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# The Quantum-Mechanical Treatment of Molecules by the Method of Spin Valence*

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The method of spin valence, developed by Born, Heitler, Rumer and Weyl for the treatment of molecular systems, becomes completely equivalent to the Slater method if the bonding forces are considered to be exerted between individual orbitals, and not between entire atoms in definite spectroscopic states. This change in the point of view eliminates several difficulties which were formerly present in the method (e.g., the obscuring of the directional properties of the valence bonds). The secular equation, for which a simplified derivation is given, is of quite a different form from the Slater equation, and the problem of its solution is considered in some detail. In addition to the rigorous methods, several approximate methods are given, of which two (applicable to unsaturated and aromatic hydrocarbons) do not require that the secular equation be set up at all. The method of spin valence is found to be more convenient than the Slater method for the treatment of systems of high multiplicity. Finally, the extension to cases of orbital, as well as spin degeneracy is briefly outlined.

## INTRODUCTION

THE method outlined by Slater[1] for the quantum-mechanical treatment of molecular structure is of such general applicability that certain other procedures which have been devised and which lead to the same final result are apt to be completely neglected. (I am not concerned here with the method[2] associated chiefly with the names of Hund and of Mulliken, since this starts from an essentially different basis and is not strictly comparable with Slater's treatment.) Van Vleck and Serber,[3] to be sure, have recently pointed out that the Dirac vector model is quite useful for many purposes, but very little attention seems to have ever been paid to the so-called method of spin valence developed by Born, Heitler, Rumer and Weyl.[4] One reason for this neglect is probably to be found in the fact that, in its usual formulation, the method treats only the interactions between entire atoms in definite spectroscopic states, and not those between the individual electrons. This makes it almost necessary to assume each atom to be in an $S$ state, and obscures the directional properties of the valence bonds to such an extent as to invalidate many of the conclusions reached. The incorrect result obtained by Markov,[5] for example, that benzene should be less stable than three acetylene molecules is apparently to be explained on this basis. This difficulty, however, is not at all essential, and, as we shall see immediately, can easily be avoided.

In the following development, a method of attack will be adopted which differs from that usually employed in that it assumes the Slater valence-bond functions at the outset. This eliminates at once the above-mentioned difficulty, and simplifies the subsequent treatment by rendering unnecessary any recourse to the unfamiliar theory of the invariants of binary forms. With this alteration, the method of spin valence becomes completely equivalent to the ordinary Slater treatment, although it remains quite different in form. It always leads to the same answer as the latter in any definite problem, but it frequently allows the calculation to be made with the expenditure of considerably less time and labor. Even in the cases in which it offers no special advantages, it is still useful in that it furnishes an independent check upon the results obtained in other ways.

## OUTLINE OF THE METHOD

For the present, the discussion will be limited to problems of spin degeneracy only, and to systems in singlet states. If we have $2N$ orbitals, $a, b, \cdots y, z$, each occupied by one electron, we

* No. 455.

[1] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[2] F. Hund, Zeits. f. Physik **73**, 1 (1931); **73**, 565 (1932). R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933) and further references given there. Cf. also E. Hückel, Zeits. f. Physik **72**, 310 (1931); **76**, 628 (1932); **83**, 632 (1933).

[3] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934). R. Serber, Phys. Rev. **45**, 461 (1934); J. Chem. Phys. **2**, 697 (1934).

[4] M. Born, Zeits. f. Physik **64**, 729 (1930); Ergebnisse d. Exakt. Naturwissenschaften, X 387 (1931). W. Heitler and G. Rumer, Zeits. f. Physik **68**, 12 (1931); H. Weyl, Nach. Ges. Wiss. Gött., M. P. Klasse, **1930**, 285; **1931**, 33; G. Rumer, ibid. **1932**, 337.

[5] M. Markov, J. Chem. Phys. **1**, 784 (1933).

can set up a Slater function for each possible way of drawing valence bonds. For bonds between $a$ and $b$, $c$ and $d$, $\cdots y$ and $z$, for example, we have[6]

$$\Psi = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_k (-1)^k R_k \sum_j (-1)^j P_j$$
$$\times \{a(1)\alpha(1)b(2)\beta(2)\cdots y(2N-1)$$
$$\times \alpha(2N-1)z(2N)\beta(2N)\}, \quad (1)$$

where $P_j$ is one of the $(2N)!$ operations of permuting the electrons among the orbital and spin functions, and $R_k$ is one of the $2^N$ operations of interchanging the spins associated with the orbitals involved in one or more bonds. $P_j$ is an even, or an odd, permutation when $j$ is even, or odd, respectively; and $R_k$ corresponds to an even, or to an odd, number of interchanges when $k$ is even, or odd, respectively. In order to avoid confusion in regard to the sign of the function, we shall adopt the following convention: Let each valence bond in the structure be represented by an arrow. Then the corresponding function is

$$\Psi = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_k (-1)^k R_k \sum_j (-1)^j P_j$$
$$\times \{a(1)\sigma_a(1)b(2)\sigma_b(2)\cdots z(2N)\sigma_z(2N)\}, \quad (2)$$

where

$$\sigma_r = \begin{cases} \alpha, \text{ if the orbital } r \text{ is at the tail of an arrow} \\ \beta, \text{ if the orbital } r \text{ is at the head of an arrow.} \end{cases}$$

In that term of the double summation for which $R_k$ and $P_j$ are both equal to the identity operator $I$, the orbitals follow in alphabetical, and the electrons in numerical order. Reversing an arrow in the structure then changes the sign of the corresponding function. In the structure represented by Eq. (1), for example, the arrows point from $a$ to $b$, $\cdots$, from $y$ to $z$.

