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MOLECULAR ENERGY LEVELS AND VALENCE BONDS

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Abstract

Electronic energy levels in molecules are discussed, by the same methods previously used in discussing atomic levels. The problem in general is much more difficult than for atoms, and less progress can be made toward quantitative solution. For the lowest electronic level in cases where there are definite valence bonds, however, approximate solutions can be set up which should be fairly accurate, and which lead to a definite verification of the ideas of the writer and of Pauling regarding directed valence and the importance of concentrated bond functions. A number of special cases are discussed, involving both spin and orbital degeneracy.

THE writer has described in a previous paper[1] a method of discussing the structure of atoms according to wave mechanics. The purpose of the present paper is to extend similar methods to a consideration of electronic levels in molecules, particularly the lowest levels, resulting in molecular binding, giving first a general discussion and then some applications to specific cases. The molecular problem is in general much more difficult than the atomic one, and the definite results which can be obtained are far fewer. Nevertheless we can obtain some general properties of polyatomic molecules, in particular the directional properties of the valence bonds, which have already been qualitatively discussed by the present writer, and independently by Pauling.[2] In this connection we should mention recent papers by Heitler and Rumer and Weyl,[3] also discussing the quantum theory of valence bonds. These discussions are in one important respect more specialized than that of the present paper: they assume that the energy involved in molecular binding is small compared with that involved in the atomic multiplet structure in the atoms which compose the molecule, so that they can neglect all but the lowest atomic levels in discussing the molecular formation. This assumption is hardly justified in actual cases; and, more important, the characteristic directional properties which we have emphasized do not appear in this approximation at all, as Heitler and Rumer find, and as we shall show in a later section. Thus we cannot regard the treatment of Heitler and Rumer as being sufficiently general to be of very great physical significance, although in some special cases it is no doubt of value.

The first part of the discussion, in sections 1 to 4, deals with the general

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

[2] J. C. Slater, Phys. Rev. **37,** 481 (1931); Linus Pauling, Journ. Am. Chem. Soc. **53,** 1367 (1931).

[3] W. Heitler and G. Rumer, Zeits. f. Physik, H. Weyl, Göttinger Nachr., 285 (1930), 33 (1931).

description of the method, and is essentially similar to the method of dealing with atoms already described in the previous paper. In section 5 we take up a variety of special cases, developing most of the characteristic features in which the treatment of molecules differs from that of atoms by means of these illustrations. Section 6 summarizes these features, and sketches a general method for treating the lowest electronic levels of molecules in which the valence binding is of a conventional sort.

This paper was written while the writer was spending the summer at the University of California. He wishes to express his appreciation of valuable discussion with various persons there, particularly Dr. Henry Eyring.

(1) The Perturbation Theory

In the perturbation theory, it is assumed that we are given initially a set of functions u_i^0, forming in some way approximations to the real solutions of the problem. Then we try to set up linear combinations of these functions, $u_i = \Sigma(k) S_{ik} u_k^0$, which form much better approximations to the solutions. If H is the Hamiltonian operator of the problem, W_i the energy value associated with this function u_i, then Schrödinger's equation $Hu_i = W_i u_i$ becomes $\Sigma(k) S_{ik} H u_k^0 = W_i \Sigma(k) S_{ik} u_k^0$. Multiplying by u_j^{0*} and integrating, we have

$$\sum(k)(H_{jk} - W_i d_{jk}) S_{ik} = 0,$$

where $H_{jk} = \int u_j^{0*} H u_k^0 \, dv$, $d_{jk} = \int u_j^{0*} u_k^0 \, dv$. These form a set of simultaneous linear equations for the S's, which in general have no nonvanishing solutions unless the determinant of coefficients $(H_{jk} - W_i d_{jk})$ vanishes. Setting this equal to zero gives an algebraic equation for the energy levels W_i, and from the resulting values we can write and solve the equations for the S's. If the set of u_i^0's formed a complete set of functions, and if the linear equations and secular equation were rigorously solved, the resulting energy values and wave functions would be exact. But actually we are always driven to use some form of approximation.

First, the conventional perturbation theory commences by assuming that each unperturbed function u_i^0 is very nearly equal to the correct function u_i. Then H_{jk} is very nearly a diagonal matrix, whose diagonal terms H_{ii} are very nearly equal to the correct energy values W_i, and S_{ik} is very nearly diagonal, the diagonal elements being nearly unity. Thus we can make a power series expansion in terms of these various small quantities, with confidence that the series will converge. The familiar perturbations of first order, second order, etc., come from the successive terms of this expansion. Although this method is treated in most discussions as if it were the standard method of perturbations, there are as a matter of fact very few cases where it can be applied.

Instead, we generally meet the problem of degeneracy. Suppose that, in the absence of some perturbation, a number of stationary states have the same energy. Then any linear combination of their wave functions forms a correct wave function associated with that energy. In general, the particular combinations which we happen to have depend on convenience in setting them up. Now if the perturbation is applied, and the energy levels split up, we no longer have this freedom of making linear combinations. The wave functions which are solutions of the unperturbed problem may be chosen as the u^0's, but then in general we shall not have one correct function u_i nearly equal to a corresponding unperturbed one u_i^0. Rather we shall have one correct one nearly equal to a certain linear combination of a set of unperturbed ones connected with the same unperturbed energy level. Thus we shall no longer have all nondiagonal matrix components of H nearly zero, and we cannot directly use the power series method. But it may happen that we choose our unperturbed functions in just such a way that these nondiagonal terms are zero anyway, and that we can expand in series after all. The perturbation method as applied to degenerate systems accomplishes just this. Its first step is to set up a so-called "zero order approximation." It does this by considering separately the small square parts of the matrix H_{jk} associated with states grouped together into a single degenerate set. By suitable linear transformations we can set up an intermediate set of functions u_i', such that just these nondiagonal components of the energy vanish. For a single square, the equations for the transformation are just like those written above for the general case, except that the indices run only over the finite set of degenerate states. Thus, at least sometimes, the problem is simple enough so that we can solve for the zero order functions u_i'. Next we can apply the regular perturbation theory, seeking a second transformation to the correct functions u_i, and solving by the power series method.

