

## On the Theory of the Structure of CH<sub>4</sub> and Related Molecules. Part I1

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## On the Theory of the Structure of $\text{CH}_4$ and Related Molecules. Part I<sup>1</sup>

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The primary purpose of the present series of papers is to give more explicit mathematical form to the theory of Mulliken and Hund, and in some instances to the alternative theories of Pauling and Slater and of Heitler and Rumer, for valence in carbon compounds. A critical comparison is given of the Slater-Pauling and Hund-Mulliken concepts of  $\text{CH}_4$ , which are based respectively on localized bonds ("electron pairs") with the Heitler-London method, and on one-electron wave functions (Mulliken's "orbitals") for a self-consistent field with tetrahedral symmetry. The H-M procedure avoids hybridization of the carbon  $2s$  and  $2p$  wave functions, but allows two (though never three or more) electrons to accumulate on one H atom, as well as up to eight on a C atom. Inadequate cognizance is thus taken of the tendency of inter-electronic Coulomb forces to keep two electrons apart. The S-P procedure avoids this excessive accumulation, but at the expense of not letting an individual wave function be of a

symmetry type (irreducible group representation) appropriate to a tetrahedral field. In particular, its  $s$ - $p$  hybridization "undiagonalizes" the internal energy of the C atom. These points are illustrated by explicit exhibition of the secular determinant, which is the main new feature. Because inter-electronic repulsions make the dynamical problem more complicated than a one-electron one, the tetrahedral symmetry need only be preserved in the properties of the total wave function of the entire system rather than that of one electron, but the departures from individual tetrahedral symmetry should be less than in the Slater-Pauling theory if the Hartree self-consistent field is really a good approximation. Thus both the H-M and S-P methods, though qualitatively exceedingly illuminating, have their own characteristic drawbacks from a quantitative standpoint unless refined by inclusion of higher approximations which ultimately merge the two methods but which practically are very difficult to make.

TWO approaches have been opened to the subject of directed or orbital valence<sup>2</sup> in polyatomic molecules. One method is that developed by Slater<sup>3</sup> and by Pauling.<sup>4</sup> Their model

is based on what Hund calls a "localization" of bonds whereby particular wave functions are assigned to "overlap" particular atoms. To explain tetrahedral carbon compounds, the so-called " $sp^3$ " valences and wave functions are introduced. Namely, Pauling and Slater show that by taking linear combinations of the usual  $2s$  and  $2p$  wave functions it is possible to build four orthogonal wave functions which project in space like the four corners of a tetrahedron. The Slater-Pauling model lends itself particularly to calculations by means of the Heitler-London method, in a generalized form given by Slater<sup>3</sup> and by Born.<sup>5</sup>

<sup>1</sup> A preliminary account was given at the Washington meeting of the American Physical Society, April, 1932, (abstract in *Phys. Rev.* **40**, 1037 (1932)).

<sup>2</sup> Since we are here confining our attention to theories of directed or orbital valence, we do not need to include in the present discussion the Heitler-Rumer treatment of carbon compounds, in which the directional properties exist only in virtue of the repulsions between the atoms attached by the central carbon atom. This Heitler-Rumer method must not, however, be overlooked and will be compared with the other methods in Part III.

<sup>3</sup> J. C. Slater, *Phys. Rev.* **37**, 481; **38**, 1109 (1931).

<sup>4</sup> L. Pauling, *J. Am. Chem. Soc.* **53**, 1367, 3225 (1931).

<sup>5</sup> M. Born, *Zeits. f. Physik* **64**, 729; **65**, 718 (1930).