If the summation over $k$ is actually performed, Eq. (1) becomes

$$\Psi = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_j (-1)^j P_j \{a(1)b(2)\cdots$$
$$\times z(2N)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\cdots$$

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[6] The first explicit statement of this rule (in a slightly different, but equivalent form) seems to have been made by G. E. Kimball and H. Eyring, J. Am. Chem. Soc. **54**, 3876 (1932).

$$\times [\alpha(2N-1)\beta(2N)-\beta(2N-1)\alpha(2N)]\}$$
$$= \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_j (-1)^j (P_j u)(P_j \varphi) \quad (3)$$

where, for convenience, we have set

$$u = a(1)b(2)\cdots z(2N)$$

and

$$\varphi = [\alpha(1)\beta(2)-\beta(1)\alpha(2)]\cdots$$
$$\times [\alpha(2N-1)\beta(2N)-\beta(2N-1)\alpha(2N)].$$

From this original structure, any other that may be desired can be obtained by redirecting the arrows in a suitable manner. Such a redirection can be represented by a permutation, $T_i$, acting upon the orbitals. If, for example, $T_i$ is the simple interchange $(by)$, the corresponding structure is that in which the arrow, which formerly had its head (or tail) at $b$, now has its head (or tail) at $y$, and vice versa. That is,

$$a \rightarrow b$$
$$\text{becomes}$$
$$z \leftarrow y$$
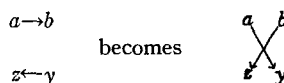


Any other bonds (such as between $c$ and $d$, etc.) remain unchanged. It is readily seen that the function which represents this new structure is

$$\Psi_i = \frac{(-1)^i}{(2^N(2N)!)^{\frac{1}{2}}} \sum_j (-1)^j (P_j T_i u)(P_j \varphi). \quad (4)$$

The factor $(-1)^i$ ensures that the direction of each arrow in the vector-bond structure will remain unchanged in the course of the permutation.

We can put Eq. (4) into a more convenient form by noting that $T_i$ can be replaced by $\hat{P}_i^{-1}$, where $P_i$ is the same permutation of the electrons, 1, 2, $\cdots 2N$, as $T_i$ is of the orbitals, $a$, $b$, $\cdots z$. This gives

$$\Psi_i = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_j (-1)^{j+i} (P_j P_i^{-1} u)(P_j \varphi). \quad (5)$$

If now we denote $P_j P_i^{-1}$ by $P_{j'}$, we have, since $P_j$ and $P_i^{-1}$ are even or odd simultaneously,

$$\Psi_i = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_{j'} (-1)^{j'} (P_{j'} u)(P_{j'} P_i \varphi),$$

or, dropping the primes and setting $P_i \varphi = \varphi_i$

$$\Psi_i = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_j (-1)^j (P_j u)(P_j \varphi_i). \qquad (6)$$

There are $(2N)!$ permutations $T_i$ and hence $(2N)!$ functions $\Psi_i$ which can be obtained in this way, but of these only $(2N)!/[N!(N+1)!] = p_N$ can be independent, since there are only $p_N$ singlet states. It is obvious, for example, that if $T_i$ is the interchange $(ab)$ in Eq. (4), the effect is merely to change the sign of the function, or to reverse the arrow between $a$ and $b$ in the corresponding structure. The general case can be described in the following manner. Arrange the orbitals formally in a circle. (This need have no relation to the actual arrangement in space.) Now draw all possible structures in which each bond lies wholly within the circle, and in which no two bonds intersect. For this purpose structures which differ only in the direction of one or more of the arrows are not to be considered as distinct. There will be exactly $p_N$ such structures, and the corresponding functions will form a complete and independent "canonical" set. Structures which contain crossed bonds can always be resolved into linear combinations of the canonical structures by repeated application of the rule[7]

$$\bigtimes = \;\rightleftarrows\; - \;\downarrow\uparrow$$

or by the procedure given by Eyring and Sun.[8]

In general no single function $\Psi_i$ will be a satisfactory representation of the molecule, and it is necessary to use a linear combination

$$\chi = \sum_{i=1}^{p_N} a_i \Psi_i \qquad (7)$$

in which the $a_i$'s are constants which are to be so chosen that $\chi$ is the best possible approximation. Instead of using the variational method, which leads to Slater's secular equation, we shall evaluate the coefficients by the ordinary first order perturbation theory. Thus, we set

$$(H-W)\chi = \sum_{i=1}^{p_N} a_i (H-W)\Psi_i = 0. \qquad (8)$$

If we should multiply Eq. (8) by $\Psi_l$ ($l=1, 2, \cdots p_N$) and integrate over all coordinates, we

[7] G. Rumer, Nach. Ges. Wiss. Gött., M. P. Klasse, **1932**, 337.
[8] H. Eyring and C. E. Sun, J. Chem. Phys. **2**, 299 (1934).

would again end up with Slater's secular equation. In the present treatment, however, we multiply by $u$, and integrate only over the spatial coordinates. In this way we obtain:

$$\sum_{i=1}^{p_N} a_i (u|H-W|\Psi_i) = \frac{1}{(2^N(2N)!)^{\frac{1}{2}}} \sum_{i=1}^{p_N} \sum_j a_i (-1)^j$$
$$\times (u|H-W|P_j u)P_j\varphi_i = 0,$$

or if we set

$$G_j = (-1)^j (u/H-W/P_j u)$$

and

$$P_j\varphi_i = \sum_{l=1}^{p_N} b_{il}{}^{(j)} \varphi_l,$$

we have

$$\sum_{i=1}^{p_N} \sum_{l=1}^{p_N} \sum_j a_i G_j b_{il}{}^{(j)} \varphi_l = 0.$$

The $\varphi_l$'s are linearly independent, and consequently the coefficient of each must vanish separately. Thus

$$\sum_{i=1}^{p_N} [\sum_j G_j b_{il}{}^{(j)}] a_i = 0, \qquad (l=1, 2, \cdots p_N). \qquad (9)$$

This set of simultaneous homogeneous linear equations for the $a_i$'s has a solution if and only if the determinant of the coefficients vanishes:

$$\begin{vmatrix} \sum_j G_j b_{11}{}^{(j)} & \cdots & \sum_j G_j b_{1 p_N}{}^{(j)} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \sum_j G_j b_{p_N 1}{}^{(j)} & \cdots & \sum_j G_j b_{p_N p_N}{}^{(j)} \end{vmatrix} = 0. \qquad (10)$$

This secular equation is quite different in form from the Slater secular equation which it replaces, and its matrix elements are obtained in quite a different way, but it clearly must lead to the same values of the energy $W$, and of the coefficients $a_i$. It is particularly to be noticed that the determinant is not in general symmetrical about the main diagonal, since $\sum_j G_j b_{il}{}^{(j)}$ is not necessarily equal to $\sum_j G_j b_{li}{}^{(j)}$.