In actual problems in atomic and molecular structure, the method of formulating the perturbation problem which seems most suitable is based on the conventional method for degenerate systems, rather than on the power series method. The essence of the scheme is that we take a finite set of unperturbed functions, set up the finite secular equation and transformation coefficients, and so solve for a finite number of almost correct functions and energy level. Thus, having only finite things to work with, we have a real chance of obtaining exact solutions. Yet instead of taking together merely those few states associated with a really degenerate group of levels, we enlarge this group when feasible, to include all the neighboring levels which influence each other in an important way. At least in principle, we can imagine that we would add to our accuracy by considering more and more levels in our secular equation, approaching in the limit the exact solution, as mentioned in a previous paragraph. The conventional description of zero order, first order, and so on, of perturbation, is not applicable in this case. By analogy with the method used for degenerate systems, we have merely a zero order approximation. Yet actually our accuracy in most cases will be better than that of the first or second order approximations of the other methods, since as far as neighboring levels are concerned, we have what might be called infinite order approximations.

Our method, then, is this. We take a finite set of functions u_k^0, $k=1 \cdots n$, and set up an equal number of linear combinations of them, $u_i=\Sigma(k=1 \cdots n) S_{ik}u_k^0$, where the S's are determined by

$$\sum(k = 1 \cdots n)(H_{jk} - W_i d_{jk})S_{ik} = 0,\ i, j = 1 \cdots n,$$

and where the energy levels W_i are the roots of the nth degree secular equation formed by setting the determinant of coefficients equal to zero.

One interesting observation relating to the method is the following: we may regard u_i as being a function containing the n parameters S_{ik}, $k=1 \cdots n$. If then we apply the variation method to our problem, stating that that function is the nearest to a solution of Schrödinger's equation which makes the mean energy $\int u_i^* H u_i \, dv$ stationary with respect to variation of the parameters, keeping $\int u_i^* u_i \, dv$ always equal to unity, then a simple application of the method of undetermined multipliers leads to equations for the S's, which are identical with the linear equations obtained above from the perturbation method. Thus our procedure can be equally well considered as a method of perturbations or of variations.

Having stated our method of perturbations, we may now proceed to the problem. There are three important parts to it, forming the subjects of the three following sections: first, setting up the unperturbed functions; second, setting up the matrix components of energy and unity with respect to these functions: third, solving the secular equation and equations for the S's.

(2) UNPERTURBED WAVE FUNCTIONS

The unperturbed wave functions u_i^0 from which we start are all functions of coordinates and spin, antisymmetric in the electrons. We build them up, for molecules as for atoms, from combinations of one-electron wave functions. In this we differ from the other writers, as Heitler and Rumer, who have worked in this field, for they assume the atomic problem already solved, and build up molecular functions out of atomic functions rather than electronic ones. There seem, however, to be essential advantages in the present method, which have been missed by the other writers.

Suppose there are N electrons in our system, whether it be an atom or a molecule. Then to set up a single unperturbed function, we assign a single set of quantum numbers, or one-electron wave functions, to the electrons. For example, let us suppose that one has the wave function A, another the function B, etc., up to a final function E, say. Each of these is a function of three coordinates of position, and one of spin, of a sort which we discuss later. Let the coordinates (of position and spin) of the first electron be denoted by 1, of the second by 2, etc. Then we could set up an approximate function as the product

$$A(1)B(2) \cdots E(N).$$

But this would not be antisymmetric in the electrons, and to set up such a function, we add together all $N!$ functions formed by making all possible permutations of the functions $A \cdots E$ (which by the exclusion principle must be all different), each with a coefficient $\pm 1/N^{1/2}$, depending on whether the permutation is even or odd. Thus if $PA(1)B(2) \cdot E(N)$ represents a function in which such a permutation has been made, we have as our function

$$\frac{1}{N^{1/2}} \sum \pm PA(1)B(2) \cdots E(N)$$

or, written as a determinant,

$$\frac{1}{N!^{1/2}}\begin{vmatrix} A(1) & A(2) & \cdots & A(N) \\ B(1) & B(2) & \cdots & B(N) \\ \cdot & \cdot & \cdot & \cdot \\ E(1) & E(2) & \cdots & E(N) \end{vmatrix}$$

The factor $1/N!^{1/2}$ is inserted in order partly to take care of normalization. If A, B, $\cdots E$ are normalized (as we assume them to be), then if they are also orthogonal, the whole function will be normalized. We do not assume A, B, etc. to be actually orthogonal, but in any case this choice of a factor simplifies the formulas.

We have seen that to each set of one-electron functions A, B, $\cdots E$ corresponds just one antisymmetric function for the whole system. In our perturbation problem, however, we consider a whole group of such antisymmetric functions, and therefore a whole group of sets of one-electron functions. The degeneracy involved arises from two sources: spin degeneracy, and orbital degeneracy. This is a direct consequence of the fact that the quantum numbers of an individual electron are divided into those depending on the orbit, and that depending on the spin, and the fact that the wave function of the electron can be written as a product of a function of the coordinates, and a function of spin.

In the first place, we consider spin degeneracy. Suppose we are given a single set of orbital one-electron functions. Corresponding to this, we have a rather large number of possible arrangements of the spins. For example, if the orbital functions are all different, each spin can be either parallel or antiparallel to the axis, so that if we consider all possibilities there will be 2^N different arrangements, and the same number of unperturbed wave functions. After solving the perturbation problem, these yield a doublet level for one electron ($2^1=2$), a singlet and a triplet for two electrons ($2^2=1+3$), two doublets and a quartet for three electrons ($2^3=2+2+4$), two singlets, three triplets, and a quintet for four electrons ($2^4=1+1+3+3+3+5$), and so on. Or if the orbital functions are not all different, some of these arrangements are not allowed on account of the exclusion principle, each pair of equal functions contributing only one possibility rather than four, so that two equivalent electrons have only a singlet level, two equivalent ones and one other a doublet, two equivalent ones and two others a singlet and triplet, and so on.

