraces the four C roots. On calculating⁵ this piece by means of (8) one finds that it gives the secular equation

$$|L(ii') - \delta_{i'i}W| = 0 \quad (9)$$

with

$$L(ii) = K(ii) + \sum_j \frac{K(ij)^2}{h\nu(ij)} - \left\{ \sum_{i', j} \frac{K(ij)K(ji')K(i'i)}{h\nu(ij)h\nu(i'j)} + \sum_{j, i', j'} \frac{K(ij)K(ji')K(i'j')K(j'j)}{h\nu(ij)h\nu(i'j)h\nu(i'j')} \right\} \quad (10)$$

$$L(ii') = K(ii') + \sum_j \frac{K(ij)K(ji')}{h\nu(i'j)} \quad (11)$$

The terms in braces are of degree λ^4 ; the others of degree λ^2 or lower. We have carried the expressions for the L 's far enough to give the expansion of (9) to λ^4 . This means that it has only been necessary to carry the off-diagonal elements (11) to the approximation λ^2 . If we were interested in individual roots of (9), instead of merely the sum, we would need to carry these elements to the approximation λ^4 , since to determine individual roots of (9) to λ^4 one would need to know the coefficients of W^2, W, W^0 to $\lambda^8, \lambda^{12}, \lambda^{16}$, respectively, whereas we are interested purely in the coefficients of W^3, W^4 . In virtue of (10), (11), (5), to our approximation the explicit form of (9) is

$$\begin{vmatrix} H_s + I_s \sum_i \sum_j (\mathbf{i} \cdot \mathbf{j}) - W & M_s \sum l_i & M_s \sum m_i & M_s \sum n_i \\ M_p \sum l_i & f(l) - W & J \sum l_i m_i & J \sum l_i n_i \\ M_p \sum m_i & J \sum l_i m_i & f(m) - W & J \sum m_i n_i \\ M_p \sum n_i & J \sum l_i n_i & J \sum m_i n_i & f(n) - W \end{vmatrix} = 0 \quad (12)$$

with

$$\left. \begin{aligned} f(q) &= W_p^C - 4\lambda^2 C_\pi + J \sum_i q_i^2 + \sum_i \sum_j q_i q_j [I_p + N(\mathbf{i} \cdot \mathbf{j})] \\ H_s &= W_s^C - 4\lambda^2 C_s - 4\lambda^2 \tau_s Q_s'^2 + 4\lambda^4 \tau_s^3 Q_s'^4, \quad J = \lambda^2 (C_\pi - C_\sigma) - \lambda^2 \tau_p Q_\sigma'^2 \\ I_k &= \lambda^4 \tau_s \tau_p D Q_s' Q_\sigma' + \lambda^4 \tau_s \tau_p \tau_k Q_\sigma'^2 Q_s'^2, \quad M_k = -\lambda^2 D - \lambda^2 \tau_k Q_s' Q_\sigma' \\ N &= \lambda^4 \tau_p^2 Q_\sigma'^2 (C_\sigma - C_\pi) + \lambda^4 \tau_p^3 Q_\sigma'^4 \end{aligned} \right\} \quad (13)$$

⁵ The matrix elements of S^{-1} needed for computing $S^{-1}KS$ are found by noting that (8) gives nearly a unit matrix, so that

$$S^{-1} = 1 - (S - 1) + (S - 1)^2 - (S - 1)^3 + \dots$$

where the i and j summations each embrace a, b, c, d and where

$$1/\tau_k = W^H + B - W_k^C > 0, \quad (k=s \text{ or } p); \quad Q_k' = Q_k + T_k(W_k^C - W), \quad (k=s \text{ or } \sigma) \quad (14)$$

$$(\mathbf{i} \cdot \mathbf{j}) = l_i l_j + m_i m_j + n_i n_j = \cos(C - H_i, C - H_j), \quad (i, j = a, b, c, d). \quad (15)$$

We have treated B as part of the H atoms' unperturbed energy in defining the τ_k or $1/h\nu(ij)$. This avoids the necessity of treating the B terms as perturbations. The rôle of the B terms is thus a trivial one, without appreciable influence on the properties of directional valence. When one drops terms beyond λ^4 , the expansion of (12) is of the form

$$(W - W_p^C)^3(W - W_s^C) + \lambda^2(a_5 W^5 + a_4 W^4 + \dots + a_0) + \lambda^4(b_7 W^7 + \dots + b_0) = 0. \quad (16)$$

The coefficients a of the λ^2 terms are easily seen to be independent of the molecular arrangement since the sum of the squares of three direction cosines is unity. The terms proportional to W^5, W^6, W^7 exist because the second relation of (14) makes the elements (13) nonlinear in W . The fact that (16) is a seventh degree expression in W gives the superficial appearance of a seventh degree secular problem, but this is only an illusion, for it is only legitimate to take the four roots which reduce to C levels at infinite C-H separations. The other three roots are devoid of any significance, as nearness to C levels was assumed in reducing the determinant to the fourth order. The occurrence of higher powers than W^4 in (16) may be obviated by depressing the higher powers of W by the approximate relation

$$W^4 = 6w^2 W^2 - 8w^3 W + 3w^4 + \lambda^2[(6a_5 w^2 + a_3) W^3 + (-8a_5 w^3 + 6a_4 w^2 + a_2) W^2 + \dots]$$

obtained by solving (16) first with $\lambda=0$ and then correcting to λ^2 inclusive. Here for simplicity we have assumed the origin for the energy so chosen that the mean root is zero when $\lambda=0$, i.e., that $W_s^C = -3w$, $W_p^C = w$ where $4w$ is the carbon s - p separation. This assumption involves no loss of generality and simplifies the calculations materially. Thus (16) is transformed into a fourth degree equation $A W^4 + B W^3 + \dots = 0$. The sum X of the four relevant roots is thus,

$$X = -\frac{B}{A} = -\frac{\lambda^2[a_3 + 6a_5 w^2] + \lambda^4[b_3 + a_3 a_4 + a_2 a_5 + w^2(6b_5 + 12a_4 a_5) - 8w^3(b_6 + a_6^2) + 39b_7 w^4] + \dots}{1 + \lambda^2 a_4 + \dots}. \quad (17)$$

It will be noted that the absence of orthogonality makes the procedure somewhat more complicated than it would otherwise be. If we were willing to assume perfect orthogonality and so set $T=0$ in (5) there would be no terms higher than W^4 in (9) or (16) and one could use the usual spur relation $X = -\sum L(ii)$ which actually is invalidated by the non-orthogonality. It is clearly to be understood that the spur in question is that of (9) or (16) and not that of (4), since we are interested in the sum of only half the roots of (4). It does not appear a legitimate approximation to assume orthogonality as (7) shows that T is of the same order of magnitude as $Q/h\nu(C; H)$ unless fortuitously Q and R are very nearly equal. Although the non-orthogonality invalidates the ordinary spur relation, it is still very much easier to calculate the sum than individual roots, as the latter would require solution of a biquadratic equation, which we have avoided.

When the explicit values of the coefficients in (16) are calculated by means of (14-15) it is found that (17) becomes

$$X = \alpha + \beta \mathbf{p}^2 + \gamma \sum_i \sum_j (\mathbf{i} \cdot \mathbf{j})^2, \quad (18)$$

where α, β, γ are independent of the arrangement of the H atoms, $(\mathbf{i} \cdot \mathbf{j})$ is defined as in (15), and \mathbf{p} is a vector of components $\sum l_i, \sum m_i, \sum n_i$. This vector is clearly proportional to the electric moment of the molecule. It is particularly noteworthy that to our degree of approximation λ^4 , the dependence of X on the molecular arrangement, i.e., on $l_i, l_j, \dots, n_i, n_j$, is only through the two combinations $\sum \sum (\mathbf{i} \cdot \mathbf{j})^2$ and \mathbf{p}^2 . The coefficients in (18) have the following values in terms of the integrals (3)

$$\beta/\lambda^4 = 2\tau_s\tau_p D[Q_\sigma Q_s + 2(T_s Q_\sigma - Q_s T_\sigma)w] + \tau_s^2\tau_p Q_s^2(Q_\sigma - 4T_\sigma w)^2 + \tau_p^2\tau_s Q_\sigma^2(Q_s + 4T_s w)^2 \\ + D(\tau_s + \tau_p)(Q_s T_\sigma + T_s Q_\sigma) + \tau_s\tau_p[2Q_\sigma T_\sigma Q_s^2 + 2Q_s T_s Q_\sigma^2 + 4(Q_\sigma^2 T_s^2 - Q_s^2 T_\sigma^2)w], \quad (19)$$

$$\gamma/\lambda^4 = \frac{1}{2}\tau_p^2(C_\sigma - C_\pi)Q_\sigma^2 + \frac{1}{2}\tau_p^3Q_\sigma^4 + 2\tau_p(C_\sigma - C_\pi)T_\sigma Q_\sigma + 2\tau_p^2Q_\sigma^3T_\sigma \quad (20)$$

with τ as in (14). The corresponding formula for α could be given, but is of no interest.