### AN EXAMPLE

In order to illustrate the method, let us consider benzene, which has already been treated by Hückel,[9] and by Pauling and Wheland.[10] We shall take into account only the interactions between the six $[p]_h$ orbitals (using Hückel's

[9] E. Hückel, Zeits. f. Physik **70**, 204 (1931).
[10] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

TABLE I.

| $T_i$ / $i$ | I | (ab) | (bc) | (cd) | (de) | (ef) | (fa) | Σ |
|---|---|---|---|---|---|---|---|---|
| A | A | $-E+A$ | $-A$ | $-D+A$ | $-A$ | $-C+A$ | $-A$ | $A(Q-W)+(C+D+E)\alpha$ |
| B | B | $-B$ | $-C+B$ | $-B$ | $-E+B$ | $-B$ | $-D+B$ | $B(Q-W)+(C+D+E)\alpha$ |
| C | C | $-B+C$ | $-C$ | $-B+C$ | $-A+C$ | $-C$ | $-A+C$ | $C(Q-W-2\alpha)+2(A+B)\alpha$ |
| D | D | $-B+D$ | $-A+D$ | $-D$ | $-A+D$ | $-B+D$ | $-D$ | $D(Q-W-2\alpha)+2(A+B)\alpha$ |
| E | E | $-E$ | $-A+E$ | $-B+E$ | $-E$ | $-B+E$ | $-A+E$ | $E(Q-W-2\alpha)+2(A+B)\alpha$ |

nomenclature) and we shall make the usual assumption that $G_i = Q - W$ if $T_i$ is the identical permutation $I$, $G_i = -\alpha$ if $T_i$ is a single interchange between adjacent orbitals, and $G_i = 0$ otherwise. There are five canonical structures,
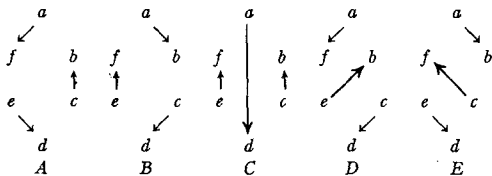


The actual calculation is given in Table I At the top are listed the permutations considered (that is, those for which $G_i \neq 0$), and on the left are listed the independent spin functions. For convenience, $\varphi_A$ is written simply $A$, and so on. The Slater function which represents the structure $A$, for example, is of course

$$\Psi_A = \frac{1}{24(10)^{\frac{1}{2}}} \sum_i (-1)^i (P_i u)(P_i \varphi_A).$$

In each square of the body of the table is given $P_i \varphi_i$ corresponding to the permutation $T_i$ above and to the spin function $\varphi_i$ at the left. As an illustration, the permutation $T_i = (ab)$ transforms the structure $A$ into
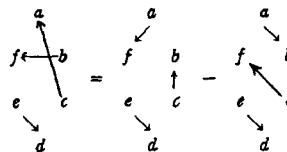


Thus, $T_i A = A - E$, and, consequently, $P_i \varphi_A = \varphi_A - \varphi_E$. In the column at the extreme right of the table are the values of

$$\sum_i G_i P_i \varphi_i = \sum_i \sum_{l=A}^{E} G_i b_{il}{}^{(j)} \varphi_l$$

obtained by summing the corresponding row. From these entries the secular equation can be written down at once:

$$\begin{vmatrix} Q-W & 0 & \alpha & \alpha & \alpha \\ 0 & Q-W & \alpha & \alpha & \alpha \\ 2\alpha & 2\alpha & Q-W-2\alpha & 0 & 0 \\ 2\alpha & 2\alpha & 0 & Q-W-2\alpha & 0 \\ 2\alpha & 2\alpha & 0 & 0 & Q-W-2\alpha \end{vmatrix} = 0. \qquad (11)$$

This gives $W = Q - 2\alpha$, $Q - 2\alpha$, $Q$, $Q - (13^{\frac{1}{2}} + 1)\alpha$, $Q + (13^{\frac{1}{2}} - 1)\alpha$, and consequently the roots are exactly the same as those found by Pauling and Wheland from the Slater secular equation, and by Hückel by a much more complicated procedure.

The eigenfunction corresponding to the lowest root, $W = Q + (13^{\frac{1}{2}} - 1)\alpha$, is before normalization $\Psi_A + \Psi_B + 0.4341(\Psi_C + \Psi_D + \Psi_E)$. This is again the same result as was obtained by Pauling and Wheland.