Next we consider orbital degeneracy. We must take, not merely one set of one-electron orbital functions, but usually a number of such sets. Each set will have all the possible spin arrangements, so that the number of unperturbed functions which we use can become considerable. We shall find, however, that we can often choose our orbital functions in advance so as to simplify the problem by obtaining groups of terms which do not influence each other. The actual way of choosing the orbital functions is a question about which there might be considerable difference of opinion. In the first place, we could choose functions which are solutions of a central field problem, as is done in the atomic case, and as Heitler and London[4] have done in discussing molecules. Or second, we could use solutions of the problem of many centers, as Lennard-Jones[5] has done in molecular problems, and as Bloch[6] has done in the problems of metals. In the present paper we shall confine ourselves to the first method, although we do not wish to indicate that the other method is not sometimes valuable. Even if we use only solutions of a central field problem, still it is not obvious which functions we should use. In an atom, it is easy to answer this question: we use functions corresponding to a definite azimuthal quantum number, and a definite component of angular momentum along a fixed direction. The essential reason for doing this is that the total component of angular momentum along a fixed direction is quantized, so that this choice of functions produces a splitting up of the terms into different groups, which do not combine, and which therefore can be treated separately, greatly simplifying the calculation. With diatomic molecules, if the axis is chosen as the axis of figure, we have the same simplifying feature. But with polyatomic molecules, unless they happen to be linear, this is no longer the case. The torques acting on the electrons are such that the component of orbital angular momentum in every direction changes with time, and no longer is quantized. The conventional wave functions, determined by the quantum numbers n, l, m_l, no longer have any particular advantage. We shall as a matter of fact find that in many cases different choices of wave functions will very decidedly simplify the calculation. Examples of this will be pointed out later. The essential idea of using such different wave functions is that in many cases we can choose them so that the lowest state of the molecule can be determined from one set of orbital functions alone, without considering any orbital degeneracy. To do this, however, requires very careful choice of the functions. We shall find in the end that they must be chosen essentially according to the criterion which has been stated by the writer and by Pauling: they must be such as to give as much overlapping as possible with the other electrons to which they are held by valence bonds, and as little as possible with electrons to which they are not held. That is to say, they must be concentrated bond functions. In many cases, too, it is necessary for these lowest states to proceed as Pauling has, using functions in which not merely the component of angular momentum along a fixed axis is not quantized but where even the total angular momentum is not determined. That is, we use functions which are not s, or p, or d electrons, but are mixtures of all these. A criterion like that of Pauling, for getting most concentrated bond functions, would be applied to know which function to use in any particular case. We shall see later by examples just how the functions should be chosen in particular cases.

(3) MATRIX COMPONENTS

Suppose we have two antisymmetric wave functions, one (U) formed from the one-electron wave functions $A \cdots E$, the other (U') from the one-electron

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[4] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[5] J. E. Lennard-Jones, Trans. Faraday Soc., **25**, 684 (1929).

[6] F. Bloch, Zeits. f. Physik **57**, 545 (1929).

functions $A' \cdots E'$. Suppose also that we have some operator F, whose matrix component we desire between these two functions. Later we may specialize by letting F be the energy, unity, or other quantities. Then by definition, using the formula for antisymmetric wave functions, our matrix component is $\int U^*FU'\,dv = (U/F/U') =$

$$\frac{1}{N!}\int \sum \pm PA^*(1)B^*(2)\cdots E^*(N)F\left(\sum \pm PA'(1)\cdots E'(N)\right)dv,$$

where we therefore have a double summation, over permutations in each function. But now on account of the fact that the only operators F which we meet are symmetric in the electrons, we see that each term of the first summation yields the same result, and since there are just $N!$ terms the result can be written as a single sum,

$$\int A^*(1)B^*(2)\cdots E^*(N)F\left(\sum \pm PA'(1)\cdots E'(N)\right)dv.$$

Each term of the summation is of the form

$$\int A^*(1)B^*(2)\cdots E^*(N)FA'(1)\cdots E'(N)dv,$$

and such an integral we shall symbolize as

$$(AB\cdots E/F/A'\cdots E').$$

We shall meet such integrals constantly, and shall write our various "exchange integrals" in this form. We can then symbolize our whole matrix component as $\Sigma \pm (AB\cdots E/F/PA'\cdots E')$.

One simplification arises when we introduce the spin part of the wave functions separately, and when F is independent of spin, or of magnetic effects. If then a is the part of the function A depending on coordinates, etc., we have $(AB\cdots E/F/A'\cdots E') = (ab\cdots e/F/a'\cdots e')$ if A and A' have the same spin, and so on down to E and E' having the same spin; but it equals zero otherwise.

In case $AB\cdots E$, $A'\cdots E'$ are all orthogonal to each other, many simplifications appear, which were met with in the atomic problem, but do not generally appear in the molecular problem. Two forms of operator are of particular interest, those of the form $F = \Sigma_i f_i$, a sum of terms each depending on the coordinates of one electron, and those of the form $G = \Sigma$ (pairs ij) g_{ij}, a sum of terms each depending on the coordinates of a pair of electrons. In this case it is easily shown that the following results hold, where U and U' represent two antisymmetric wave functions:

$$(U/F/U) = \Sigma(a)\ (A/f/A)$$

$$(U/F/U') = (A/f/A'),\ \text{if } U' \text{ differs from } U \text{ by just one index, } A \neq A',$$
$$= 0 \text{ otherwise.}$$