The all important question is now the signs of β and γ . These are both positive because of the following considerations. We have already mentioned after Eq. (3) that the C , D , Q , T may all be considered positive, and τ is positive in virtue of (14). Furthermore $C_\sigma - C_\pi$ is positive since the σ_i wave function overlaps the hydrogen atom H_i much more than do the π_i functions. Hence every term in (20) is positive. Eq. (19) contains two negative terms, but these are of subordinate importance for the following reasons. In the first place, the carbon s - p separation $4w$ may be small compared to the separation τ between the H and C levels. If this is the case Tw will be small compared to Q , since (7) shows that T is of the order of magnitude Q/τ inasmuch as Q and R are usually very roughly of the same order. Furthermore, even if the s - p interval should be so large that Tw and Q are of the same order of magnitude, there are so many positive terms that it would be only with a very curious and unreasonable collection of values for the integrals (3) that the negative terms could predominate. In particular, if the s and p bonds are nearly equal, the value of $T_\sigma Q_s$ will not differ greatly from that of $T_s Q_\sigma$, so that the factors $(T_s Q_\sigma - Q_s T_\sigma)$ and $(Q_\sigma^2 T_s^2 - Q_s^2 T_\sigma^2)$ are comparatively small.

The most stable molecular arrangement is that which minimizes (18), since $2X$ is the binding energy. A convenient alternative way of writing (18) is

$$X = \alpha + (16/3)\gamma + (\beta - \frac{2}{3}\gamma)\mathbf{p}^2 \\ + 2\gamma \sum_{i, j} [(i \cdot j) + \frac{1}{3}]. \quad (21)$$

Eqs. (18) and (21) are identical inasmuch as $\mathbf{p} = \sum \mathbf{i}$, $\mathbf{i} \cdot \mathbf{i} = 1$, and as the sum in (18) included $j \leq i$ in addition to $j > i$. Now the tetrahedral model alone possesses *both* of the two following properties: (a) absence of an electric moment \mathbf{p} ; (b) a common value $-\frac{1}{3}$ for every term of the form $\mathbf{i} \cdot \mathbf{j}$ ($i \neq j$). (The easiest way to see that the tetrahedron fulfills (b) is to note that the

projections on C-H_a of unit vectors directed along C-H_b, C-H_c, C-H_d are all equal, and of magnitude $-\frac{1}{3}$ because of the absence of an electric moment). Eq. (21) shows immediately that the tetrahedral model possesses the least energy of all models if $\beta \geq \frac{2}{3}\gamma$. It is not unlikely that the latter inequality is fulfilled. For instance, if we suppose that the Q , T are more important than the C , D terms, that Tw/Q is small, that $\tau_s = \tau_p$ and that the s and p bonds are of equal intensity (i.e., $Q_\sigma = Q_s$, $T_\sigma = T_s$), Eqs. (19-20) show that $\frac{2}{3}\gamma$ is between one-sixth and one-third as large as β ; actually the s bonds are weaker than the p , but perhaps not enough to make $\frac{2}{3}\gamma > \beta$.

One can also see beyond all reasonable doubt from (18) or (21) that the tetrahedral model is superior even if $\beta < \frac{2}{3}\gamma$. It is an immediate consequence of (21) that the tetrahedron has the least energy of all models devoid of an electric moment, since with $\mathbf{p} = 0$ the question of the sign of $\beta - \frac{2}{3}\gamma$ does not enter. Among the models with an electric moment, the only arrangement that seems at all probable is a pyramidal model with the C atom at its apex and the four H atoms at the corners of a square base. One easily finds that in this model the sum $\sum (\mathbf{i} \cdot \mathbf{j})^2$ has its minimum value when each C-H axis is inclined at $\cos^{-1} 3^{-\frac{1}{2}} = 54.7^\circ$ to the axis of the pyramid. Then some of the $(\mathbf{i} \cdot \mathbf{j})$ ($i \neq j$) have the value $+\frac{1}{3}$, the rest the value $-\frac{1}{3}$. The 54.7° pyramid thus gives the same value for the third term of (18) as the tetrahedron, but the pyramid has an electric moment and so gives a larger value of the second term. Of course this still does not disprove the possibility of some freak, unsymmetrical model with an electric moment, but we must not forget the physical fact that dielectric constant data unquestionably reveal that CH₄ has no moment. Irrespective of this fact, one can progress a step further towards complete mathematical rigor by noting that the tetrahedral model, regardless of the

sign of $\beta - \frac{2}{3}\gamma$, fulfills the analytical criterion

$$\sum_i [\mathbf{i} \times \mathbf{j}] (\mathbf{i} \cdot \mathbf{j}) = 0 \quad (22)$$

that $\sum_{ij} (\mathbf{i} \cdot \mathbf{j})^2$ be an extremum. That (22) is the condition for the minimum of this sum can be verified by writing the sum explicitly in terms of the l 's, m 's, and n 's, and then differentiating with respect to, say, the m 's after the n 's have been eliminated by the relations $l_i^2 + m_i^2 + n_i^2 = 1$. Satisfaction of (22) by the tetrahedron shows that it is stable with respect to adjacent arrangements, but this does not say that there are not radically different arrangements also satisfying (22) and conceivably giving still lower energy if there is an electric moment. The 54.7° pyramid, the square coplanar model, and collinear arrange-

ments $\mathbf{i} \cdot \mathbf{j} = \pm 1$ are all solutions of (22), but each gives a higher value of (18) than the tetrahedron.

Case $W^C - W^H \gg Q$. This is another limiting ionic case, differing from the preceding in that the drift of electronic charge is from C to H rather than from H to C, making the model nearly $C^{4+}(H_4)^{4-}$. This case can be treated by the same kind of perturbation development as the preceding one, but we shall omit the calculations. Without appreciable computation, one can show that the tetrahedral model has the least energy if one neglects the corrections for non-orthogonality, so that one can use the spur theorem.⁶ Of course the corrections are important, but in the preceding case, at least, they reinforced rather than counteracted the other terms.

3. ANOTHER METHOD OF APPROXIMATION WITH THE HUND-MULLIKEN METHOD

When Q is of the same order of magnitude as, or larger than, the separation $W^H - W^C$ between the C and H levels, the molecule is no longer usually highly polar, and it is naturally no longer legitimate to use the perturbation developments employed in Section 2. Because of this difficulty it appears no longer possible to find the binding energy for arbitrary arrangements. Instead it is necessary to restrict our attention to models with some degree of symmetry so as to permit factorization of the secular determinant (4). Fortunately the symmetrical models are, of course, the most likely. Three types of symmetrical models will be described and calculated below under (a), (b), (c), and it will be shown that of these the tetrahedron is the most stable. Even with the symmetrical types the calculation is too complicated to be tractable⁷ without the following three simplifications: (I) neglect of the s - p separation in carbon; (II) neglect of the C and D terms in (4-5); (III) neglect of terms arising from want of orthogonality (the T terms in 4-5).

Assumption (I), *viz.*, that $W_p^C - W_s^C$ is very small compared to Q , means conditions such that s - p hybridization would be a good approximation were the calculation to be made by the Heitler-London method. It is not necessary to make the more stringent restriction that $|W^H - W^C| \ll Q$, as the latter proves to permit little additional simplification beyond that arising from $W_p^C = W_s^C = W^C$. We can clearly suppose that $W^H - W^C$ is at most of the order Q , since if $W^H - W^C \gg Q$ we would merely revert to the case already covered by perturbation theory. In consequence of this fact, we shall show in the next paragraph that (II) and (III) are good approximations if (I) is granted.

Assumption (II) means that the molecular bonds are supposed to arise mainly from the Hund resonance (our Q) terms rather than from penetration (our C, D) terms. In the preceding cases

⁶ If we set $T=0$, the root sum Y which interests us when $W^C - W^H \gg Q$ is $Z - X$ where Z is the spur of the complete matrix (4) and X is our previous root sum. The value of Z is independent of the angles, and hence Y has an extremum when X does. When $W^C - W^H \gg Q$ the tetrahedral arrangements gives a minimum of $Z - X$ and a maximum of X rather than the reverse as previously. This is because sign changes in τ and in certain of the integrals (3), occasioned by the electronic drift being from C to H rather than from H to C, make the expressions β, γ defined in (19, 20) become negative.

⁷ For the regular tetrahedron, which is a special case of the models of class (a) or (c), and which has the most symmetry of all, none of the approximations (I), (II), (III) are necessary, and an exact expression can be derived for the energy, which was given in Eq. (4), Part I. The constants employed in Part I have the following significance in terms of the integrals (3), etc.

$$\begin{aligned} a + 3b &= 4C_s + W_s^C, & a - b &= \frac{1}{4}C_\sigma + \frac{3}{4}C_\pi + W_p^C, \\ \bar{c} + 3e &= 2(-Q_s + T_s W_s^C), & c - e &= -(\frac{1}{4})^\frac{1}{2}(Q_\sigma - T_\sigma W_p^C), \\ d + 3f &= -2T_s, & d - f &= -(\frac{1}{4})^\frac{1}{2}T_\sigma, & g &\sim 0, & h &\sim 0, & k &= W^H + B. \end{aligned}$$

we stated that it was not allowable to forget the C, D terms, even though $C, D \ll Q$, inasmuch as they affected the dependence of energy on arrangement in the approximation CQ^2, DQ^2 , whereas Q alone appeared only in the fourth order (cf. Eqs. (19-20)). In the present case, however, the development in ascending powers of $Q/h\nu(\text{H}; \text{C})$ is no longer used and in consequence the Q terms will influence the energy of spatial arrangement in the first rather than fourth approximation, thus surely becoming more important than the C terms. This can be seen concretely from later specific energy formulas; the situation is roughly similar to that of an expression like $(a^2 + b^2 \cos^2 \theta)^{\frac{1}{2}} + (a^2 + b^2 \sin^2 \theta)^{\frac{1}{2}}$, which depends on angle in the approximation b^4/a^3 if $b^2 \ll a^2$, but in terms of the order b otherwise. Likewise neglect of orthogonality is a much better approximation than when $W^H - W^C \gg Q$. This can be seen from dimensional considerations. The expressions T_s, T_v are dimensionless and small compared to unity, while Q has the dimensions of energy. Terms of the form $Q^x(W^H - W^C)^y T^z$ can thus appear along with those of the form Q^{x+y} and could be coordinate in importance with the latter in the previous cases where $|W^H - W^C| > Q$ but not in the present one, where $W^H - W^C$ is at most comparable with Q .