The other approach is that due to Hund<sup>6</sup> and to Mulliken,<sup>7</sup> and is a generalization of their diatomic configuration theory. In Mulliken's recent model, an electron is not assigned to a particular valence but is allowed to move in a field of the same symmetry as that of the molecule in question; e.g., a field of tetrahedral symmetry in CH<sub>4</sub>. Great simplicity rests in the fact that with this model the dynamics are that of a "one electron system," for instance the two center problem in diatomic molecules, the five center one in CH<sub>4</sub>. Electrons are, so to speak, fed to the molecule one at a time, and by the Pauli principle not more than two of them can be digested in the same orbital state. Inter-electronic repulsions can, in principle, be included to the extent to which they may be represented by a Hartree self-consistent field of the given symmetry. If the molecule is symmetrical, several solutions of the "one-electron" wave equation may have the same energy. The degree of degeneracy can be determined from that famous paper of Bethe<sup>8</sup> in which the different representations of the rotation group are resolved into their irreducible portions in various crystallographic groups. In particular in the tetrahedral models the two-quantum levels split in the same fashion as for a central field, *viz.*, into one isolated term (the  $2s$  wave function) and one triply degenerate term (three arbitrary orthogonal linear combinations of the usual  $2p$  wave functions). It is to be particularly noted that Mulliken's tetrahedral model does not demand or even allow "hybridization," i.e., intermingling of the  $2s$  and  $2p$  wave functions in linear combinations. The method of calculation with the Mulliken model is essentially a generalization of one devised by Hund for simple cases, and is at least superficially very different from the Heitler-London method, as we shall see. The new contribution of Mulliken's recent paper, as compared to Hund's previous work, is the qualitative consideration of the arrangement of energy levels under molecular fields of given symmetry types.

Both the Slater-Pauling and Hund-Mulliken schemes predict a right-angled model for H<sub>2</sub>O if one neglects (a) the forces between the two H

atoms, (b) the finite separation of the  $1S$ ,  $3P$ ,  $1D$  terms arising from the configuration  $p^4$  of O, and (c) the bonding power of the two  $2s$  electrons of O. This right-angled feature has already been demonstrated common to both methods in the literature, but we may here call attention to the fact that they give nearly similar energies of formation of H<sub>2</sub>O when the constants are determined by an assumed value of the energy of OH. Namely both schemes are readily seen to yield the result that the energy of the reaction  $2H + O = H_2O$  is double that of  $H + O = OH$ , if we neglect items (a), (b), and (c) above, also (d) interaction terms between  $1s$  of H and  $2p\pi$  of O, which are surely subordinate to those between  $1s$  and  $2p\sigma$ , and (e) allowance in the Heitler-London-Slater-Pauling method for the fact that the electron pairing is imperfect, i.e., the valences not 100 percent "pure" in Weyl's sense. Slater mentions that the heat of formation of OH from O and H is probably about 5 volts, and hence both schemes agree in predicting that the heat of H<sub>2</sub>O from O and 2H is in the neighborhood of 10 volts, in accord with experiment.<sup>9</sup>

#### CRITICAL COMPARISON OF MULLIKEN AND SLATER-PAULING WAVE FUNCTIONS: PROS AND CONS OF HYBRIDIZATION

Our next point will be a mathematical calculation exhibiting explicitly why the  $s$  and  $p$  wave functions do not hybridize in the Mulliken model of CH<sub>4</sub>. We shall start with a system of representation in which the  $sp^3$  wave functions are used, and show that proper solution of the secular problem introduces a canonical transformation which destroys the hybridization. Following Hund, we shall assume that an idealized localized valence bond between an  $sp^3$  wave function of C and a  $1s$  wave function of H can be represented by using a wave function of the form  $\alpha\psi(1s; H) + (1 - \alpha^2)^{1/2}\psi(sp^3; C)$  where the axis of the  $sp^3$  function is, of course, to be taken coincident with the C-H axis. When we use a notation such as  $\psi(1s; H_i)$  we mean a  $1s$  wave

<sup>9</sup> A. S. Coolidge has recently made a calculation of H<sub>2</sub>O by the Slater-Pauling method without the use of as many approximations as (a)–(e); (Phys. Rev. **42**, 189 (1932)). Unfortunately the accord with experiment is poor, suggesting that the close agreement achieved with the less refined calculations is perhaps somewhat accidental.