Also

$$
\begin{aligned}
(U/G/U) &= \Sigma \text{ (pairs } AB\text{) } ((AB/g/AB) - (AB/g/BA))\\
(U/G/U') &= \Sigma(B \neq A)\, ((AB/g/A'B) - (AB/g/BA')), \text{ if } U' \text{ differs from } U\\
&\quad \text{by one index, } A' \neq A\\
&= (AB/g/B'A') - (AB/g/B'A'), \text{ if } U' \text{ differs from } U \text{ by two}\\
&\quad \text{indices, } A' \neq A,\ B' \neq B\\
&= 0 \text{ otherwise.}
\end{aligned}
$$

In these equations,

$$(A/f/B) = \int A(1) f_1 B(1) dv_1$$

$$(AB/g/CD) = \iint A(1)B(2) g_{12} C(1) D(2) dv_1 dv_2.$$

If in particular F and G do not involve the spins, we have just functions of the coordinates coming into the expressions above: $(A/f/B)$ is zero unless a and b are connected with the same spin, in which case it equals $(a/f/b)$, where a and b are orbital functions, and $(AB/g/CD)$ is zero unless A and C are connected with the same spin, and also B and D, in which case it equals $(ab/g/cd)$. Although in molecular problems we generally have one-electron functions which are not orthogonal to each other, still they do not depart far from orthogonality, and for that reason terms which are entirely absent according to the rules above are likely to be small for molecules. Thus for instance, since energy operators are of the form F and G, the components of energy are small between two functions which differ in respect to more than two electrons.

It is worth while to consider the form which the matrix components of energy will take in actual cases. The energy operator for a molecule with fixed nuclei is

$$H = -\frac{h^2}{8\pi^2 m} \sum_i \nabla_i^2 - \sum_{i\alpha} \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{\alpha\beta} Z_\alpha Z_\beta / r_{\alpha\beta} + \sum_{ij} e^2/r_{ij}.$$

In this, the summations over i and j are over the electrons, those over α and β are over the nuclei. The Z's represent the nuclear charges, in electronic units, and the r's the distances of separation. We now allow this operator to act on a function $a(1) \cdots e(n)$. In doing this, we note the equations which the functions a, etc., satisfy. These are of the form

$$\frac{-h^2}{8\pi^2 m} \nabla^2 a = (V_a - E_a) a$$

where V_a is a potential function for the one electron problem, E_a an energy level. Substituting, we have

$$
\begin{aligned}
Ha(1) \cdots e(n) = \Bigg(\sum_a (V_a - E_a) &- \sum_{i\alpha} Z_\alpha e^2 / r_{i\alpha}\\
&+ \sum_{\alpha\beta} Z_\alpha Z_\beta / r_{\alpha\beta} + \sum_{ij} e^2/r_{ij} \Bigg) a(1) \cdots e(n).
\end{aligned}
$$

All terms but the last are either constants or functions of single electrons, and so form the functions f; the last sum represents a sum over all pairs of electrons, and so is the sum of g's.

When now we multiply this by another wave function, and integrate, we obtain terms of two sorts. First, there are the small terms which result entirely from lack of orthogonality of the functions. Similar terms to these would also be found in the matrix of unity, and in the final calculation most of them will cancel out. For instance, in computing the mean value of a constant term in the energy over any unperturbed function, we must get just this constant itself. Yet this often comes about by having such terms in an energy expression in a numerator of a fraction, and corresponding terms in matrix elements of unity in a denominator, so that finally these terms just balance out. These terms, then, though they must be considered in the actual calculation, are not of particular theoretical interest, and need not be discussed further.

The terms of the second sort are similar to the Coulomb and exchange integrals which Heitler and London found in the problem of the diatomic molecule, or to the similar integrals within the atoms which we meet in complex atomic spectra. Thus for instance if we have the Coulomb integral $(ab \cdots e/H/ab \cdots e)$, the result is essentially similar to a sum of Coulomb interactions between all pairs of electrons in the molecules. With the simple resonance integral, $(ab \cdots e/H/ba \cdots e)$, where the two functions differ just in the interchange of functions a and b, connected with different atoms, the leading terms form just the sort of exchange integral between a and b that Heitler and London would have found if the molecule contained no other electrons. If the two functions differ by a cyclic permutation of three electrons, as $(abc \cdots e/H/cab \cdots e)$, we have an integral which would be zero if the functions were orthogonal, and which will be much smaller than the simple exchange integrals in any case. It is hardly worth while in a general discussion to go more into details about the various integrals. One thing should be noted, however, for the guidance of any one making actual calculations: it is necessary to analyze carefully the exact relations of the functions V_a and the various terms in $1/r$ in the energy. Some of the terms refer to interactions within the various atoms, others to interactions between atoms, and a careful separation of them is essential. It is much safer to formulate the problem in a general way, including all electrons of the problem, as we have sketched here, and then eventually to show that some terms are independent of interatomic distance and lead to atomic energies, than just to start out as if the atoms consisted only of valence electrons surrounding a nucleus of some effective nuclear charge, even though the latter method gives qualitatively the correct interpretation of multiplet levels, valence, and so on.

(4) SOLUTION OF THE SECULAR EQUATION

In the last two sections, we have sketched the method to be used in setting up unperturbed wave functions, and in calculating matrix components of the energy and of unity with respect to them. We are now able to set up the secular equation for the energy, and the next problem is to try to solve it. The equation is an algebraic one of high order, and without special devices we cannot hope to attack it successfully. In the atomic problem, it was generally possible to find enough special properties of the equation to permit of its complete solution, without any difficulty whatever. In the first place, each unperturbed state was characterized by two quantities, the component of orbital and spin angular momentum along a fixed axis, which we called M_L and M_S respectively, which remained constant when we applied the perturbations. As a result of this, we could divide the states into groups, each with a particular M_L, M_S, and each such group could be treated independently of the others. H had no matrix components from one group to another, so that the secular equation broke up into a product of factors, each connected with one group. This automatic factoring of the equation helped with the solution, but a further principle also was of service. It could be proved by independent methods that all the roots of the partial equation connected with a given M_L, M_S, were also roots of the equations connected with any group with smaller M_L or M_S. Thus we knew some, at least, of the roots of each partial equation, provided we had already solved the equations connected with larger M_L and M_S. As a matter of fact, proceeding in a systematic manner, it was found that in every case discussed, all but one root of each partial equation could be determined in this way. Now when all but one of the roots of an algebraic equation are known, it is very easy to solve for the other one. We can merely use the theorem that the sum of the roots equals the coefficient of the next to the highest power of the unknown, provided the coefficient of the highest power in unity. Thus by subtracting the known sum of all but one root from the known sum of all the roots, we get immediately the desired root. Since our equation is written in the form of a determinant, it can be shown immediately that the desired coefficient, equal to the sum of roots, is simply the sum of all the diagonal elements H_{ii} appearing in the determinant. Thus in the atomic case we were actually able to dispense with the calculation of all elements except these diagonal ones, and we encountered no equations except linear ones, so that all energies were linear functions of the various integrals.