## USE OF SYMMETRY OF THE MOLECULE IN SIMPLIFYING THE TREATMENT

The calculation as carried out above is of about the same difficulty as that by the Slater treatment, but it can be greatly simplified if the energy of only the lowest state is desired. This follows from the fact that the degree of the secular equation can be reduced by taking advantage of the symmetry of the molecule.[11] It is obvious, for example, that the structures $A$ and $B$ must enter the complete eigenfunction for the ground state with the same coefficient, and that $C$, $D$ and $E$ must do likewise. (In order for this statement to hold, it is necessary that each arrow in each structure point from an odd numbered to an even numbered orbital, the orbitals being numbered in sequence around the circle in either direction. The starting point for the enumeration is arbitrary, but must be the same for all structures. The purpose of this convention is to ensure that the integral $(\Psi_i, \Psi_j) > 0$ for all $i$ and $j$.) There are thus only two independent coefficients, and in consequence the secular equation can be made a quadratic. It is not necessary, however, to set up the original fifth degree equation at all, since it is possible to obtain the quadratic in one step. The procedure in the general case is as follows: Let there be several different types of structure, of which characteristic representatives are $A$, $B$, $\cdots F$, respectively, and let there be $g_A$ structures of type $A$, all with coefficient $a_A$, $g_B$ structures of type $B$, all with coefficient $a_B$, and so on. Of course $g_A + g_B + \cdots + g_F = p_N$, the total number of independent spin functions. Now, using only the structures $A$, $B$, $\cdots F$ as a basis, construct a

table similar to Table I. If the carrying out of a permutation upon a given member of the set $A, B, \cdots F$ leads to a structure not a member of the set, this latter is represented in the table by that member of the set which belongs to the same type. The secular equation is then written down from the table in the same manner as before. If the coefficients $a_A$, $a_B$, $\cdots a_F$ are desired, they can be obtained from the equations

$$\sum_{R=A}^{F} (M_{RS} - \delta_{RS}W)a_R g_R = 0, \quad (S = A, B, \cdots F), \quad (12)$$

where $M_{RS} - \delta_{RS}W$ is the $RS$ element of the secular equation. These equations take the place of (9), from which they can be readily derived by equating all the $a_i$'s that should be equal, and by then adding together the equations for which $l$ refers to structures of the same type.

As an application of this procedure, we shall consider cyclooctatetrane, which has already been treated by Penney[12] by the Slater method. There are 8 electrons and hence 14 canonical structures, of which 2 are of type $A$ below, 8 of type $B$, and 4 of type $C$. The remaining structures of each type are obtained from the characteristic example by rotation about the eightfold axis.
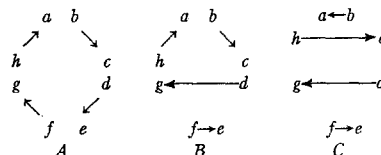


The results of the different permutations are given in Table II. It is understood of course that the entry corresponding to $T_j = (de)$ and $\varphi_i = C$, for example, does not mean that the result of the

[11] This is a special case of quite general group theoretical considerations. Cf. H. Eyring, A. A. Frost and J. Turkevich, J. Chem. Phys. 1, 777 (1933); A. E. Stearn, C. H. Lindsley and H. Eyring, ibid. 2, 410 (1934).

[12] W. G. Penney, Proc. Roy. Soc. A146, 223 (1934).

TABLE II.

| $\varphi_i$ \ $T_j$ | $I$ | $(ab)$ | $(bc)$ | $(cd)$ | $(de)$ | $(ef)$ | $(fg)$ | $(gh)$ | $(ha)$ | $\Sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $A$ | $A$ | $-B+A$ | $-A$ | $-B+A$ | $-A$ | $-B+A$ | $-A$ | $-B+A$ | $-A$ | $A(Q-W)+4B\alpha$ |
| $B$ | $B$ | $-C+B$ | $-B$ | $-B+B$ | $-A+B$ | $-B$ | $-A+B$ | $-B+B$ | $-B$ | $B(Q-W)+(2A+C)\alpha$ |
| $C$ | $C$ | $-C$ | $-B+C$ | $-A+C$ | $-B+C$ | $-C$ | $-B+C$ | $-A+C$ | $-B+C$ | $C(Q-W-4\alpha)$ $+(2A+4B)\alpha$ |

permutation $(de)$ upon $C$ is actually equal to $-B+C$, but merely that it is equal to $-(a$ structure of type $B)+(a$ structure of type $C)$. The secular equation is now

$$\begin{vmatrix} Q-W & 4\alpha & 0 \\ 2\alpha & Q-W & \alpha \\ 2\alpha & 4\alpha & Q-W-4\alpha \end{vmatrix} = \begin{aligned} &(Q-W)^3-4(Q-W)^2\alpha \\ &-12(Q-W)\alpha^2+40\alpha^3=0. \end{aligned}$$

This gives $W=Q+3.3022\alpha$ for the lowest root, in complete agreement with the value found by Penney. The work involved here is much less than by the Slater treatment, which necessitates actually setting up the entire fourteenth degree equation, and then reducing it to a cubic.

## APPROXIMATE SOLUTION OF THE SECULAR EQUATION

### First method

For still more complicated molecules, the secular equation becomes of unmanageably high degree, even after all the reduction arising from symmetry has been taken into account. In such cases it is desirable to have some method of approximation. In the Slater treatment this is quite easy, since one has only to equate the coefficients of all the first excited structures, those of all the second excited structures, and so on. One can furthermore entirely neglect the very highly excited structures since these have but little effect upon the total energy. Sherman has shown[13] by a detailed discussion of naphthalene that this procedure results in only a small error, and is a very good approximation indeed. In the present treatment, however, the secular equation is of quite a different form. In particular, it is not symmetrical about the main diagonal, and, as a consequence, the sign of the error which is

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[13] J. Sherman, J. Chem. Phys. **2**, 488 (1934).

introduced by the various approximations cannot be known beforehand with any certainty. Furthermore, the precise significance of the energy value obtained when the equation is not solved rigorously is no longer clear. Consequently, we cannot be sure, without further discussion, that the same approximate procedure as was used with the Slater equation will be legitimate here, but we can apply it, nevertheless, to several problems, and see how well it works in practice. This will give only an empirical check upon the method; but a rigorous theoretical treatment would be quite difficult.