<sup>6</sup> F. Hund, *Zeits. f. Physik* **73**, 1, 565; **74**, 429 (1931–2).

<sup>7</sup> R. S. Mulliken, *Phys. Rev.* **40**, 55; **41**, 49 (1932).

<sup>8</sup> H. Bethe, *Ann. d. Physik* **3**, 133 (1929).

function for an H attracting center. The subscript  $i$  ( $i = a, b, c, d$ ) is inserted only when it is necessary to distinguish between the four different H nuclei involved in CH<sub>4</sub>. Similarly  $\psi(2p; C)$  denotes a  $2p$  wave function for a C attracting center,  $\psi(sp^3; C)$  an  $sp^3$  one, etc. When we come to

CH<sub>4</sub> we can no longer hope to express the molecular wave functions as linear combinations of two wave functions, as in a diatomic problem, but instead must use linear combinations of the following eight wave functions, denoted by I-IV'

$$\left. \begin{aligned} \text{I} &= \psi(1s; H_a), \quad \text{II} = \psi(1s; H_b), \quad \text{III} = \psi(1s; H_c), \quad \text{IV} = \psi(1s; H_d); \\ \text{I}', \text{II}', \text{III}', \text{IV}' &= sp^3 \text{ wave functions of C directed along} \\ &\quad \text{C-H}_a, \text{C-H}_b, \text{C-H}_c, \text{C-H}_d \text{ respectively.} \end{aligned} \right\} \quad (1)$$

The secular determinant is of the form

$$\begin{vmatrix} a-W & b & b & b & c-dW & e-fW & e-fW & e-fW \\ b & a-W & b & b & e-fW & c-dW & e-fW & e-fW \\ b & b & a-W & b & e-fW & e-fW & c-dW & e-fW \\ b & b & b & a-W & e-fW & e-fW & e-fW & c-dW \\ c-dW & e-fW & e-fW & e-W & k-W & g-hW & g-hW & g-hW \\ e-fW & c-dW & e-fW & e-fW & g-hW & k-W & g-hW & g-hW \\ e-fW & e-fW & c-dW & e-fW & g-hW & g-hW & k-W & g-hW \\ e-fW & e-fW & e-fW & c-dW & g-hW & g-hW & g-hW & k-W \end{vmatrix}. \quad (2)$$

The rows and columns are indexed with respect to I', ..., IV', I, ..., IV. The constants  $c, e$  are Hund resonance terms between the C and H atoms, and  $g$  a similar term between the H atoms themselves. By a resonance term or integral we mean a matrix element  $\int \psi' \mathbf{H} \psi dv$  in which  $\psi', \psi$  are single electron wave functions for different atoms and in which  $\mathbf{H}$  is the Hamiltonian operator. It is not to be confused with "exchange integrals," which have a meaning only in two-or-more electron systems and in which electrons are permuted rather than simply one electron transferred from one atom to another. The term  $b$  exists because the hybridization prevents  $l$  being a good quantum number. The energy  $W$  appears off the diagonal because the wave functions of different attracting centers are not mutually orthogonal. On the other hand the C wave functions are orthogonal to each other, and hence  $W$  does not appear off the diagonal in the upper left quarter of (2). We shall not attempt at present to express the various constants in terms of the familiar integrals of the two-center problem, but substantially this will be done in Part II in connection with more general models (cf. especially note 7 of Part II). The occurrence

of the same letter in several places in (2) is, of course, a consequence of the tetrahedral symmetry and complete parity of the four  $sp^3$  wave functions except for direction. Clearly the Hund resonance term has one value  $c$  for pairs of wave functions such as (I, I'), (II, II') ..., (IV, IV') and another common value, say  $e$ , for (I, II'), (II, I'), (I, III'), etc., while  $g$  denotes the value for H-H pairs such as (I, II), etc.