In the molecular problem, the method is not so easy. The orbital angular momentum is no longer quantized, and the only special fact which we have left is that the levels are separated into groups with different values of M_S, resulting in a factoring of the equation into sub-equations, and the occurrence of all the roots of one equation in the next lower equation. The net result of this is that we can break up the terms into groups, each containing all the terms of the same multiplicity. Thus if there is just one term of a given multiplicity, its energy will be given linearly in terms of the various integrals; if there are two the energies will be given as roots of a quadratic, and so on. In other words, for practical purposes we are limited, as far as exact solutions are concerned, to cases where no more than two terms of the same multiplicity occur. For example, suppose our problem is one in which all electrons have different but definite orbital wave functions, and in which the only degeneracy is that of spin. Then two electrons give a singlet and triplet, each of which we can get explicitly (as Heitler and London did in the case of H_2, an example of this case). Three electrons give a quartet and two doublets, and the quartet comes linearly in terms of the integrals, the two doublets as the two roots of a quadratic. Four electrons give a quintet, which can be obtained, three triplets, which could be found only as the roots of a cubic, and two singlets, the roots of a quadratic. Fortunately the molecular levels of lowest multiplicity are stable, so that with four electrons we can still get the energy of the lowest level explicitly. But with five or six electrons there are five doublets, or five singlets, respectively, and the solution can no longer be found by elementary methods. In diatomic molecules, special properties of symmetry in the nuclei, and other such things can produce a possibility of still further factoring, and can simplify the solution. But in general such methods are not applicable in polyatomic molecules, and we shall therefore not make particular use of them.

Fortunately the cases which we can solve exactly include some important ones, in which we can examine the relative sizes of various terms. When we do this, it appears that certain approximate methods can be legitimately used, when we are interested only in the lowest molecular level. These methods amount to choosing a particular combination of unperturbed functions as the most likely one, by a method suggested by the chemical method of drawing valence bonds, and using as the energy simply the mean value of H averaged over this combined wave function. We shall show that this gives results which are quite satisfactory in the cases where we can check them up, and that it leads in general to physical results concerning energy levels and valence bonds which are of great interest. The special cases will be discussed in the next section, and these general considerations will be described in the concluding section.

(5) Illustrations in Typical Cases

(a) Two atoms, each with one *s* electron

As a first simple illustration, we take the interaction of two atoms each containing a single *s* electron (H_2, Na_2, NaK, etc.).[7] Let a be the wave function (of coordinates only, not involving spin), of an electron on the first nucleus, b the function of an electron on the second. Since the electrons are *s* electrons, there is no orbital degeneracy to consider. As a result of spin degeneracy, there are four unperturbed functions: In this table, + means that the component of the electron's spin along an arbitrary axis is $+\frac{1}{2}h/2\pi$, and − means that it is $-\frac{1}{2}h/2\pi$. A total spin of 1 means really $1h/2\pi$. Now a triplet has

	Spin of a	Spin of b	Total spin
I	+	+	1
II	+	−	0
III	−	+	0
IV	−	−	−1

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[7] This problem has been discussed in detail by N. Rosen, Phys. Rev. **38**, 255 (1931).

three degenerate levels, of total spin 1, 0, -1, and a singlet has one level, of spin 0. Hence we have a triplet and a singlet. Further, if we work out matrix components of energy and unity, we find that there are no components between states of different spin, so that I, IV stand all by themselves, and II and III are grouped together. Now we can work out our matrix components according to the rules of section 3. We have

$$H_{\mathrm{I},\mathrm{I}} = (ab/H/ab) - (ab/H/ba)$$
$$d_{\mathrm{I},\mathrm{I}} = (ab/1/ab) - (ab/1/ba) = 1 - (ab/1/ba),$$

if a and b are normalized. Thus we have as one factor of the secular equation merely

$$((ab/H/ab) - (ab/H/ba)) - W(1 - (ab/1/ba)) = 0,$$

or

$$W = \frac{(ab/H/ab) - (ab/H/ba)}{1 - (ab/1/ba)}.$$

This is evidently the energy of the triplet. Next we compute the other components:

$$H_{\mathrm{II},\mathrm{II}} = (ab/H/ab) = H_{\mathrm{III},\mathrm{III}}$$
$$H_{\mathrm{II},\mathrm{III}} = H_{\mathrm{III},\mathrm{II}} = -(ab/H/ba)$$
$$d_{\mathrm{II},\mathrm{II}} = d_{\mathrm{III},\mathrm{III}} = 1$$
$$d_{\mathrm{II},\mathrm{III}} = d_{\mathrm{III},\mathrm{II}} = -(ab/1/ba).$$

Then we have the following secular equation between states II and III:

$$\begin{vmatrix} (ab/H/ab) - W & -(ab/H/ba) + (ab/1/ba)W \\ -(ab/H/ba) + (ab/1/ba)W & (ab/H/ab) - W \end{vmatrix} = 0,$$

or $((ab/H/ab)-W)^2-(-(ab/H/ba)+(ab/1/ba)W)^2=0$. This equation can be factored at once into

$$((ab/H/ab) - (ab/H/ba) - (1 - (ab/1/ba))W)\times$$
$$((ab/H/ab) + (ab/H/ba) - (1 + (ab/1/ba))W) = 0.$$

Setting the first factor equal to zero, we obtain just the triplet solution already found. In fact, if we did not know how to factor or otherwise solve our quadratic, we could have divided it through by this linear factor, and the resulting linear equation would have given us the singlet directly. This gives as the singlet energy

$$W = \frac{(ab/H/ab) + (ab/H/ba)}{1 + (ab/1/ba)}.$$

When we examine the meaning of the integrals, we see that $(ab/H/ab)$ is Heitler and London's H_1, $(ab/H/ba)$ is their H_2, and $(ab/1/ba)$ is their S^2. Thus these results agree exactly with the ones which they derive.