(a) One type of model which is readily treated and which we shall call class (a) is obtained by the following scheme. Let the coordinates of the C atom be 0, 0, 0 and those of the four other atoms be $x, 0, z; -x, 0, z; 0, y', z'; 0, -y', z'$; Let $\omega = \tan^{-1} z/x$ and $\omega' = \tan^{-1} z'/y'$. This class includes the regular tetrahedron as the special case $\omega = -\omega' = \tan^{-1} 2^{-\frac{1}{2}} = 35.3^\circ$ and the Guillemin-Henri pyramidal model (H atoms at corners of square base, C at vertex) as the special case $\omega = \omega', z = z'$. In order to make our calculations applicable to molecules of the form CH_2X_2 as well as just CH_4 , we shall

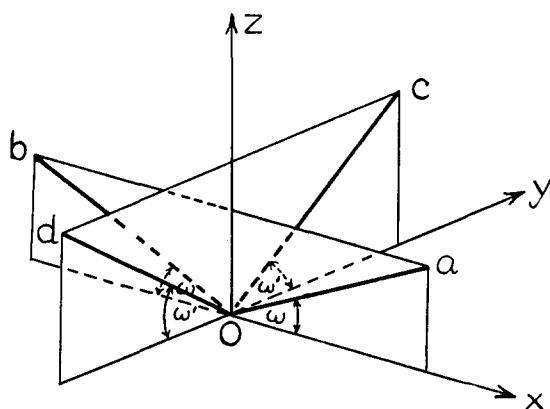


FIG. 1 (class (a)). For CH_4 or CH_2X_2 . Here $Oa = Ob; Oc = Od$, with H atoms at c, d and a C atom at O . The atoms at a, b are either both H or both X. The regular tetrahedron is the special case $\omega = -\omega' = \tan^{-1} 2^{-\frac{1}{2}} = 35.3^\circ$. In the text the notation \mathfrak{N} or P is used for integrals involving either a or b ; and N or Q for those involving c or d .

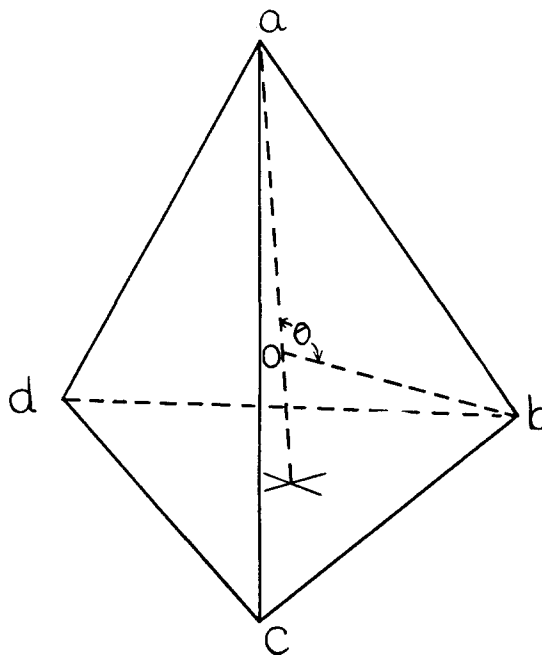


FIG. 2 (class (c)). For $\text{CH}_4, \text{CH}_2\text{X}$, or NH_3 . Here $Ob = Oc = Od$ and $ab = ac = ad$ with H atoms at b, c, d ; a C (or N) atom at O and an H or X (or no) atom at a . The z axis is directed along Oa and the xz plane contains aOb . The regular tetrahedron is the special case $\theta = \cos^{-1} -\frac{1}{3} = 109.5^\circ$. The integrals \mathfrak{N} or P apply to a ; and N or Q to b, c, d .

not assume that the atoms in the xz plane are the same as those in the yz plane.⁸ It will not be necessary to suppose⁹ $x^2+z^2=y'^2+z'^2$, i.e., that the two kinds of atoms are equidistant from the C atom, but unfortunately it must be assumed for tractability that they all have the same energy W^H . The resonance integrals between the C atom and the atoms in the xz plane will be denoted by the letter P rather than Q in order to exhibit the fact that they are held by bonds of different intensity than those in the yz plane. It is convenient to choose the eight wave functions as follows

$$\begin{aligned} & [\psi(2s), \frac{1}{2}(\psi_a+\psi_b+\psi_c+\psi_d), \psi(2\sigma_z), \frac{1}{2}(\psi_a+\psi_b-\psi_c-\psi_d)], \\ & [\psi(2\sigma_x), 2^{-\frac{1}{2}}(\psi_a-\psi_b)], \quad [\psi(2\sigma_y), 2^{-\frac{1}{2}}(\psi_c-\psi_d)]. \end{aligned} \quad (23)$$

with notation as in Eq. (1) except for obvious contractions. The secular determinant, originally of degree 8 (cf. Eq. (4)) then factors into a biquadratic and two quadratics. The biquadratic is a quadratic in $(W-W^H)(W-W^C)$ and so easily soluble. Wave functions bracketed together belong to the same factor. The factorization is readily verified and explicit form of the factorized determinants constructed from the transformation property (6) of the carbon p wave functions under rotation. Four of the roots are as follows:

$$W_1 = F(P_\sigma^2 \cos^2 \omega), \quad W_2 = F(Q_\sigma^2 \cos^2 \omega'), \quad (24)$$

$$W_\pm = G_\pm(P_\sigma^2 \sin^2 \omega + Q_\sigma^2 \sin^2 \omega' + P_s^2 + Q_s^2; 2P_\sigma Q_s \sin \omega - 2P_s Q_\sigma \sin \omega'), \quad (25)$$

where $F(a) = \frac{1}{2}(W^H + W^C) - \frac{1}{2}\sqrt{[(W^H - W^C)^2 + 8a]}$, (26)

$$G_\pm(b; c) = \frac{1}{2}(W^H + W^C) - \frac{1}{2}\sqrt{[(W^H - W^C)^2 + 4b \pm 4(b^2 - c^2)^{\frac{1}{2}}]}.$$

The radical sign is used throughout to denote the positive square root. The other four roots are similar except that the factor before the radical sign is $+\frac{1}{2}$ rather than $-\frac{1}{2}$. These other roots are "anti-bonding," i.e., give higher energy than the lesser of the two quantities W^H , W^C , and hence are of no interest to us. The Pauli principle allows two electrons to each bonding root, and so the molecule's energy is

$$2X = 2(W_1 + W_2 + W_+ + W_-). \quad (27)$$

We first note that for given absolute values of ω , ω' , and nonvanishing P , Q , the expression (27) has a lower value when ω and ω' have opposite rather than similar signs. This follows from (24-26) and the inequality

$$G_+(b; c') + G_-(b; c') < G_+(b; c) + G_-(b; c) \quad (b \geq c' > c > 0).$$

Hence for any molecule of the type CH_4 or CH_2X_2 the pyramidal model is never that of least energy.

Now let us make the specialization $Q=P$ appropriate to CH_4 if all four H atoms are equidistant from C, and plot (27) as a function of the variables ω , ω' . The value of (27) is then symmetric with respect to the line $\omega = -\omega'$ in the ω , ω' plane, as well as with respect to $\omega = \omega'$. Hence if we consider the behavior of (27) along any curve in the ω , ω' plane, (27) will have extremums where the curve crosses either of these lines. Furthermore, an extremum of (27) along the line $\omega = -\omega'$ occurs at $\omega = \tan^{-1} 2^{-\frac{1}{2}}$, as can be verified by differentiation of (27) with respect to ω after first setting $\omega' = -\omega$. Hence the regular tetrahedron gives an extremum of the energy, which closer examination shows

⁸ Most commonly the atoms X will be halides, in which case they will be in $2P$ rather than in $2S$ states like hydrogen. Despite this difference, the analysis is still applicable if we suppose that in the halide's incomplete shell $ms^2 mp\pi^4 mp\sigma$, the axis of $mp\sigma$ is directed towards the central atom C and if we neglect the bonding power of ms and $mp\pi$. Such a choice of the axis of $mp\sigma$ is clearly demanded for overlapping favorable to bonding. With these assumptions, only the $2p\sigma$ electron of the halide is involved in the secular problem (4), and the integrals

(3) obviously are to be calculated for an $mp\sigma$ rather than $1s$ state of X. Also no harm is done if the letter H similarly symbolize some atom other than hydrogen and not necessarily in an S state. Thus the conclusions of our calculations also apply to compounds such as CCl_4 , CCl_2Br_2 , CCl_3Br , as well as CH_4 , CH_2X_2 , CH_3X .

⁹ The assumption $x^2+z^2=x'^2+z'^2$ is, however, always needed for the simplification $P=Q$ which we make in connection with CH_4 .

to be a minimum rather than maximum. The tetrahedral model is thus stable with respect to adjacent models. This is not quite the same as demonstrating rigorously that it has the least energy of all models of the class, as conceivably there might be a lower minimum at some other values of ω , ω' . Because of algebraic difficulties, it would be difficult to solve the equations $\partial X/\partial \omega = \partial X/\partial \omega' = 0$ explicitly for ω , ω' , but rough inspection of the behavior of (27) for various values of the arguments shows that the occurrence of a lower minimum is exceedingly unlikely. In fact the only other minimum appears to be the 54.7° pyramid ($\omega = \omega' = 35.3^\circ$), which is a minimum along the line $\omega = \omega'$, but is a higher minimum because of the considerations in the preceding paragraph. It is interesting to note that this pyramid and the tetrahedron are minima for all values of the relative intensity Q_s/Q_σ of the s and p bonds, including $Q_s/Q_\sigma = 0$ and excluding only the trivial case $Q_s/Q_\sigma = \infty$ where there is no directional valence. The existence of a nonvanishing Q_s is necessary only to make the two minima unequal, as the signs of ω , ω' are immaterial in (24–25–26) if $Q_s = P_s = 0$. Hence just as in Section 2 the tetrahedron takes precedence over the 54.7° pyramid only because of the interplay between the s and p bonds.