The fact that the nonvanishing off-diagonal elements of (2) are not confined to the places (I; I'), (II; II'), ..., (IV; IV'), of course, shows that localization is impossible, i.e., that twofold linear combinations of the form  $\alpha I + (1 - \alpha^2)^{1/2} I'$ , etc., are inadequate wave functions. Great simplification can, however, be achieved by making a canonical transformation corresponding to the introduction of the eight new wave functions<sup>10</sup>

<sup>10</sup> In unpublished work, Mulliken has also independently found that the functions  $\psi_1, \psi_2, \psi_3, \psi_4$  defined in (3) are linear combinations of the H wave functions appropriate to the tetrahedral symmetry. Mulliken's method of obtaining the combinations was a study of general symmetry properties rather than of the secular determinant. He has also thus deduced independently the trigonal wave functions to be given in Eq. (29) of Part II.

$$\begin{aligned}
\psi_1 &= \frac{1}{2}[\text{I} + \text{II} + \text{III} + \text{IV}], & \psi_2 &= \frac{1}{2}[\text{I} + \text{II} - \text{III} - \text{IV}], \\
\psi_3 &= \frac{1}{2}[\text{I} - \text{II} + \text{III} - \text{IV}], & \psi_4 &= \frac{1}{2}[\text{I} - \text{II} - \text{III} + \text{IV}] \\
\psi_1' &= \frac{1}{2}[\text{I}' + \text{II}' + \text{III}' + \text{IV}'], & \psi_2' &= \frac{1}{2}[\text{I}' + \text{II}' - \text{III}' - \text{IV}'], \\
\psi_3' &= \frac{1}{2}[\text{I}' - \text{II}' + \text{III}' - \text{IV}'], & \psi_4' &= \frac{1}{2}[\text{I}' - \text{II}' - \text{III}' + \text{IV}']
\end{aligned} \tag{3}$$

in place of  $\text{I} \cdots \text{IV}'$ . One verifies that the secular determinant then factors into four second order determinants, of which three are identical. The determinantal equations occurring once and thrice are given respectively by the upper and lower choice of sign in the following Eq. (4):

$$\begin{vmatrix} a + (b \pm 2b) - W & c + (e \pm 2e) - dW - (f \pm 2f)W \\ c + (e \pm 2e) - dW - (f \pm 2f)W & k + (g \pm 2g) - W - (h \pm 2h)W \end{vmatrix} = 0. \tag{4}$$

The pairs of wave functions which are associated with the four second order determinants are respectively  $(\psi_1, \psi_1'), (\psi_2, \psi_2'), (\psi_3, \psi_3'), (\psi_4, \psi_4')$ . All but the first of these pairs are correlated with the lower choice of sign in (4). The transformation (3) which simplifies (2) to (4) completely eliminates the  $sp^3$  hybridization, since  $\psi_1'$  does not combine with  $\psi_2', \psi_3', \psi_4'$ , and since further  $\psi_1'$  is merely an ordinary  $2s$  wave function. The latter statement follows from the fact that the  $sp^3$  functions are of the form<sup>3,4</sup>  $\frac{1}{2}\psi(2s) + f(r)(\mathbf{r} \cdot \mathbf{1}_i)$ , where  $\mathbf{1}_i$  is a unit vector directed along  $\text{C}-\text{H}_i$ , whence  $\mathbf{1}_a + \mathbf{1}_b + \mathbf{1}_c + \mathbf{1}_d = 0$ . Also  $\psi_2', \psi_3', \psi_4'$  are ordinary  $2p$  wave functions.

One thing must be particularly noted. According to the ideas of Hund and Mulliken we must fill twice each of the lower roots of the four second order equations:—twice because the Pauli principle allows two electrons to a given orbital state. The total wave function for the eight electron  $\text{CH}_4$  system is (forgetting, as we do throughout, the  $K$  shell of C)

$$\Phi_1(1)\Phi_1(2)\Phi_2(3)\Phi_2(4)\Phi_3(5)\Phi_3(6)\Phi_4(7)\Phi_4(8) \tag{5}$$

with

$$\begin{aligned}
\Phi_i &= \beta_i \psi_i + (1 - \beta_i^2)^{1/2} \psi_i' \quad (i = 1, \dots, 4) \\
\beta_2 &= \beta_3 = \beta_4. \tag{6}
\end{aligned}$$

Here  $\Phi_i(j)$  means that the coordinates involved as arguments of  $\Phi_i$  relate to electron  $j$ . The values of  $\beta_1, \beta_2$  are determined by finding the transformation matrices connected with the two secular problems (4).