It is worth while to solve also for the coefficients determining the correct linear combinations of wave functions. We find of course that I and IV give directly two of the three components of the triplet. Substituting the energy values into the equations for II and III, we find that except for a normalizing factor, the third function connected with the triplet is II+III, and the singlet function is II−III. It is to be noted that this result seems at first sight strange, when compared with the well-known fact that the triplet functions are antisymmetric in the coordinates of the two electrons, while the singlet functions are symmetric. We might at first sight expect the signs to be reversed. But if we actually put in the functions of coordinates and of spin, we find that the singlet function II−III is really symmetric in the coordinates, antisymmetric in spin, so that it is all right.

(b) Three electrons, with only spin degeneracy

The preceding case was really the general one of two electrons, with orbital wave functions a and b, with only spin degeneracy. Next we consider the case of three such electrons, with functions a, b, and c. We expect a quartet and two doublets. There are eight unperturbed functions. State I and VIII by themselves give two of the four states of the quartet. II, III, IV give a cubic, one of whose roots gives another state of the quartet, and the other two roots give the two doublets. Similarly V, VI, VII yield the fourth state of the quartet, and the other two states of the doublets. We have then

	Spin of a	Spin of b	Spin of c	Total spin
I	+	+	+	3/2
II	+	+	−	1/2
III	+	−	+	1/2
IV	−	+	+	1/2
V	−	−	+	−1/2
VI	−	+	−	−1/2
VII	+	−	−	−1/2
VIII	−	−	−	−3/2

$$H_{\mathrm{I},\mathrm{I}} = (abc/H/abc) - (abc/H/bac) - (abc/H/acb) - (abc/H/cba) + (abc/H/bca) + (abc/H/cab)$$

$$d_{\mathrm{I},\mathrm{I}} = 1 - (abc/1/bac) - (abc/1/acb) - (abc/1/cba) + (abc/1/bca) + (abc/1/cab).$$

The energy of the quartet is then

$$W = \frac{(abc/H/abc)-(abc/H/bac)-(abc/H/acb)-(abc/H/cba)+(abc/H/bca)+(abc/H/cab)}{1-(abc/1/bac)-(abc/1/acb)-(abc/1/cba)+(abc/1/bca)+(abc/1/cab)}$$

It is worth noting that if the functions a, b, c are nearly orthogonal, the last two terms of numerator and denominator will be small compared with the others, since they correspond to interchange of three electrons. Thus to an approximation we may write the formula without these terms. Of if we wish an even rougher approximation, we may leave out the terms in the denominator altogether, as we could if the functions were really orthogonal, obtaining a formula for the quartet

$$W = (abc/H/abc) - (abc/H/bac) - (abc/H/acb) - (abc/H/cba),$$

or the first term, minus the terms obtained by making each possible interchange of two electrons.

To investigate the doublet terms, we must consider the secular equation between II, III, and IV. We have

$$\begin{aligned}
H_{\text{II},\text{II}} &= (abc/H/abc) - (abc/H/bac)\\
H_{\text{III},\text{III}} &= (abc/H/abc) - (abc/H/cba)\\
H_{\text{IV},\text{IV}} &= (abc/H/abc) - (abc/H/acb)\\
H_{\text{II},\text{III}} &= (abc/H/cab) - (abc/H/acb)\\
H_{\text{III},\text{IV}} &= (abc/H/cab) - (abc/H/bac)\\
H_{\text{II},\text{IV}} &= (abc/H/cab) - (abc/H/cba).
\end{aligned}$$

The matrices of unity are just the same, with 1 substituted for H. In the last formula, we have used the fact that $(abc/H/bca) = (abc/H/cab)$. This follows from the following two steps: $(abc/H/bca) = (cab/H/abc)$, since from definition we can make any permutation of the first set of indices, if only we make an identical permutation of the second set at the same time; and $(cab/H/abc) = (abc/H/cab)$, since the matrices are Hermitian and real.

Instead of trying to solve the cubic equation between II, III, and IV, we shall adopt a method which we shall find useful in many cases. We introduce four linear combinations of the three functions, which we shall call A, B, C, and D, by the equations

$$\begin{aligned}
A &= 1/2^{1/2}(\text{II} - \text{III})\\
B &= 1/2^{1/2}(\text{III} - \text{IV})\\
C &= 1/2^{1/2}(\text{IV} - \text{II})\\
D &= \tfrac{1}{2}(\text{II} + \text{III} + \text{IV}).
\end{aligned}$$

These four functions cannot of course be linearly independent; as a matter of fact, as one immediately sees, $A+B+C=0$. Thus one can use three independent ones, as A, B, and D, for setting up a new secular equation. When we compute the matrices of H and of unity with respect to these functions, we discover immediately that all matrices between D and any one of the other three functions are zero. That means that our secular equation is already factored: one energy level is that obtained directly from D, or $H_{D,D}/d_{D,D}$, and the other two are roots of a quadratic obtained, say, from the functions A and B. Now the first energy value proves to be just the energy of the quartet, so that we see that D is the wave function of the quartet. The wave functions for the doublets are then two orthogonal linear combinations of A and B