As a first example, let us consider cyclo-decapentane. With 10 electrons there are 42 canonical structures, which belong to the 6 types
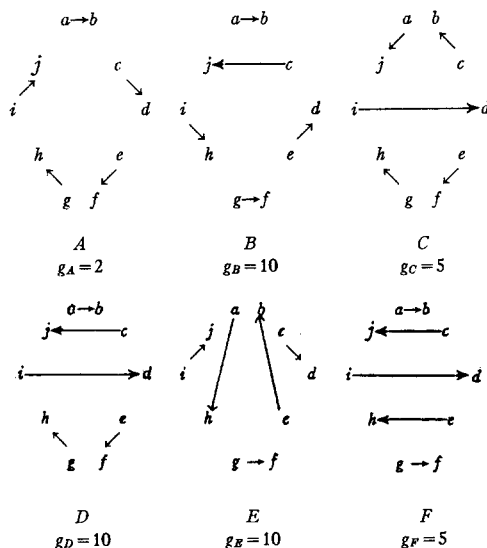


The secular equation is found in the usual manner to be:

$$\begin{vmatrix} Q-W & 5\alpha & 0 & 0 & 0 & 0 \\ 2\alpha & Q-W-2\alpha & 2\alpha & 0 & 2\alpha & 0 \\ 0 & 4\alpha & Q-W-2\alpha & 2\alpha & 0 & 0 \\ 2\alpha & 0 & 2\alpha & Q-W-4\alpha & 2\alpha & \alpha \\ 0 & 5\alpha & 0 & 2\alpha & Q-W-4\alpha & 0 \\ 0 & 4\alpha & 0 & 4\alpha & 0 & Q-W-6\alpha \end{vmatrix} = 0. \qquad (13)$$

This equation, being of the sixth degree, is still not too complicated to be treated rigorously. On multiplying out the determinant, we obtain

$$(Q-W)^6 - 18(Q-W)^5\alpha + 84(Q-W)^4\alpha^2$$
$$+ 104(Q-W)^3\alpha^3 - 1520(Q-W)^2\alpha^4$$
$$+ 3104(Q-W)\alpha^5 - 1600\alpha^6 = 0$$

of which the lowest root is $W = Q + 4.031\alpha$. The correct value will serve as a useful check upon the approximate treatment, which we now apply.

Before we can do this, however, we need to observe that while the secular equation enters the calculation as the condition of compatibility of the set of Eqs. (12) for the $a_{R}g_{R}$'s, it can also be considered as the condition of compatibility of a different set

$$\sum_{S=A}^{F} (M_{RS} - W\delta_{RS})c_S = 0 \quad (R = A, B, \cdots F). \quad (14)$$

In the Slater treatment, the constants $c_S$ are just

equal to the corresponding $a_S$'s, since the secular equation is symmetrical, but in the present treatment, this is not necessarily true. The $c$'s here are in general quite complicated functions of the $a$'s, and their precise significance is not at all clear. Consequently we have no intuitive reason (as we do in the case of the $a$'s) to believe that the $c$'s for structures of the same degree of excitation should be approximately equal to each other. We assume, however, that they are, and check the legitimacy of the assumption by comparing the result thus obtained with the rigorous solution. We are justified in doing so, since the present approximate treatment is almost entirely empirical and exploratory in nature.

The procedure now is first to multiply each row of the secular equation by the corresponding $g_R$ value,[14] and then to add the rows and columns which refer to structures whose coefficients are to be equated. Thus the Eq. (13) becomes

$$\begin{vmatrix} 2(Q-W) & 10\alpha & 0 & 0 \\ 20\alpha & 15(Q-W)+10\alpha & 30\alpha & 0 \\ 20\alpha & 70\alpha & 20(Q-W)-40\alpha & 10\alpha \\ 0 & 20\alpha & 20\alpha & 5(Q-W)-30\alpha \end{vmatrix} = 0 \quad (15)$$

when we group together the first excited structures $B$ and $C$, and the second excited structures $D$ and $E$. On multiplying out the determinant, we find

$$100[3(Q-W)^4 + 22(Q-W)^3\alpha - 27(Q-W)^2\alpha^2$$
$$- 348(Q-W)\alpha^3 - 380\alpha^4] = 0$$

or $W = Q + 4.022\alpha$, for the lowest root. This value is in error by only $0.009\alpha$, and consequently is very good. If now we introduce the further simplification of neglecting the third excited structure $F$, we have merely to solve the cubic equation obtained by dropping the fourth row and column from (15). This leads to an energy of $W = Q + 3.954\alpha$, in error by $0.077\alpha$, which is still fairly satisfactory. If, however, the second excited structures, $D$ and $E$, are neglected as well, the energy obtained from the resulting quadratic equation is only $W = Q + 2.937\alpha$; and if all excited structures are neglected, the energy is simply $W = Q$. Thus the neglect of the highly

excited structures is not as satisfactory here as in the Slater treatment, and must be employed with considerable caution.

These same general conclusions are reached in a consideration of naphthalene. Here there are again 10 electrons and 42 canonical structures, but the symmetry of the molecule allows the reduction of the secular equation to be carried only as far as the sixteenth degree. Sherman[13] has given a complete treatment of this problem by the Slater method, and has shown that the rigorous solution is $W = Q + 4.0400\alpha$. We shall not solve the present equation rigorously,[15] but shall reduce it to the fifth degree by equating the coefficients of the first excited structures, those of the second, and those of the third. This gives

[14] The purpose of this step is to ensure that the subsequent adding of rows will equate the coefficients $a_R$, and not the products $a_{R}g_{R}$.