(b) **Plane models.** Consider a plane model formed by placing the C atom at the center of a parallelogram, an atom X at each of two opposite corners, and an atom H at each of the two other corners. In this type of model the energy obviously has the same value when the angle α between the diagonals of the parallelogram has the value α as when it has the value $\pi - \alpha$. Hence $\alpha = \pi/2$ gives an extremum, easily seen to be a minimum. With such a value of α , this plane model is merely the special case $\omega = \omega' = 0$ of the models of class (a) and hence has higher energy than the tetrahedron.

Another readily soluble model in which all atoms are in the same plane is that in which the X atoms are at the upper corners, the H atoms at the lower corners, of an isosceles trapezoid, with C on the axis of symmetry. This model is obtainable from class (a) by rotating the plane labelled dOc in Fig. 1 by 90° around the z axis. We can thus take the coordinates of the atoms to be the same as in class (a) except that those of the last two atoms become $x', 0, z'$; $-x', 0, z'$ and $\omega' = \tan^{-1} z'/x'$. The selection of wave functions and factorization are the same as in (23) except that $\psi(2\sigma_y)$ gives an isolated root W^c , while the other three wave functions in the second line of (23) give a cubic of which one root is W^H . Two of the roots are still given by (25) while (24) is replaced by

$$W_1' = F(0), \quad W_2' = F(P_\sigma^2 \cos^2 \omega + Q_\sigma^2 \cos^2 \omega'). \quad (28)$$

Using (26) one finds $W_1' + W_2' > W_1 + W_2$, and so the plane model is less firmly bound than the spatial model of the same ω , ω' .

(c) Another tractable case, which we shall call class (c) and which is illustrated in Fig. 2, is that in which the C atom is at the center of a polar coordinate system r, θ, φ while the coordinates of the other four atoms are $r, 0, 0$; $r', \theta, 0$; $r', \theta, \frac{2}{3}\pi$; $r', \theta, \frac{4}{3}\pi$. In order to make our calculations applicable to CH₃X, we shall not necessarily assume that the atom a on the polar (z) axis is identical with the other three atoms held by the C atom, which we may take to be identical H atoms. As before, resonance integrals connected with the C–X bond are denoted by the letter P . Only in the particular case CH₄ shall we suppose $r = r'$. The regular tetrahedron is included as the special case $\theta = \cos^{-1}(-\frac{1}{3}) = 109.5^\circ$. The choice of wave functions and factorization are indicated by the following scheme:

$$\begin{aligned} & [\psi(2s), \psi(2\sigma_z), \psi_a, 3^{-\frac{1}{2}}(\psi_b + \psi_c + \psi_d)], \\ & [\psi(2\sigma_x), (\frac{2}{3})^{\frac{1}{2}}(\psi_b - \frac{1}{2}\psi_c - \frac{1}{2}\psi_d)], \quad [\psi(2\sigma_y), 2^{-\frac{1}{2}}(\psi_c - \psi_d)] \end{aligned} \quad (29)$$

and the bonding roots are

$$W_1 = W_2 = F(\frac{3}{4}Q_\sigma^2 \sin^2 \theta), \quad W_\pm = G_\pm(\frac{1}{2}P_\sigma^2 + \frac{3}{2}Q_\sigma^2 \cos^2 \theta + \frac{1}{2}P_s^2 + \frac{3}{2}Q_s^2; 3^{\frac{1}{2}} \cos \theta P_s Q_\sigma - 3^{\frac{1}{2}} P_\sigma Q_s) \quad (30)$$

with notation as in (26). One verifies by differentiation with respect to θ , that with (30) and the specialization $P = Q$ appropriate to CH₄, the root sum (27) has a minimum at the tetrahedral angle $\theta = 109.5^\circ$.

4. CASE $W^H - W_s^C$ BUT NOT $W^H - W_p^C$ LARGE COMPARED TO Q IN HUND-MULLIKEN METHOD

This case is a mixture of those in Sections 2 and 3, and is perhaps a better approximation than either to reality since the s - p separation in C is not small, and is probably greater than $W^H - W_p^C$. Here the $2s$ state of C is assumed to lie much deeper than either W^H or the $2p$ states of C. One twice-filled root of the secular determinant is then substantially a carbon $2s$ level; in other words by far the largest coefficient in the corresponding linear combination of wave functions is that of the carbon $2s$ one. If $W^H = W_p^C$, and if we neglect the interaction between s and p bonds, which is small in the present case, the six electrons not absorbed by $2s$ will in the mean be distributed equally between the totality of the four H atoms and the three p levels of C. Thus the $2s$ but not the $2p$ part of the problem will be amenable to the near-ionic approximation and the molecule will be substantially of the structure $C^+(H_4)^-$, except insofar as $W^H \neq W_p^C$. As a first approximation, the bonding effect of the $2s$ wave functions of C can be neglected, since this could be treated by proper adaptation of the "near-ionic" perturbation method of Section 2, and so will give rise only to terms of order $Q^2/h\nu(H; C_s)$ and higher. Such terms are small compared to the p bonding energies, which are of the order Q . A further, less important effect enhancing the importance of the p as compared to the s bonds is the fact that the $2s$ wave functions represent firmer binding in the C atom and so less "overlapping"

of the H atoms than do the $2p$ functions, thus making $Q_s > Q_p$. As a first approximation the bonding action of the $2p$ states may be treated by the method of Section 3 with $Q_s = P_s = 0$. There is now, to be sure, the difference that there are six rather than eight electrons in the secular problem, since two electrons have been absorbed and isolated by the deep $2s$ level. This difference, however, is immaterial inasmuch as in each example of Section 3 one root W_- becomes nonbonding when $Q_s = P_s = 0$, and we have merely to eject $2W_-$, which is now independent of angular arrangements, from the sum (27). The analysis of Section 3 can thus be used and shows that the two most stable models are the regular tetrahedron and the 54.7° pyramid. We saw that with $Q_s = P_s = 0$ these two models were on a par. However, correction for the fact that the s - p interplay (not to mention H-H repulsions) is not completely negligible will make the tetrahedron have the lower energy of the two. This could be demonstrated by introducing the interaction between the s and p bonds as a perturbation of order $Q^2/h\nu(H; C_s)$ and above. We shall, however, omit the proof, since most readers will probably consider the result sufficiently obvious in view of the fact that the present case is intermediate between the cases of Sections 2 and 3, and in both these cases we showed that the s - p interplay favored the regular tetrahedron over the 54.7° pyramid.

5. CALCULATION BY HEITLER-LONDON-PAULING-SLATER METHOD OF ELECTRON PAIRS

It unfortunately appears impossible without undue labor to make calculations by the Heitler-London method for anything like as great a variety of arrangements as in the preceding Hund-Mulliken procedure. The difficulty with the H-L method is that the secular determinant is of degree 14 and hence is too complicated for explicit solution without either the assumption of electron pairing, wherein the members of a pair have their spins anti-parallel, or else the Heitler-Rumer assumptions to be discussed in Part III. A pair, of course, represents a saturated chemical bond, and the total wave function is invariant when the purely orbital coordinates of the members of a pair are permuted. The qualitative idea of electron pairs as units of chemical structure is due originally to Lewis,¹⁰ who proposed it before the days of quantum mechanics and hence without the wave-mechanical interpretation.

Since the carbon p wave functions are proportional to x, y, z , and so transform like vectors, the most general real linear combination of the carbon s and p wave functions is of the form

¹⁰ G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chem. Cat. Co., 1923.

$$\psi_i^C = \alpha_i \psi(2s) + \beta_i \psi(2\sigma_i). \quad (31)$$

Clearly the H atom to be paired with this wave function should be located on the axis of quantization C- i of the p term in (31), as then the overlapping is the largest possible. This concept is the basic idea of the Slater-Pauling theory of directed valence. Unfortunately it is impossible to construct four wave functions of the form (31) which are normalized and mutually orthogonal and which project respectively in four *arbitrary* directions $i = a, b, c, d$. This is true since the requirements of normalization and orthogonality yield 10 relations while there are only eight coefficients α_1, \dots, β_4 at our disposal. The need of orthogonality is vital, since two electrons with non-orthogonal wave functions have a constraint on the angle between their spins and so are not free to make valence bonds with electrons in other atoms. (The easiest way of seeing this is to pass to the limiting case in which the non-orthogonal functions are identical: the spins associated with the two functions are then anti-parallel and the valences of the two electrons are hence saturated intra-atomically. Abandonment of normalization would not increase the number of allowable directions, as it merely would introduce a trivial constant factor.)