(or A and B and C, which comes to the same thing). To set up the secular equation between A and B, we make use of one fact: since $A+B+C=0$, we have at once

$$\begin{aligned} H_{AA} + H_{AB} + H_{AC} &= 0 \\ H_{AB} + H_{BB} + H_{BC} &= 0 \\ H_{AC} + H_{BC} + H_{CC} &= 0. \end{aligned}$$

Eliminating from these equations, we have $H_{AB}=\frac{1}{2}(H_{CC}-H_{AA}-H_{BB})$. That is, we can write our nondiagonal elements of energy in terms of the diagonal elements. The same result holds for the matrix of unity. Now substituting in the secular equation, and using the abbreviations

$$H_{AA} = P,\ H_{BB} = Q,\ H_{CC} = R,\ d_{AA} = p,\ d_{BB} = q,\ d_{CC} = r,$$

we easily find that the solutions of the quadratic are

$$\begin{aligned} W = {} & \frac{P(p-q-r)+Q(-p+q-r)+R(-p-q+r)}{p^2+q^2+r^2-2pq-2qr-2pr} \\ & \pm \frac{2(P^2qr+Q^2pr+R^2pq+PQr(r-p-q)+QRp(p-q-r)+PRq(q-p-r))^{1/2}}{p^2+q^2+r^2-2pq-2qr-2pr}. \end{aligned}$$

This equation takes an interesting form in the case where we can neglect the lack of orthogonality of the functions II, III, IV. For then we have $p=q=r=1$, and the limiting form is

$$\begin{aligned} W &= \frac{P+Q+R}{3} \pm \frac{2}{3}(P^2+Q^2+R^2-PQ-QR-PR)^{1/2} \\ &= \frac{P+Q+R}{3} \pm \frac{2}{3}\left(\tfrac{1}{2}((P-Q)^2+(Q-R)^2+(R-P)^2)\right)^{1/2}. \end{aligned}$$

It is easily found that the diagonal elements of the matrix of H, required in these formulas, are

$$\begin{aligned} H_{AA} = P &= (abc/H/abc) + (abc/H/acb) - \tfrac{1}{2}((abc/H/bac) + (abc/H/cba)) \\ &\quad - (abc/H/cab) \\ H_{BB} = Q &= (abc/H/abc) + (abc/H/bac) - \tfrac{1}{2}((abc/H/acb) + (abc/H/cba)) \\ &\quad - (abc/H/cab) \\ H_{CC} = R &= (abc/H/abc) + (abc/H/cba) - \tfrac{1}{2}((abc/H/acb) + (abc/H/bac)) \\ &\quad - (abc/H/cab). \end{aligned}$$

The formulas for p, q, r, are the same with unity in place of H. In the limiting case where $p=q=r=1$, we can then use $P-Q=3/2((abc/H/acb)-(abc/H/bac))$, etc., obtaining[8]

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[8] F. London, Zeits. F. Electrochem. **35**, 552 (1929); Sommerfeld Festschrift, Hirzel, p. 104.

$$W = (abc/H/abc) - (abc/H/cab) \pm \left\{\tfrac{1}{2}(((abc/H/acb) - (abc/H/bac))^2 + ((abc/H/bac) - (abc/H/cba))^2 + ((abc/H/cba) - (abc/H/acb))^2)\right\}^{1/2}.$$

The method we have used deserves a certain amount of comment for its physical interest. The function A is essentially II–III. Now if the electron a were removed to a large distance from b and c, so that we had large interaction just between b and c, we should have the case of a diatomic molecule, and from the preceding section we see that this function would give just the singlet state of that molecule, the one givng strongest molecular binding. Thus A corresponds essentially to a valence bond between electrons b and c. Similarly B corresponds to a bond between a and b, and C to a bond between a and c. The real situation appears as a combination of these, taking some of the character of each. Generally one of the three bonds will appear much stronger than the others, and then the real wave function is much nearer the function A, B, or C, as the case may be, as we can find by actually working out the transformation coefficients.[9] The energy in such a case takes on a particularly simple form. We can get at this in either of two ways. First, we can expand the quadratic, regarding certain interaction integrals as being large, others small. For example, if the electron a were removed to a large distance, the integral $(abc/H/acb)$ would still be large, for it is essentially an exchange integral between b and c, but the integrals $(abc/H/bac)$ and $(abc/H/cba)$ would be small. Expanding the quadratic, taking for simplicity the case $p=q=r=1$, we have

$$W = (abc/H/abc) - (abc/H/cab) \pm (abc/H/acb) - \tfrac{1}{2}((abc/H/bac) + (abc/H/cba)).$$

The diatomic molecule bc by itself would have the energy $(abc/H/abc) \pm (abc/H/acb)$, where the a in the integrals plays a purely formal role. Thus we see that the addition of the electron a has two results: first, the small term $(abc/H/cab)$, coming from cyclic permutation of electrons, is introduced. This is unimportant. But second, the exchange integral $(abc/H/acb)$ between the electrons b and c is diminished by half the integrals $(abc/H/bac)$ and $(abc/H/cba)$ between a and b and c respectively. For example, if we take the negative sign, the interaction integral between b and c would normally give an attraction between these atoms. Then the interaction between a and the other atoms will be one of repulsion, but this repulsion will be only half as great as if b and c were not bound into a molecule. Physically, then, if a univalent atom approaches a diatomic molecule formed of two univalent atoms, the single atom will repel the molecule. On the other hand, if the atom approaches too closely, the approximation no longer holds, and it may even become bound to one of the atoms of the molecule, liberating the remaining atom of the molecule in the process, and resulting in a chemical reaction. The necessary energy which the molecule must have to rise over the hill of potential to the valley corresponding to the other form of molecule is the heat of activation, as has been shown by Eyring and Polanyi.[10]

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[9] Compare W. Heitler, Phys. Rev. **38**, 243 (1931).

[10] Eyring and Polanyi, Zeits. physik. Chem. **B12**, 279 (1931).