[15] Dr. J. Sherman and the author, however, have proved that it is completely equivalent to the Slater equation. The proof rests upon the fact that it can be made identical with the latter by the use of the familiar transformations

$$\begin{vmatrix} Q-W-\alpha & 0 & 6\alpha & 0 & 0 \\ 0 & 2(Q-W)-2\alpha & 12\alpha & 0 & 0 \\ 14\alpha & 20\alpha & 16(Q-W)-10\alpha & 38\alpha & 2\alpha \\ 8\alpha & 12\alpha & 72\alpha & 19(Q-W)-47\alpha & 12\alpha \\ 4\alpha & 8\alpha & -4\alpha & 20\alpha & 4(Q-W)-20\alpha \end{vmatrix} = 0.$$

(The same energy would be obtained if this equation were reduced still further to the fourth degree, by grouping the two different types of unexcited structures; i.e., by adding the first two rows and columns.) The lowest root is found to be $W = Q + 4.0241\alpha$, in error by only $0.0159\alpha$. This is somewhat better than the value of $W = Q + 4.0175\alpha$ which Sherman obtained by applying the same approximate treatment to his Slater-type equation. The neglect of the third excited structures leads to an energy of $W = Q + 3.7231\alpha$, which is to be compared with the value of $W = Q + 4.0172\alpha$, obtained by Sherman with the same assumption. Again we see that this latter approximation is not very satisfactory in the present method.

### Second method

It is readily seen by comparing (12) and (14) that the equation

$$\sum_R \sum_S a_R g_R (M_{RS} - \delta_{RS} W) c_S = 0 \qquad (16)$$

is rigorously true for any arbitrary choice of the constants $c_S$ if the $a$'s are correct, and for any arbitrary choice of the constants $a_R$ if the $c$'s are correct. Consequently, it must be very nearly true if both the $a$'s and the $c$'s are approximately correct. Rough values of the various coefficients can be obtained for this purpose most easily by the method of successive approximations. That is, we first arbitrarily insert in the Eqs. (12)—or (14)—any values of the $a$'s—or of the $c$'s—that may seem reasonable. In this way, we obtain a set of linear equations for $W$, the roots of which will not be mutually consistent unless the assumed values of the coefficients are accidentally correct. We then proceed systematically to improve the consistency by varying the coefficients one or two at a time. With a little practice,

of determinants (i.e., adding columns, etc.). This gives a practically complete check upon both equations.

this becomes quite a simple operation, and no great labor is required to obtain fairly satisfactory values. For example, in the case of cyclodecapentane, we find very easily that

$$a_A : a_B : a_C : a_D : a_E : a_F \cong 1:1/3:1/4:1/15:1/10:1/80,$$

and

$$c_A : c_B : c_C : c_D : c_E : c_F \cong 1:4/5:4/5:18/25:18/25:3/5.$$

When these values are inserted into Eq. (16), the resulting energy, $W = Q + 4.037\alpha$, is in error by only $0.006\alpha$.

### FURTHER APPROXIMATE METHODS APPLICABLE TO UNSATURATED AND AROMATIC HYDROCARBONS

If no great accuracy is desired, this last procedure can be made into a very simple one by the use of merely estimated coefficients. A fairly satisfactory empirical rule for doing this with the hydrocarbon molecules is as follows: Let $a = c = 1$ for all unexcited structures; $a = 3/10$ and $c = 5/6$ for all first excited structures; $a = (3/10)^2$ and $c = (5/6)^2$ for all second excited structures; and so on.* The sort of results that can be obtained by this method is indicated in Table III (third column from the left).

A still rougher approximation consists in letting all the $c$'s be equal to unity. Then Eq. (16) becomes

$$\sum_R \sum_S a_R g_R (M_{RS} - \delta_{RS} W) = 0$$

or

$$W = \sum_R \sum_S a_R g_R M_{RS} / \sum_R a_R g_R. \qquad (17)$$

Now, if we examine the various secular equations which have been set up above, we notice a very striking regularity, namely, that in all cases

* *Note added in proof:* Further investigation has shown that this rule is greatly oversimplified. The author expects to discuss the problem in further detail in a later paper.

TABLE III. *Approximate energies of unsaturated and aromatic hydrocarbons.*

| Compound | Correct[a] | Energy Approximate | | |
|---|---|---|---|---|
| | | I[c] | II[d] | III[e] |
| Benzene | $Q+2.61\alpha$ | $Q+2.58\alpha$ | $Q+2.68\alpha$ | $Q+2.5\alpha$ |
| Cyclooctatetrane | $3.30\alpha$ | $3.31\alpha$ | $3.34\alpha$ | $3.3\alpha$ |
| Cyclodecapentane | $4.03\alpha$ | $4.03\alpha$ | $3.99\alpha$ | $4.2\alpha$ |
| Naphthalene | $4.04\alpha$ | $4.02\alpha$ | $4.11\alpha$ | $4.0\alpha$ |
| Butadiene | $1.73\alpha$ | $1.75\alpha$ | $1.77\alpha$ | $1.8\alpha$ |
| Hexatriene | $2.48\alpha^b$ | $2.54\alpha$ | | $2.7\alpha$ |
| Octatetrane | $3.2\alpha^b$ | | $3.1\alpha$ | $3.5\alpha$ |
| Phenylethylene | $3.3\alpha^b$ | | $3.35\alpha$ | $3.3\alpha$ |
| Diphenylethylene | $5.6\alpha^b$ | | | $5.7\alpha$ |
| Triphenylethylene | $7.8\alpha^b$ | | | $8.0\alpha$ |
| Tetraphenylethylene | $10.1\alpha^b$ | | | $10.3\alpha$ |
| Biphenyl | $4.9\alpha^b$ | | $4.8\alpha$ | $4.8\alpha$ |
| Diphenylbenzene | $7.1\alpha^b$ | | | $7.2\alpha$ |
| Triphenylbenzene | $9.3\alpha^b$ | | | $9.5\alpha$ |

[a] L. Pauling and J. Sherman, J. Chem. Phys. 1, 679 (1933).
[b] These values were obtained by the Slater method, with only unexcited and first excited structures taken into consideration. Consequently the coefficients of $\alpha$ appearing here are lower limits to the true values.
[c] Values in this column were obtained from Eq. (16) with the use of estimated coefficients: $a = (0.3)^i$ and $c = (5/6)^i$ for all $i$th excited structures.
[d] Values in this column were obtained from Eq. (19) with $a$'s estimated as in column I.
[e] Values in this column were obtained from Eq. (21).