The only models, other than highly unsymmetrical ones, for which it appears possible to construct wave functions with the necessary directive and orthogonality properties are those of class (c), Section 3, for which $\cot^2 \theta \leq \frac{1}{2}$ and those of class (a) for which

$$\cos 2\omega \cos 2\omega' = \sin \omega^2 \sin \omega'^2 \quad \text{with} \quad |\omega'| \leq \frac{1}{2}\pi, |\omega| \leq \frac{1}{2}\pi, \quad \omega'/\omega < 0. \quad (32)$$

The highly unsymmetrical models presumably would be needed for say CWXYZ, but are quite unlikely for CH₄, CH₃X, or CH₂X₂, so that we shall not consider them. For class (c) the proper set of orthogonal functions is

$$\psi_a^C = (1 - 2 \cot^2 \theta)^{\frac{1}{2}} \psi(2\sigma_a) - 2^{\frac{1}{2}} \cot \theta \psi(2s), \quad (33)$$

$$\psi_j^C = (\frac{2}{3} \operatorname{cosec}^2 \theta)^{\frac{1}{2}} \psi(2\sigma_j) + (\frac{1}{3} - \frac{2}{3} \cot^2 \theta)^{\frac{1}{2}} \psi(2s) \quad (j = b, c, d),$$

while for (a)

$$\psi_j^C = (1 + \cos 2\omega)^{-\frac{1}{2}} [\psi(2\sigma_j) + (\cos 2\omega)^{\frac{1}{2}} \psi(2s)] \quad (j = a, b), \quad (34)$$

$$\psi_k^C = (1 + \cos 2\omega')^{-\frac{1}{2}} [\psi(2\sigma_j) + (\cos 2\omega')^{\frac{1}{2}} \psi(2s)] \quad (j = c, d)$$

with notation as in Section 3. The orthogonality is readily established with the aid of the relation $\int \int \int \psi(2\sigma_i) \psi(2\sigma_j) dv = \cos(i, j)$ after the cosine is expressed in terms of θ or of ω, ω' with the restriction (32). When $\cos \theta = -\frac{1}{3}$ or $\tan \omega = -\tan \omega' = 2^{-\frac{1}{2}}$ the models reduce to the regular tetrahedron, and then (33) or (34) become the usual Slater-Pauling sp^3 functions.

Because of the inability to find many symmetrical models which permit natural C-H paired bonds, it is in a certain sense impossible to demonstrate in completely quantitative fashion that the tetrahedral model is the most stable in the Heitler-London method. Pauling's criteria of "maximum overlapping," to be sure, make this model very reasonable indeed, as he has shown.¹¹ Quite irrespective of this fact, the mere inability to "localize" the bonds with symmetrical models other than those cited must be regarded as strong evidence that other models do not fit naturally into the scheme of things and so yield less bonding energy.¹²

¹¹ L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

¹² Essentially this point has also been noted in an interesting paper by R. Hultgren, Phys. Rev. **40**, 891 (1932). His wave functions are more general than ours in that d states are admitted to the linear combinations, but less general in that all the functions are supposed to have the same hybridization ratio. Eqs. (33) and (34) each involve two such ratios. Four would be required for CWXYZ. Presumably the number of different ratios

required is the same as the number of different kinds of atoms attached by C. If this is the case then all the C wave functions of CH₄ have the same ratio and the tetrahedral model follows uniquely simply from the requirement of orthogonality. Nevertheless it seems of some interest for us to verify that introduction of two unequal ratios in place of one raises the value of (35) in CH₄.

There is no difficulty in showing that for CH_4 the regular tetrahedron has the least energy of all the models of class (c) with $\cot^2 \theta \leq \frac{1}{2}$ or of class (a) obeying (32). Under the assumption of perfect pairing and neglect of everything but exchange terms the molecular energy is

$$W = \sum_i J_{ii} - \frac{1}{2} \sum_{i, j(i \neq j)} J_{ij} + \text{constant} \quad (35)$$

where J_{ij} is the exchange integral for the combination ψ_i^H, ψ_j^C . Eq. (35) is the embodiment of the well-known results that the exchange energy associated with a saturated bond a, b , is $+J_{ab}$ and that this energy is $-\frac{1}{2}J_{bc}$ between a member b of a pair and any other electron c not its mate in the pair.¹³ As usual, we shall neglect all H-H forces or H-H overlapping. By means of the transformation relation (6) it is possible to express (35) in terms of θ or ω, ω' and the essentially diatomic integrals

$$N_{kl} = - \int \int \int \int \int \psi_H(1) \psi_k(2) \mathbf{H} \psi_l(1) \psi_H(2) dv_1 dv_2 \quad (k, l = 2s, 2p\sigma, \text{ or } 2p\pi \text{ of C}). \quad (36)$$

The minus sign has been inserted in order to make most of the N_{kl} positive. Except for sign, the expressions (36) are exchange integrals when $k=l$. The value of $N_{\sigma\pi}$ is zero. It is readily shown, from band spectrum data or by approximate calculation, that $N_{\sigma\sigma}$ and N_{ss} are both positive, while $N_{\pi\pi}$ is negative.^{13a}

In the case of (33) we find

$$W = -\frac{5}{2}N_{\sigma\sigma} + 4N_{\pi\pi} + \frac{1}{2}N_{ss} + 2^{\frac{1}{2}}(1 - 2\cot^2 \theta)^{\frac{1}{2}}(-3\operatorname{cosec} \theta + 3\cot \theta)N_{\sigma s} - (\mathfrak{N}_{\sigma\sigma} - N_{\sigma s})(1 - 3\cot^2 \theta) \\ + (\mathfrak{N}_{ss} - N_{ss})(\frac{1}{2} - 3\cot^2 \theta) + \mathfrak{N}_{\pi\pi} - N_{\pi\pi} + 2^{\frac{1}{2}}(3\mathfrak{N}_{\sigma s} - 3N_{\sigma s})\cot \theta(1 - 2\cot^2 \theta)^{\frac{1}{2}}. \quad (37)$$

In order to make our calculations adaptable to CH_3X or CHX_3 , we have allowed atom a in Fig. 2, Section 3, to be different from the other three atoms b, c, d held by C, and so yield values of the integrals (36) which may be different than those for the other bonds and which are distinguished by being printed in German type. Thus in CH_3X , \mathfrak{N} denotes (36) with subscript X substituted for H, while $\mathfrak{N} = N$ in dealing with CH_4 . When one sets $\mathfrak{N} = N$, (37) depends on θ only in the terms proportional to N_{ss} , which are peculiar to s - p hybridization. One verifies by differentiation with respect to θ that then if $N_{ss} > 0$, $\mathfrak{N} = N$, Eq. (37) has a minimum at $\cos \theta = -\frac{1}{3}$, giving us the regular tetrahedron. The assumption $N_{ss} > 0$ is correct, for the charge cloud of a $2p\sigma$ wave function is dumb-bell shaped with opposite signs for $\psi(2\sigma)$ on the two ends, so that the sign of N_{ss} is dependent on which end of the dumb-bell one places the H atom. To obtain favorable bonding one must choose the end for which N_{ss} is positive, as is obvious from "overlapping" considerations or from the fact that the minimum of (37) is higher with $N_{ss} < 0$ than with $N_{ss} > 0$. When $\cot^2 \theta = \frac{1}{2}$ the three axes C- b , C- c , C- d are mutually orthogonal; there is then no hybridization and atom a is held only by an s bond; under these conditions it is not necessary to restrict atom a to the axis $\theta=0$, as it is easily shown that the energy is independent of the alignment of C- a relative to the three orthogonal axes C- b , C- c , C- d .

In the case of models of class (a) with the restriction (32) one finds that (35) becomes

$$W = -\frac{5}{2}N_{\sigma\sigma} + 4N_{\pi\pi} + \frac{1}{2}N_{ss} + \mathfrak{N}_{\sigma s}g(\omega', \omega) + N_{\sigma s}g(\omega, \omega') + (\mathfrak{N}_{ss} - N_{ss})[1 - 2f(\omega') + f(\omega)] \\ + (\mathfrak{N}_{\sigma\sigma} - N_{\sigma\sigma})[-2f(\omega) + \cos^2 2\omega f(\omega) + 2\sin^2 \omega \sin^2 \omega' f(\omega')] \\ + (\mathfrak{N}_{\pi\pi} - N_{\pi\pi})[\sin^2 2\omega f(\omega) + 2f(\omega')(1 - \sin^2 \omega \sin^2 \omega')] \quad (38)$$

with

$$f(\omega) = (1 + \cos 2\omega)^{-1}, \quad g(\omega', \omega) = -2(\cos 2\omega)^{\frac{1}{2}}[1 + f(\omega)] + 4(\cos 2\omega')^{\frac{1}{2}}f(\omega') \sin \omega \sin \omega'.$$

In order to make the calculations applicable to CH_2X_2 , we have allowed atoms a and b to be different

¹³ Cf. for instance J. C. Slater, Phys. Rev. **34**, 1307 (1929). His K is our J .

^{13a} See, for example the table given by Coolidge, Phys. Rev. **42**, 198 (1932).

from c , d , and so give rise to integrals \mathfrak{N} rather than N . As before, when we make the specialization $\mathfrak{N} = N$ appropriate to CH₄, a dependence of W on angle exists only in virtue of the terms involving N_{ss} . That (38) then has an extremum at the tetrahedral configuration is most easily demonstrated by a symmetry argument: *viz.*, when $\mathfrak{N} = N$ the expression (38), regarded as a function of ω , ω' , is symmetric about the line $\omega = -\omega'$ in the ω , ω' plane, and so will have an extremum along the curve (32) at the intersection of this curve with this line. The coordinates of the intersection are $\omega = -\omega' = \tan^{-1} 2^{-\frac{1}{2}}$, the tetrahedral values.