*Accumulation of electrons on one nucleus.* If we express (5) in terms of the original functions  $\text{I}, \dots, \text{IV}'$  by means of (3) we see that (5) will involve terms of the form  $\text{I}(1)\text{I}(2) \cdots \text{I}(8)$ . The

physical interpretation of such terms is that there is a finite probability of all eight electrons being piled momentarily on one hydrogen atom, since  $\text{I}(j)$  means a hydrogen wave function in which electron  $j$  is attached to nucleus  $a$ . There are also other terms involving accumulation of from 2 to 7 electrons on the same H atom. Analogous results are found in Hund's calculations for  $\text{H}_2$  and  $\text{H}_2\text{O}$ , where respectively 2 and 4 electrons can accumulate on an H atom. Fortunately, all these remarks apply only as long as we take the wave functions to be simple products such as (5) of "one-electron functions." Actually, the seriousness of the accumulation effects is considerably diminished from the foregoing when one includes the spin and "antisymmetrizes" so as to satisfy the Pauli principle. One must, of course, take the antisymmetrical linear combinations, inclusive of spin functions, since the wave function (5) is not unique because of the possibility of permutation of electrons. As long as we have agreed to include electron repulsions only insofar as they can be represented by the self-consistent field, the process of taking such combinations will have no effect upon the energy provided we neglect terms resulting from the want of orthogonality of the wave functions  $\text{I}, \text{I}', \dots, \text{IV}'$  etc., i.e., provided we neglect the elements  $dW, fW, hW$  in (2). When linear combinations are taken in accordance with the Pauli principle, it is found that not more than two electrons can accumulate on a given nucleus. In other words, the final wave function will involve terms such as  $\text{I}(1)\text{I}(2)\text{II}(3) \cdots$ , but none such as  $\text{I}(1)\text{I}(2)\text{I}(3) \cdots$ . For this observation the writer is indebted to Professor Slater. Similarly in Hund's model of  $\text{H}_2\text{O}$ , only

two electrons can accumulate on one H nucleus when the exclusion principle is taken into account.

To prove that the exclusion principle reduces accumulation as stated above, one utilizes the well-known result of Slater's paper on complex spectra,<sup>11</sup> that the complete wave function, inclusive of spin, can be written as a sum of determinants. The elements of a determinant consist of the product of a spin factor and an orbital wave function. Elements of the same column have the same coordinate and spin arguments, i.e., relate to the same electron, but have different spin or orbital functions, while elements of the same row all involve the same functions but with different arguments. In our case the orbital factors of each element may without loss of generality be considered to be one of the eight expressions  $I \cdots IV'$ , since provision for linear combinations is made when it is stated that the complete wave function is the *sum* of determinants. Because the spin factor can only assume two different values  $\delta(-\frac{1}{2}; m_s)$ ,  $\delta(\frac{1}{2}; m_s)$ , any given one of the expressions  $I \cdots IV'$  cannot appear in more than two rows of any determinant without the latter vanishing. From this it follows that the expansion of the complete wave function cannot involve terms in which any one of these expressions appears as a factor more than twice, Q.E.D.