$$\sum_S M_{RS} = Q + n_R, \qquad (18)$$

where $n_R$ is the number of strong bonds between adjacent orbitals in the structure $R$. That is, $n_R = N$ for the unexcited structures, $n_R = N-1$ for the first excited structures, and so on. This rule is easily shown to be quite general, as long as the only interchanges to be considered are those between odd numbered and even numbered orbitals, the enumeration being carried out as described above. (page 234.) (In the type of problem under consideration, this is equivalent to the restriction that only interchanges between adjacent orbitals be considered, and that the molecule contain no odd-membered rings.) Thus, putting Eq. (18) into (17), we find

$$W = Q + \sum_R a_R g_R n_R / \sum_R a_R g_R. \qquad (19)$$

This relation makes it possible to calculate the approximate energy of the molecule *without setting up the secular equation at all.* One needs only to know the factors $g_R$ and the approximate values of the coefficients $a_R$. Some results obtained in this way—with the same assumptions as before in regard to values of the $a$'s—are given in Table III (second column from the right). It will be seen that these are really quite good. The value of this method—and of the immediately preceding—lies in the fact that the calculated

energy is not very sensitive to small changes in the coefficients, as long as these are of reasonable magnitudes.

Since Eq. (19) is rigorously true when the correct values of the $a$'s are inserted, it gives a very valuable check upon the results obtained by other methods. For example, when the coefficients given by Sherman[13] (column 1a in Table III, page 491) for the 16 different types of structure of naphthalene are used, the resulting energy is $W = Q + 4.0403\alpha$, in almost complete agreement with his value of $W = Q + 4.0400\alpha$. Consequently one can be quite certain that there is no large error in his work. When the degree of the secular equation is reduced by equating coefficients arbitrarily, Eq. (19) is no longer necessarily exactly true. Thus, with Sherman's fifth degree coefficients (column 1b in Table III), the energy becomes $W = Q + 4.0545\alpha$, which is different from the solution of the corresponding equation—$W = Q + 4.0175\alpha$.

There is one final approximate method which is useful for order-of-magnitude calculations. Like the last, it does not require that the secular equation be set up at all, and, in addition, it does not require any knowledge of the factors $g_R$. If all unexcited structures are given the coefficient $c = 1$, and all first excited structures the coefficient $c = \bar{c}$, then one can easily show that any equation of the set (14), for which $R$ refers to an unexcited structure, can be expressed in the form

$$Q - W + [N(2 - \bar{c}) + B(\bar{c} - 1)]\alpha = 0. \qquad (20)$$

Here $B$ is defined as the number of interchanges in the molecule for which the corresponding exchange integral is equal to $\alpha$—i.e., 6 for benzene, 11 for naphthalene, and so on. (The derivation of (20) assumes that all unexcited structures can be canonical simultaneously, and also that there are no "phantom orbitals," as in the case of the free radicals.[16]) The extreme variation of $\bar{c}$ seems to be approximately from 0.75 to 0.9 (this would give an upper and a lower limit to the energy), although it is possible that this limitation may not be valid in molecules widely different from those studied so far. If a rounded-off average value of $\bar{c} = 5/6$ is used, Eq.

[16] Cf. L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933).

(20) becomes

$$W = Q + \tfrac{1}{6}(7N - B). \qquad (21)$$

The results of a number of calculations by this method are given in the last column of Table III. It will be seen that these are considerably better than one would have any right to expect.

## STATES OF HIGHER MULTIPLICITY

The method of spin valence is especially advantageous in the treatment of systems of high multiplicity. The Slater method, of course, can also be extended to these cases, but, as far as the author is aware, no very convenient procedure for doing so has yet been described. The device of formally reducing the system to a singlet by the introduction of "phantom orbitals"[17] becomes very cumbersome as the multiplicity increases, and is hardly practicable except for doublet, and perhaps for triplet levels. The difficulty lies in the fact that this procedure does not allow the states under consideration to be separated from all those of lower multiplicity. The simplest possible example is the triplet level of the $H_2$ molecule. Here it is necessary to introduce two phantom orbitals, $x$ and $y$, in addition to the real ones, $a$ and $b$. There are then two structures,

$$
\begin{array}{ccccc}
a & b & & a\text{---}b \\
| & | & & \\
y & x & & y\text{---}x,
\end{array}
$$

which must be considered. (It is not legitimate to neglect the second, as would seem reasonable at first sight.) The secular equation is found in the usual way to be

$$
\begin{vmatrix}
Q - W - \tfrac{1}{2}\alpha & \tfrac{1}{2}(Q - W) + \tfrac{1}{2}\alpha \\
\tfrac{1}{2}(Q - W) + \tfrac{1}{2}\alpha & Q - W + \alpha
\end{vmatrix} = 0
$$

or $\qquad W = Q + \alpha, \quad Q - \alpha.$

Here, as before, $Q$ is the coulomb integral, and $\alpha$ is the single exchange integral between $a$ and $b$. All exchange integrals involving the phantom orbitals $x$ and $y$ vanish. Of the two roots, one corresponds to the singlet, and the other to the triplet level, but, before we can tell which is which, we have to calculate the singlet energy independently. This is found to be $W = Q + \alpha$, and consequently, the desired triplet energy is given by the second root, $W = Q - \alpha$. In the general

[17] Cf. L. Pauling, J. Chem. Phys. **1**, 280 (1933); L. Pauling and G. W. Wheland, ibid. **1**, 362 (1933).

case, the calculation can become quite complicated. In order to find the 20 quintet levels of an 8-electron problem, for example, we would have to solve a secular equation of the 132nd degree. Of the 132 roots thus obtained, 28 would correspond to the 14 singlet states (each occurring twice), 84 would correspond to the 28 triplet states (each occurring three times), and the remaining 20 would correspond to the desired quintet states.