Slater¹⁴ has remarked that the Heitler-London and Hund-Mulliken methods are equivalent in the last analysis as they reach the same goal when pushed to final accuracy by inclusion of higher approximations (notably addition of polar terms in the H-L and antisymmetrization and inclusion of electron repulsion in the H-M). Of course what Slater says is ultimately true, but when one stops at the first approximation the resemblance between the two methods is very remote in polyatomic molecules. The superiority of the tetrahedron over other molecules which could be calculated was shown above to owe its existence in the H-L-P-S method entirely to the integral N_{ss} which represents the interplay between the s and p bonds and epitomizes the s - p hybridization. On the other hand in the H-M method the p bonds alone were sufficient to insure the superiority of the tetrahedron over all other models with the single exception of the 54.7° pyramid. The tetrahedron was superior to this pyramid because, unlike the latter, the tetrahedron involved no s - p hybridization at all!

6. CONFIGURATION OF SOME OTHER MOLECULES, NOTABLY CHX₃, CH₂X₂, CWXYZ, BeX₂, OX₂

The "near-ionic" perturbation calculation given in Section 2 can be extended without particular difficulty to the case in which the central atom is not necessarily carbon, and attaches any number of other atoms, provided only that in all there are precisely eight electrons available for the bonding. There are, of course, in general, plenty of electrons of lower principal quantum number, but these are treated as nonbonding. In place of (18) one finds

$$X = \alpha' + \sum_i \sum_j \beta_{ij} (\mathbf{i} \cdot \mathbf{j}) + \sum_i \sum_j \gamma_{ij} (\mathbf{i} \cdot \mathbf{j})^2 \quad (39)$$

where \mathbf{i} , \mathbf{j} are unit vectors along the axes C- i , C- j and where β_{ij} , γ_{ij} are defined nearly as in (19), (20) except that they are symmetrical in i , j . For instance

$$D^i \tau_s^i Q_s^j \tau_p^j Q_p^i + D^j \tau_s^j Q_s^i \tau_p^i Q_p^j$$

replaces $2\tau_s \tau_p D Q_s Q_p$ in the first term of (19). Superscripts are, of course, now added to indicate that the integrals (3) have different values for a bond involving atom i than one involving atom j , and instead of (14) one has $1/\tau_k^i = W^i + B_i - W_k^c$ with W^c , W^i denoting respectively the unperturbed energy of the central atom and that of atom j . Our discussion does not apply to double or multiple bonds, and so

¹⁴ J. C. Slater, Phys. Rev. **41**, 255 (1932).

we must suppose that atoms i , j , \dots each have only one solution of Schrödinger's equation which is important for bonding.

Eq. (39) throws considerable light on molecular arrangement. When we remember that the β_{ij} and γ_{ij} are positive and that the terms γ_{ij} are due purely to the bonding by the carbon p wave functions, while the β_{ij} are due to the interplay between the s and p bonding actions (cf. Eqs. (19, 20)), we see that the axes C- i , C- j joining any two atoms i , j to the central atom seek to align themselves at right angles to each other if the p wave functions alone are important for bonding. However, if the s - p interplay is appreciable, the angle i -C- j will tend to increase towards 180°, as $\mathbf{i} \cdot \mathbf{j}$ has its minimum value at 180° as compared with 90° for $(\mathbf{i} \cdot \mathbf{j})^2$ ($i \neq j$). Of course it is impossible for all bonds to be mutually at right angles if more than three atoms are attached to the central atom, and in CH₄ the tetrahedral arrangement represents, so to speak, the nearest the bonds can come to such angles. In molecules in which the attached atoms are not all alike, the values of β_{ij} , γ_{ij} will be greater for certain pairs of bonds than for others. These pairs will tend to set themselves at the optimum angles even though this involves making some of the other axes inclined to each other at

unfavorable angles. For instance, consider a hypothetical ideal case in which γ_{12} , γ_{13} , γ_{23} , γ_{14} , γ_{24} are infinitely large compared with γ_{34} and with any β . Then atoms 1, 2, 3 would be located along three mutually orthogonal axes with origin at the central atom, and atom 4 would be located on the axis C-3 (probably on the opposite side of C from 3) though this leads to the worst possible value of the term involving β_{12} , β_{13} , β_{23} , β_{14} , β_{24} , γ_{34} . In short, the most important pairs of bonds are greedy and tend to assume the most favorable angles at the expense of their fellows. Hence the correct structure when the carbon atom attaches four atoms not all of the same type may be described as a distorted tetrahedron. (Strictly speaking the model is still a tetrahedron, but not a regular one. We insert the adjective "distorted" because we use the word tetrahedron usually only in connection with the regular type.) One can easily see that pyramidal models, where all four attached atoms are on one side of a plane containing the central atom, and plane models will yield higher values of (39) than a properly chosen distorted tetrahedron. Some particular molecules are the following:

CH_2X_2 . Here the model will be one of type (a), shown in Fig. 1, Section 3, but with in general $-\omega' \neq \omega \neq \tan^{-1} 2^{-\frac{1}{2}}$ unless the C-H and C-X bonds are very nearly equal. If P_s is large compared with P_s , Q_s , and Q_s , the angle ω will be nearly 45° and ω' nearly 0.

CH_3X or CHX_3 . The appropriate model is one of type (c), shown in Fig. 2, with the tetrahedral value 109.5° for θ in CH_3X only if $\beta_{\text{HX}} = \beta_{\text{HH}}$, $\gamma_{\text{HX}} = \gamma_{\text{HH}}$. If $\gamma_{\text{HH}} \gg \gamma_{\text{HX}}$ and $\gamma \gg \beta$ then θ will be nearly $\tan^{-1} 2^{-\frac{1}{2}}$, and the three C-H axes will be nearly at right angles. If $\gamma_{\text{HX}} \gg \gamma_{\text{HH}}$ and $\gamma \gg \beta$ the value of θ will be nearly 90° , and the plane of the three H atoms will almost contain the central atom.

NH_3 . For mathematical purposes the ammonia molecule is equivalent to a special case of CH_3X in which atom X is held by a bond of zero intensity (i.e., $\beta_{\text{HX}} = \gamma_{\text{HX}} = 0$) and so is effectively non-existent. As already stated, the fact that the central atom is N rather than C is immaterial for formal considerations so long as there are precisely eight electrons. The value of θ is found by minimization of (39) to be $\cos^{-1} [(\gamma - \beta)/3\gamma]^{\frac{1}{2}}$

if $\beta \leq \gamma$ and 90° if $\beta \geq \gamma$. Thus θ is bounded by 54.7° and 90° . If $\beta = 0$ is a good approximation, θ will be 54.7° and the three NH axes will be inclined at 90° . If the s - p interplay β were the most important thing, which is surely not so, the angle θ would be 90° , and the model would be coplanar. Actually, Lueg and Hedfeld determine θ from band spectra to be 73° , while Dennison and Uhlenbeck find $\theta = 68^\circ$ by a different method but likewise based in part on band spectra.¹⁵ Either of these values is within the critical range predicted by the theory.

CWXYZ. Here, naturally, none of the angles should in general be equal.

All the above conclusions are seemingly based on (39) and hence on a "near-ionic" approximation which is not usually an especially close one. To remove this objection we have therefore given another method of approximation for CH_2X_2 and CH_3X (or CHX_3) in Section 3, which applies under different conditions, *viz.*, items (I), (II), (III) of Section 3, and the assumption $W^H = W^X$. These other conditions are more likely to be met when the molecule is primarily nonpolar, and agree with (39) in predicting that the angles cease to be exactly tetrahedral in CH_2X_2 and CH_3X or CHX_3 , as (27) ceases to have a minimum at $-\omega' = \omega = \tan^{-1} 2^{-\frac{1}{2}}$ (with Eqs. (24-25)) or at $\cos \theta = -\frac{1}{3}$ (with Eqs. (30)) when $P \neq Q$. The distorted tetrahedra were again found in Section 3 to be better than the corresponding pyramidal and plane models. Similar results can also be obtained with the intermediate method of Section 4, which uses the near-ionic approximation only for the $2s$ part of the problem. The same conclusions thus hold in our three methods of approximation based on the Hund-Mulliken viewpoint. Additional confidence is supplied by the fact that in the Heitler-London-Pauling-Slater method the tetrahedral angles disappear as soon as the calculations are adapted to CH_2X_2 , CH_3X or CHX_3 , since (37) and (38) cease to have minima at exactly the above values of θ or ω , ω' if $\mathfrak{N} \neq N$.

¹⁵ Lueg and Hedfeld, *Zeits. f. Physik* **75**, 559 (1932); D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932) or N. Rosen and P. M. Morse, *ibid.* **42**, 210 (1932); these determinations are presumably more accurate than older spectroscopic work which gave values of θ in the neighborhood of 60° .

That the tetrahedral angles are not preserved in CH₂X₂ and CHX₃ is in agreement with x-ray data¹⁶ which reveal the following values for the angles between the two C—Cl axes: CHCl₃, 116.4°; CH₂Cl₂, 123.8°, whereas the value disclosed for CCl₄ is 109.5°, exactly the tetrahedral value. The deviations from 109.5° in CHCl₃ and CH₂Cl₂ are in the direction to be expected from our theory. Namely, it is known experimentally that C—H bonds (94 kg cal./g mol.) are firmer than C—Cl ones (72 kg cal./g mol.). Hence if the *p*-bonding effects overshadow the *s* ones, as they doubtless do, both the H—M and H—L—P—S methods predict that the angles H—C—H and Cl—C—H will become nearer 90° than in the regular tetrahedron, but this entails making the angle Cl—C—Cl greater than 109.5°. It is clear that the deviation should be smaller in CHCl₃ than in CH₂Cl₂ since in the latter there are more H—C—H or H—C—Cl angles, causing more overpowering of Cl—C—Cl directional valency. If the latter and *s*-bonding were negligible, the angle Cl—C—Cl would be 120° in CHCl₃ and 180° in CH₂Cl₂.