Another unpleasant feature is that much of the expansion of (5) represents terms of the structures  $C^{4+}(H_4)^{4-}$ ,  $C^{3+}(H_4)^{3-}$ ,  $\dots$ ,  $C^{4-}(H_4)^{4+}$ , even though in the mean the molecule is not ionic. For instance, if  $\beta_1^2 = \beta_2^2 = \frac{1}{2}$  and if we neglect corrections for non-orthogonality, the C and collectively the four H atoms share the 8 electrons equally on the average but one calculates that then the molecule spends the following percentages of the time in various structures:  $C^0(H_4)^0$ , 27 percent;  $C^+(H_4)^-$ , 22;  $C^-(H_4)^+$ , 22;  $C^{2+}(H_4)^{2-}$ , 11;  $C^{2-}(H_4)^{2+}$ , 11;  $C^{3+}(H_4)^{3-}$ , 3;  $C^{3-}(H_4)^{3+}$ , 3;  $C^{4+}(H_4)^{4-}$ ,  $\frac{1}{2}$ ;  $C^{4-}(H_4)^{4+}$ ,  $\frac{1}{2}$ . (The process of antisymmetrizing does not affect the percentages of distribution between C and 4H, but does show that in  $C^{4+}(H_4)^{4-}$  the 8 electrons are always distributed evenly between the 4 hydrogen nuclei.) This is entirely too much instantaneous polarity. The excessive instantane-

ous polarity demanded by the Hund-Mulliken method is glaringly revealed in the case of  $H_2$ , where this method predicts the molecule to be  $H^+H^-$  and  $H^-H^+$  half the time, whereas calculation shows that it probably is so constituted only 1/64 of the time.<sup>12</sup> If the transfer effects are as frequent in CH as in  $H_2$ , and if those in  $CH_4$  can be roughly estimated by fourfold superposition of those in CH, then this value 1/64 suggests that methane should be  $C^+(H_4)^-$  or  $C^-(H_4)^+$  each only 3 percent of the time and be in doubly or more ionic states (all kinds combined) less than 1 percent. The excessive accumulation effects can be eliminated by extending Mulliken's method by adding to (5) other solutions in which one or more electrons settle in the higher<sup>13</sup> roots of the determinants (4). Essentially because the presence of nodes increases materially the normalization constants for the higher states, the amount of such states which must be added to (5) is surprisingly small, at least in  $H_2$ , where Mulliken notes<sup>12</sup> that the accumulation effect is properly reduced by adding<sup>14</sup>  $\psi_u(1)\psi_u(2)$  to  $\psi_g(1)\psi_g(2)$  in the ratio of only 1 to 8. This suggests that it probably would be quite a good approximation if we could make a calculation in which (5) is augmented by linear combination with states in which only one or two electrons settle in the higher roots of (4). Such a calculation, however, presents serious mathematical difficulties, and without it the Hund-Mulliken method must be regarded more as a qualitative rather than quantitative procedure.

The preceding result that two electrons can occasionally accumulate on one atom is, of course, in sharp contrast to the high degree of localization found in the Slater-Pauling model, and related Heitler-London methods of calculation which assign one and only one electron to an H atom. Naturally, accurate inclusion of the electron repulsion prevents accumulation being realized to the extent predicted by the preceding

<sup>12</sup> See discussion by R. S. Mulliken, *Phys. Rev.* **41**, 69-71 (1932) based on a calculation by Slater, *ibid.* **35**, 514-515 (1930).

<sup>13</sup> Do not confuse our references to the higher and lower roots of an individual determinant of (4) with the upper and lower choices of sign which yield the two determinants.

<sup>14</sup> Here, as usual, the notation  $\psi_g$ ,  $\psi_u$  means wave functions respectively even and odd with respect to reflection in the midpoint of the internuclear axis. The corresponding notation in reference 12 is  $\phi_0$ ,  $\phi_1$ .