A more straightforward application of the Slater method to such cases consists in actually setting up the proper number of independent wave functions, in the manner given by Kimball and Eyring,[6] and then evaluating the various matrix elements which occur in the secular equation. This latter is quite a laborious process, however, since no simple rules have yet been worked out for the states of higher multiplicity, analogous to those given by Kimball and Eyring[6] and by Pauling[17] for the singlet states.*

In contrast to the above, however, the method of spin valence is very simply applicable to systems of high multiplicity. The justification of the following procedure is quite straightforward, and will be left to the reader.[18] We introduce a *single* phantom orbital $L$, no matter what the multiplicity of the molecule may be, and to it we bond all the unshared electrons. (This apparent violation of the Pauli exclusion principle is legitimate here in consequence of the purely formal nature of the treatment.) Thus, for the triplet state of the $H_2$ molecule, we have the single structure

$$
\begin{array}{ccc}
a & & b \\
 \searrow & & \swarrow \\
 & L &
\end{array}
$$

The corresponding function is

$$\Psi = \tfrac{1}{2}\sum_i (-1)^i P_i \{ a(1)b(2)[\alpha(1)l_- - \beta(1)l_+]$$
$$\times [\alpha(2)l_- - \beta(2)l_+] \},$$

where $l_+$ and $l_-$ are constants, which are transformed under a rotation of axes in the same manner as $\alpha$ and $\beta$, respectively. The function $\Psi$ is readily seen to be a linear combination of the three components of the triplet. There are only

[18] Cf. M. Born, Ergebnisse d. Exakten Naturwiss. 1931, 387.
* *Note added in proof:* Since the above was written, a method has been given by R. S. Bear and H. Eyring, J. Chem. Phys. **3**, 98 (1935).

TABLE IV.

| $T_j$ / $\phi_i$ | $I$ | $(ab)$ | $(bc)$ | $(cd)$ | $(da)$ | $\Sigma$ |
|---|---|---|---|---|---|---|
| $A$ | $A$ | $-A$ | $A+B$ | $A$ | $C-B$ | $A(Q-W)-(A+C)\alpha$ |
| $B$ | $B$ | $B-A$ | $-B$ | $B-C$ | $B$ | $B(Q-W)+(A-2B+C)\alpha$ |
| $C$ | $C$ | $C$ | $C+B$ | $-C$ | $A-B$ | $C(Q-W)-(A+C)\alpha$ |

two permutations to be considered, the identity $I$, and the single interchange $(ab)$, both of which leave the structure unaltered. The secular equation is accordingly

$$|G_I+G_{(ab)}|=0 \quad \text{or} \quad |Q-W-\alpha|=0.$$

Thus the energy is simply $W=Q-\alpha$, in agreement with the result above.

A somewhat more complicated problem is that of the triplet states of cyclobutadiene. There are three structures to be considered
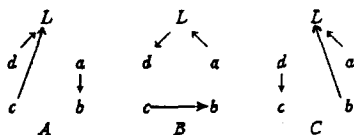


As before, a complete independent set of functions is obtained by arranging the orbitals in a circle and drawing all structures in which no two bonds intersect. The usual rules apply to the resolution of structures with crossed bonds, in terms of the canonical set. The functions are set up in a manner analogous to the one above for $H_2$. Corresponding to $A$, for example, we have

$$\Psi_A=\frac{1}{4(6)^{\frac{1}{2}}}\sum_i(-1)^iP_j\{a(1)b(2)c(3)d(4)$$

$$\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$\times[\alpha(3)l_--\beta(3)l_+][\alpha(4)l_--\beta(4)l_+]\}.$$

The calculation is given in Table IV.

The corresponding secular equation is

$$\begin{vmatrix} Q-W-\alpha & 0 & -\alpha \\ \alpha & Q-W-2\alpha & \alpha \\ -\alpha & 0 & Q-W-\alpha \end{vmatrix}=0.$$

The solutions are $W=Q$, $Q-2\alpha$, $Q-2\alpha$, in complete agreement with the results obtained by Hückel.[9]

As in the case of the singlet states, it would be

possible to carry through a discussion of such matters as the reduction of the secular equation by taking advantage of the symmetry of the molecule, and the approximate methods of solving the secular equations. This would lead to nothing essentially new, however, and consequently need not be discussed here in any further detail.

ORBITAL DEGENERACY

The problem of orbital degeneracy can also be treated by the method of spin valence. As in the case of the Slater method, however, the treatment becomes too complicated to be of very much use, except in actual numerical calculations for quite simple systems. We can represent a general wave function as

$$\chi=\frac{1}{(2^N(2N)!)^{\frac{1}{2}}}\sum_i\sum_k\sum_j(-1)^ja_{ik}(P_ju_i)(P_j\varphi_k),$$

where the $u_i$'s are functions of the spatial coordinates (analogous to the $u$ of Eq. (3)), the $a_{ik}$'s are constants to be chosen so as to give the best possible function $\chi$, and the other symbols have the same significance as before. Some simplification is afforded by the fact that whenever $u_i$ assigns two electrons, say $r$ and $s$, to the same orbital, then $a_{ik}$ will vanish unless $\varphi_k$ contains the factor $[\alpha(r)\beta(s)-\beta(r)\alpha(s)]$. If we apply perturbation theory by setting $(H-W)\chi=0$ and by then proceeding in the same manner as before, we obtain

$$\sum_i\sum_k\sum_j a_{ik}G_{ji}b_{kl}^{(j)}=0 \quad (l=1, 2, \cdots p_N).$$

This set of simultaneous homogeneous linear equations for the $a_{ik}$'s takes the place of the set (9), and, like it, gives rise to a corresponding secular equation from which the energy can be obtained. It is doubtful if this method offers any advantages over the usual one, with which it is equivalent. It is given here only for the sake of completeness.