The same general conclusions on NH₃ as before with (39) are also obtained if one uses the other methods. With the method of Section 3 one minimizes (27) with *P*=0 in (30). The resulting value of *θ* is given by

$$\cos^2 \theta = \frac{1}{3} - \frac{2}{3}(Q_s^2/Q_\sigma^2) \quad \text{if } Q_s^2 \leq \frac{1}{2}Q_\sigma^2 \quad (40)$$

and $\theta = \pi$ otherwise. The method of Section 4 predicts θ to be slightly greater than $54.7^\circ = \cos^{-1}(\frac{1}{3})^{\frac{1}{2}}$. With the Slater-Pauling method one uses the wave functions (33) but assigns two electrons to ψ_{Ca} since nitrogen has five electrons. The resulting expression for the energy is (37) with *N*=0 but augmented by a contribution

$$\begin{aligned} & \frac{2}{3}(1 - 2 \cot^2 \theta) \cos^2 \theta N_{\sigma\sigma} \\ & - 3 \times 2^{\frac{1}{2}}(1 - 2 \cot^2 \theta)^{\frac{1}{2}} \cot \theta \cos \theta N_{ss} \\ & + 2 \cot^2 \theta N_{ss} + (1 - 2 \cot^2 \theta)(W_p - W_s) \end{aligned} \quad (41)$$

due to the fifth electron. The minimum can only be found numerically, but is located at a somewhat greater angle than 54.7°. The term proportional to *W_p*—*W_s* has been inserted in (41) to make some allowance for the influence of the finite *s*-*p* separation of the central atom upon the variation of the energy with angle. That the *s*-*p* separation does give an angular term is obvious from the fact that with the wave functions now being used, the N atom is in the configuration *s*²*p*³ at $\theta = 54.7^\circ$ and in the configuration *sp*⁴ at $\theta = 90^\circ$, so that the internal energy of the N atom

is raised in passing from 54.7° to 90°. When we use notation such as *sp*⁴ here we do not mean that individual electrons are of the 2*s* or 2*p* types but that the sum of the squares of the 2*s* and 2*p* parts of the individual functions add to 1 and 4, respectively. The specific form of the term proportional to *W_p*—*W_s* in (41) is obtained by examination of the sum of the squares of the 2*s* and 2*p* parts for various angles. The corresponding term was omitted in our formulas (39), (38) for CH₄, CH₂X₂, CH₃X; its inclusion would merely introduce an additive constant *W_p*—*W_s* independent of angle, inasmuch as our models of these molecules always involved the aggregate configuration *sp*³ whereas the normal state of C is *s*²*p*². It must be cautioned that even with such additions we make no allowance for the dependence of the energy of the central atom on *L* and *S* in distinction from on the individual *l*'s. The correction for the *L*, *S* structure will be studied in Part III.

In the cases of the molecules CH₂X₂, CH₃X, or CHX₃, attempts could be made to calculate quantitatively the deviations of the angles from the tetrahedral values by finding what values of ω , ω' or θ minimize (27), (37), (38), and (39), and so determine the values of the constants (3) or (36) which will yield agreement with experiment. However, this procedure involves algebraic difficulties not encountered in NH₃, where simple formulas for θ were derived, and is promising only in a rough way, since, as in NH₃, the precise minimizing angles will depend on the type of approximation used. For instance, the minimum of (27) with (24–25) does not yield values of ω , ω' conforming to (32). If in particular, as in the method of Section 4, one neglects all *s* bonding effects by setting *P_s*=*Q_s*=0 in (24–25) the minimum of (27) is easily found and comes at

$$\begin{aligned} P_\sigma^2 \cos^2 \omega = Q_\sigma^2 \cos^2 \omega' = \frac{1}{3}(P_\sigma^2 + Q_\sigma^2) & \quad \text{if } \frac{1}{2} \leq P_\sigma^2/Q_\sigma^2 \leq 2; \\ \omega = 45^\circ, \quad \omega' = 0 & \quad \text{if } P_\sigma^2/Q_\sigma^2 \geq 2; \\ \omega = 0, \quad \omega' = 45^\circ & \quad \text{if } P_\sigma^2/Q_\sigma^2 \leq \frac{1}{2}. \end{aligned}$$

This is for CH₂X₂; for CH₃X (Eqs. (30) in (27)) the corresponding values are

$$\begin{aligned} 9Q_\sigma^2 \sin^2 \theta = 6Q_\sigma^2 + 2P_\sigma^2 & \quad \text{if } P_\sigma^2/Q_\sigma^2 \leq \frac{3}{2}; \\ \theta = 90^\circ & \quad \text{if } P_\sigma^2/Q_\sigma^2 \geq \frac{3}{2}. \end{aligned}$$

(If instead, (39) is used, the neglect of *s* bonding means $\beta=0$, and the minimizing angles for CH₃X, for instance, are the same as those just given except that γ_{HX} , γ_{HH} replace *P_s*², *Q_s*². If the approximations (I), (II), (III) of Section 3 are made, γ_{HH}/γ_{HX} reduces to *Q_s*²/*P_s*², as should be.) The fact that $\pi - 2\omega = \theta = 90^\circ$ if $P_\sigma^2 \gg Q_\sigma^2$ is, of course, an illustration of the tendency of the most important bond angles to become 90° if the *p* bonding effects predominate.

At this point we may mention a modification which we believe should be made in some of the statements in Pauling's important paper.¹¹ It conveys the impression that even when there are only two atoms attached the tetrahedral angle 109.5° is the best possible one, whereas we have already intimated that this angle is characteristic

¹⁶ L. Bewilogua, Phys. Zeits. 32, 265 (1931); P. Debye, Zeits. f. Electrochemie 36, 612 (1930).

only of four equivalent attached atoms, and that two sole (or the two firmest out of many) attached atoms tend to set their bonding axes at an angle between 90° and 180° whose precise magnitude depends on the relative importance of pure p -bonding and s - p interplay. This can be seen not merely from the near-ionic approximation (39) but also with the two other methods of approximation for the Hund-Mulliken theory given in Sections 3-4, or with the Heitler-London-Pauling-Slater method. The assumptions of Section 4 largely suppress s bonding and so make the valence angle in CX_2 nearly 90° . To calculate this angle with the procedure of Section 3 one has only to set $Q=0$ in (24-25) since CX_2 is formally equivalent to CH_2X_2 with the C-H bonds made infinitely small. The minimum of (27) then comes at $P_\sigma^2 \cos 2\omega = P_s^2$ if $P_s \leq P_\sigma$ and at $2\omega = 180^\circ$ if $P_s \geq P_\sigma$; whether there are four, eight or some intermediate number of electrons is immaterial in this particular case, since two of the roots (24-25) are nonbonding when $Q=0$, making any electrons beyond four superfluous. Similarly in the Heitler-London-Pauling-Slater method, the behavior of CX_2H_2 in the limiting case that the C-H bonds are very weak is given by Eq. (38) if one sets $N=0$ and remembers that ω' is a function of ω given by (36). An explicit formula for the value of the angle $\pi-2\omega$ between the two C-X axes which then minimizes (38) cannot be given because of algebraic difficulties, but the terms of (38) which involve $\mathfrak{N}_{\sigma\sigma}$ have their minimum at $2\omega=90^\circ$ and those which involve \mathfrak{N}_{ss} or \mathfrak{N}_{ss} , their minimum at $\omega=0$, making it clear that the minimum will in general come at a value of $\pi-2\omega$ intermediate between 90° and 180° whose precise magnitude depends on the relative sizes of $\mathfrak{N}_{\sigma\sigma}$, \mathfrak{N}_{ss} , and $\mathfrak{N}_{\pi\pi}$. Terms containing $\mathfrak{N}_{\pi\pi}$ are unimportant because $\mathfrak{N}_{\pi\pi}$ is small. The reason why Pauling appeared to obtain 109.5° quite generally is that he used semiquantitative criteria of "overlapping" rather than the more exact Eq. (35) and assumed a particular value of the relative intensity of the s and p bonds. Of course 109.5° is in the critical range 90° - 180° , and may not be far removed from the actual best angle since the p bonding effects favoring 90° are probably the most important factor. In fact, according to Mecke,¹⁷ the actual angle in H_2O is between 103° and 106° .

CX_2 , BeX_2 , OX_2 . We must mention that when the H atoms are completely removed from CH_2X_2 , the wave functions appropriate to the third and fourth electrons of C are probably not correctly given by ψ_c^C, ψ_d^C in (34). When the H atoms are missing, these two electrons have no attached atoms with which to be paired, and so need not have equal hybridization ratios as assumed in (34). Also they may even be in the same state, with their spins mutually paired. Another possible choice for the third and fourth wave functions in place of those in (34) is¹⁸

¹⁷ R. Mecke and W. Baumann, Phys. Zeits. 33, 833ff. (1932).