<sup>11</sup> J. C. Slater, *Phys. Rev.* **34**, 1293 (1929).

calculation. We have agreed to neglect this repulsion except via the self-consistent field, and under such neglect the question of accumulation is irrelevant for the time being, but any wave functions giving pronounced accumulation will be rather severely perturbed, and hence cannot be regarded a good approximation, if the theory is refined by introducing accurate consideration of the electron repulsions as a perturbation. Strict localization of one electron to an H atom could have been achieved if we had not taken the linear combinations (3) but had instead kept the hybridized  $sp^3$  wave functions and had used only twofold linear combinations of the form  $\alpha I + (1-\alpha^2)^{1/2} I'$  etc., which, as already stated, represent purely localized bonds. Such a mode of securing localization would involve the error of neglecting the elements  $b, e, f, g, h$  in (2) since these elements cannot be brought onto the diagonal by taking such twofold (rather than eightfold) linear combinations. This error we shall call for brevity the neglect of individual symmetry type inasmuch as the wave functions representing  $sp^3$  bonds are thus inadequate to diagonalize (2) or in other words lack the symmetry properties characteristic of irreducible representations of the tetrahedral group. The word "individual" is inserted because the symmetry considerations relate to wave functions of an isolated electron. When electron repulsions are accurately included, the dynamical problem ceases to be that of a one-electron system, and so symmetry properties for individual electrons are no longer preserved. Nevertheless, they will not be seriously impaired if the Hartree self-consistent field has been a good approximation.

The seriousness of neglecting symmetry type is gauged by the magnitude of  $b, e, f$  in (2), or more succinctly, by the separation of the lower roots<sup>13</sup> of the two determinants (4) since if these roots coincided their wave functions could be combined by a process more or less the reverse of (3) into those representing localized  $sp^3$  bonds. If the carbon levels are lower than the hydrogen ones, the two lower roots of (4) are  $W = a + 3b$ ,  $W = a - b$  when  $c = d = e = f = 0$ , as is the case when all interaction between the C and H atoms is neglected. Hence  $4b$  has the significance of being the carbon  $s-p$  separation, and neglect of individual symmetry type will be a poor approximation if this separation is greater than or

comparable with the C-H bonding energy. Actually the  $s-p$  interval in carbon amounts to a few volts, and hence is not negligible compared to the energy of a C-H bond (4 volts). (The value of the  $s-p$  interval in C depends on which spectral terms are selected from the configurations  $sp^3$  and  $s^2p^2$ ; the lowest state  $^3P$  of  $s^2p^2$  is 1.6 volts below  $^5S$  of  $sp^3$ , according to rather indirect evidence from band spectra,<sup>15</sup> and is definitely known to be from 8 to 10 volts below most<sup>16</sup> other terms ( $^1P, ^3P, ^1D, ^3D$ ) belonging to  $sp^3$ . Since a one-electron model is inadequate to take account of different term values for the same configuration, it is perhaps fairest for our purposes to compare the mean of all terms arising from  $s^2p^2$  with the mean of all terms from  $sp^3$ . When allowance is made for the fact that the two other terms  $^1D, ^1S$  of  $s^2p^2$  are 1 and 2 volts higher than  $^3P$ , the difference between the two means is found to amount to 6 or 7 volts.) Even if the  $s-p$  separation of carbon were zero, the neglect of individual symmetry type would not be a good approximation as the two determinants (4) are not identical even when  $b=0$ . The situation is thus quite different from that which Hund<sup>6</sup> encounters in a strictly right-angled model of  $H_2O$ , where only  $p$  wave functions are used for the O valences, and where he shows that the two lower roots of his two determinants exactly coincide, so that the error due to neglect of individual symmetry type in securing localized bonds is nil.

To summarize, the Slater-Pauling localized bonds avoid excessive electronic accumulation on the same atom, but give rather too great departures from individual symmetry type. These properties were, in fact, already known in a very general way, but it seems instructive to us to have deduced them more concretely by means of the secular determinant (2).

In Part II we shall give calculations which aim to show that the tetrahedral model of  $CH_4$  is firmer than other models in both the Hund-Mulliken and Slater-Pauling methods, even without invoking H-H repulsions.

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<sup>15</sup> W. Heitler and G. Herzberg, *Zeits. f. Physik* **53**, 52 (1929).

<sup>16</sup> The location of the remaining term  $sp^3\ ^3S$  is unknown.