¹⁸ It seems quite probable that the functions (42) and first two of (34) are the proper wave functions for C double bonds, rather than the tetrahedral sp^3 functions assumed by Pauling and Slater. At any rate it is certain

$$\psi_c' = \psi(2\sigma_y),$$

$$\psi_d' = [k(\omega)]^{\frac{1}{2}} [-\operatorname{cosec} \omega (\cos 2\omega)^{\frac{1}{2}} \psi(2\sigma_z) + \psi(2s)] \quad (42)$$

with $k(\omega) = 1/(\operatorname{cosec}^2 \omega \cos 2\omega + 1)$. Here the y axis has been taken perpendicular to the plane of X-C-X, and the z axis bisects the angle X-C-X. The exchange energy between the third and fourth electrons and the X atoms is minimized by placing both these electrons in the state ψ_c' . The total energy is¹⁹ then

$$W = W' - 2\mathfrak{N}_{ss} + 2\mathfrak{N}_{\pi\pi} + [1 + k(\omega)][W_p - W_s],$$

where W' denotes the value of the expression (38) when one sets $N=0$ and strikes out all terms involving $f(\omega')$ (including those through $g(\omega', \omega)$). More likely, however, the third and fourth electrons both decide to settle in ψ_d' , as this makes the carbon configuration nearly s^2p^2 rather than nearly p^4 if 2ω is nearly 90° . The total bonding energy is then

$$W = W' - 2\mathfrak{N}_{ss} + [1 - k(\omega)][W_p - W_s] + 2k(\omega)[\cos 2\omega(\mathfrak{N}_{\sigma\sigma} + \cot^2 \omega \mathfrak{N}_{\pi\pi}) - 2(\cos 2\omega)^{\frac{1}{2}} \mathfrak{N}_{ss} + \mathfrak{N}_{ss}]. \quad (43)$$

If the third and fourth electrons are entirely missing, as in BeX_2 , this energy is $W' - 2\mathfrak{N}_{ss} + [1 + k(\omega)][W_p - W_c]$. If there are six electrons in the central atom, as in H_2O or OX_2 , there are probably two electrons each to the states ψ_c', ψ_d' , and the energy is the expression (43) augmented by $2\mathfrak{N}_{\pi\pi}$. In all cases the first two electrons are assigned one each to the first two states of (34). None of these modifications change the critical region in which the best value of the angle X-C-X is located.

The foregoing discussion of CX_2 , BeX_2 or OX_2 presupposes the two attached atoms to be identical. Calculations can also be made for the case that they are not equal, but we shall not give them, as they yield nothing qualitatively new regarding the favored angles. When the two attached atoms are not identical and hence not held by bonds of equal strength, one can no longer assume that they are held by pairing with electrons of the central

that the s - p hybridization ratios for double bonds will not be the same as for CH_4 . We suggest this combination of (42) with (34) because it gives three directed coplanar valences, viz., those corresponding to $\psi_a^C, \psi_b^C, \psi_d'$. The C-C bond is here to be located along the z axis, so as to bisect X-C-X. This subject of double bonds will be discussed more fully in a paper by W. G. Penney.

¹⁹ This and shortly following formulas for the bonding energy are obtained by application of (35) and (6), with allowance for the finite s - p separation in the same fashion as in connection with (41). The addition of $-2\mathfrak{N}_{ss}$ and the omission of $f(\omega')$ are consequences of the fact that in (38) those terms containing $\mathfrak{N}_{\sigma\sigma}, \mathfrak{N}_{\sigma s}, \mathfrak{N}_{\pi\pi}$ which arise from interaction of the third and fourth electrons of C with X_2 , are proportional to $f(\omega')$, while the corresponding terms containing \mathfrak{N}_{ss} are proportional to $1-f(\omega')$. Such terms must be dropped and new terms added because of the substitution of new wave functions in place of the third and fourth of (34).

atom which are represented by the first and second wave functions of Eq. (34). Instead the s - p hybridization ratios appropriate to the two bonds may be unequal, whereas (34) assumes equality.

7. STRUCTURE OF CH₃ AND CH₄⁺

All of our conclusions concerning the superiority of the tetrahedral or distorted tetrahedral arrangement are contingent upon there being eight electrons available for bonding, so that each of the four lowest roots of the secular Eq. (4) are filled twice. When there are only seven electrons available, as in CH₃ and CH₄⁺, the results are sometimes different. In the Hund-Mulliken method they depend upon the particular type of approximation which can be employed, and are as follows.

(i) The near-ionic approximation of Section 2, if allowable, predicts that the most stable models of both CH₃ and CH₄⁺ are plane provided the s state of C is beneath the p states by an energy difference large compared to the bonding energy. This can be seen from the following simple argument. In the near-ionic approximation, by far the largest part of the linear combination involved in the wave function is the carbon portion, so that it has a meaning to label the electrons $2s$, $2p$, etc., as in carbon. We showed in Section 2 that the energy of an eight electron system is invariant of the spatial arrangement to the approximation λ^2 . The bonding power of any individual electron, however, is of the order λ^2 . Hence the arrangements of the H atoms in CH₃ or CH₄⁺ which give the lowest energy will be the same as the arrangements of CH₃⁻ or CH₄ for which one $2p$ electron is removed most easily. The plane models possess this characteristic, since when all the H atoms are in the xy plane, the wave function $\psi(2\sigma_z)$ is nonbonding, except for the small term C_x in (3). Another way of saying the same thing is that with the seven electron configuration $2s^2 2\sigma_x^2 2\sigma_y^2 2\sigma_z$, increased overlapping is secured by placing all the H atoms in the xy plane, whereas this is clearly not true of the more symmetrical, eight-electron configuration $2s^2 2\sigma_x^2 2\sigma_y^2 2\sigma_z^2$.

(ii) The method of approximation of Section 3 is the same for CH₃ as NH₃. The determination of the best value of θ is unaffected by the fact that the energy is now $2W_1 + 2W_2 + 2W_+ + W_-$

instead of the sum (27) appropriate to an eight electron system, for W_- in (30) is a nonbonding root independent of θ , Q when $P=0$. Hence θ is given by (40) and the model is pyramidal if the s bonds are not too intense. On the other hand one finds with this method²⁰ that CH₄⁺ will be plane even if the s bonds are weak unless, also, Q_σ is sufficiently large compared to $W^H - W^C$.

(iii) With the method of approximation of Section 4, which is near ionic only for the $2s$ electrons, one concludes that the best models of CH₃ and CH₄⁺ are respectively models of type (c) with atom a missing and type (a) shown in Figs. 1, 2, Section 3, with the following values of θ or ω , ω'

$$\sin^2 \theta = \frac{8}{9} + \frac{1}{18Q_\sigma^2} (W^H - W_p^C)^2$$

if $(W^H - W_p^C)^2 < 2Q_\sigma^2$;

$$\cos^2 \omega = \cos^2 \omega' = \frac{8}{9} + \frac{1}{24Q_\sigma^2} (W^H - W_p^C)^2$$

if $(W^H - W_p^C)^2 < \frac{8}{3}Q_\sigma^2$;

$\theta = \pi$ or $\omega = \omega' = 0$ otherwise.

These results are obtained by minimizing²¹ $2W_1 + 2W_2 + W_+$ with $P_\sigma = P_s = Q_s = 0$ in (30) or with $P_\sigma = Q_\sigma$, $P_s = Q_s = 0$ in (24-25). The values $\theta = \pi$, $\omega = \omega' = 0$ represent plane models, and so we conclude that the spatial model is obtained by the procedure of Section 4 only if Q is sufficiently large compared with $W^H - W_p^C$.

To study CH₃ by the H-L-P-S method one uses the wave functions (33) and sets $\eta = 0$ in (37). The minimum of (37) then falls at²²

$$\cot^2 \theta = -\frac{1}{4} + \frac{3}{4} \frac{(N_{\sigma\sigma} - N_{ss})}{[4N_{\sigma\sigma}^2 + (N_{\sigma\sigma} - N_{ss})^2]^{\frac{1}{2}}}$$

if $N_{\sigma\sigma} \geq N_{ss} + 2^{-\frac{1}{2}}N_{ss}$ (44)

²⁰ For instance when $P=Q$, $\omega = \pm \omega'$, one finds $W_1 + 2W_2 < W_1' + 2W_2'$ only if $Q_\sigma^2 \cos^2 \omega > 3(W^H - W^C)^2$. Here W_1 , W_2 and W_1' , W_2' are levels for certain spatial and plane models as given in (24), (28). The remaining roots (25) are common to both models.

²¹ Only five electrons are involved in this sum because two are absorbed by the deep $2s$ states.

²² Eq. (44) would also give the best value of θ for NH₃ in the H-L-P-S method were it not for the fact that the energy of NH₃ involves the additional terms (41). The term proportional to $W_p - W_s$ in (41) will tend to make θ smaller in NH₃ than in CH₃.

and at $\theta = \pi$ otherwise. Hence this method predicts a pyramidal model only if $N_{\sigma\sigma}$ be sufficiently large compared with N_{ss} , $N_{\sigma s}$. The structure of CH_4^+ cannot be simply studied by the H-L-P-S procedure since no natural scheme of electron pairing is possible.

In view of all the above it is likely that CH_3 has a larger value of θ than does NH_3 , and may conceivably even be plane. One thing is particularly clear: there is no reason for CH_4^+ to be a regular tetrahedron like CH_4 . Instead CH_4^+ should be a flattened tetrahedron, i.e., a model of type (a), Section 3, with $\omega = -\omega'$, $|\omega| \leq 35.3^\circ$, and possibly $\omega = \omega' = 0$.

With all three variants (i-ii-iii) of the H-M method, one electron of CH_3 is more loosely bound than the rest. In fact, in (ii) one root is nonbonding, and in (i) nearly so. The H-L-P-S method also predicts one loose electron in CH_3 , viz., that electron of C which is unpaired to an H partner. Experimental confirmation is provided by the fact that the ionization potential 10.3 volts of CH_3 is lower than that, 14.5, of CH_4 , an observation due to Mulliken.²³ From qualitative consideration of the wave functions, he has, in fact, suggested a pyramidal model of CH_3 with one loosely held electron.

²³ R. S. Mulliken, Phys. Rev. **40**, 56 (1932).