The second way in which we may get at the approximate energy, when the wave function is very nearly one corresponding to a pure valence bond is to notice that the functions A, B, C correspond exactly to these bonds, and that by first order perturbation theory the diagonal energy values of these states give the best approximations to the energy. Thus for the bond between atoms a and b, we have the state A, and we see that the diagonal energy $H_{AA}=P$ is exactly the same that we found by expanding the quadratic. More accurately, we should take the energy to be $H_{AA}/d_{AA}=P/p$. By taking advantage of this fact, we can avoid the necessity of expanding in quadratics entirely in many cases, although of course not in finding activation energies, for in that problem we must be able to pass continuously from one limiting case to another. For discussing a single molecule, however, the linear formula is in general sufficient, as we shall see as we progress. And we may well state in words the characteristic of the wave function and energy level which we have to express this case. The wave function is made up of the two unperturbed functions for which the electrons to be bound have opposite spins, the two functions being added with opposite signs. And the energy is the sum of the Coulomb interaction $(abc/H/abc)$, the exchange term $(abc/H/acb)$ between the electrons being bound, diminished by half the exchange term between the remaining electron and the two bound in the molecule, and further corrected by the cyclic term. As we progress, we shall find this general situation characteristic of valence binding.

(c) Four electrons, with only spin degeneracy

The case of four electrons, with functions a, b, c, d is similar in most respects to that of three. There are one quintet level, three triplets, and two singlets, so that we cannot get the triplets in explicit form without solving a cubic. Since the levels in which we are most interested are the singlets, we limit ourselves to solving for them. There are sixteen unperturbed functions, of which we list those having positive or zero total spin. The function I is a quintet function. II, III, IV, and V give a biquadratic equation, of which one root is the quintet energy, the others the three triplet energies. Finally VI–XI lead to a secular equation of the sixth degree, having as roots the roots of the biquadratic, and also the two singlet energy levels. If we now

	Spin of a	Spin of b	Spin of c	Spin of d	Total spin
I	+	+	+	+	2
II	+	+	+	−	1
III	+	+	−	+	1
IV	+	−	+	+	1
V	−	+	+	+	1
VI	+	+	−	−	0
VII	+	−	+	−	0
VIII	+	−	−	+	0
IX	−	+	+	−	0
X	−	+	−	+	0
XI	−	−	+	+	0

evaluate the fourth power and sixth power equations, as polynomials in W, we must find that the sixth power one is divisible by the fourth power one, leading to a quadratic equation. We can greatly simplify the calculation, however, if we introduce at the outset seven linear combinations of the functions VI . . . XI. These combinations may be denoted as follows:

$$\begin{aligned}
&A{:}\tfrac{1}{2}(\mathrm{VI}-\mathrm{VIII}-\mathrm{IX}+\mathrm{XI})\\
&B{:}\tfrac{1}{2}(\mathrm{VIII}-\mathrm{VII}-\mathrm{X}+\mathrm{IX})\\
&C{:}\tfrac{1}{2}(\mathrm{VII}-\mathrm{VI}-\mathrm{XI}+\mathrm{X})\\
&D{:}1/2^{1/2}(\mathrm{VII}-\mathrm{X})\\
&E{:}1/2^{1/2}(\mathrm{VIII}-\mathrm{IX})\\
&F{:}1/2^{1/2}(\mathrm{VI}-\mathrm{XI})\\
&G{:}1/6^{1/2}(\mathrm{VI}+\mathrm{VII}+\mathrm{VIII}+\mathrm{IX}+\mathrm{X}+\mathrm{XI})
\end{aligned}$$

As with three electrons, the functions A, B, C are not independent, but instead $A+B+C=0$. When now we compute the matrix components of H and of unity with respect to the functions $A\cdots G$, using for this purpose the components between the functions VI $\cdots$ XI, we find that the functions fall into three groups: A, B and C, D, E, and F, and G, such that the matrix components between the groups are exactly zero. In this way we have an automatic factoring of the secular equation into a quadratic, a cubic, and a linear equation. Simple discussion shows that two combinations of A, B, and C correspond to the singlets, D, E, and F to the triplets, and G to the quintet level. To solve for the singlets, then, we need only use the quadratic secular equation between states A and B.

Since $A+B+C=0$, we have just the same situation that we did in the case of three electrons. All the calculation goes through as before, and we need not even rewrite the solutions of the quadratic equation. The only difference is in the values of the diagonal energies, H_{AA}, H_{BB}, H_{CC}, or P, Q, and R. These are

$$\begin{aligned}
P = {}&(abcd/H/abcd)+(abcd/H/cbad)+(abcd/H/adcb)\\
&-\tfrac{1}{2}((abcd/H/bacd)+(abcd/H/dbca)+(abcd/H/acbd)+(abcd/H/abdc))\\
&-\tfrac{1}{2}((abcd/H/cabd)+(abcd/H/bdca)+(abcd/H/dbac)+(abcd/H/acdb)\\
&+(abcd/H/bcad)+(abcd/H/dacb)+(abcd/H/cbda)+(abcd/H/adbc))\\
&+((abcd/H/badc)+(abcd/H/cdab)+(abcd/H/dcba))\\
&+((abcd/H/bcda)+(abcd/H/dabc))\\
&-\tfrac{1}{2}((abcd/H/bdac)+(abcd/H/cdba)+(abcd/H/cadb)+(abcd/H/dcab))\\
Q = {}&(abcd/H/abcd)+(abcd/H/bacd)+(abcd/H/abdc)\\
&-\tfrac{1}{2}((abcd/H/cbad)+(abcd/H/dbca)+(abcd/H/acbd)+(abcd/H/adcb))\\
&-\tfrac{1}{2}((abcd/H/cabd)+(abcd/H/bdca)+(abcd/H/dbac)+(abcd/H/acdb)\\
&+(abcd/H/bcad)+(abcd/H/dacb)+(abcd/H/cbda)+(abcd/H/adbc))
\end{aligned}$$

$$\begin{aligned}
&+ ((abcd/H/badc) + (abcd/H/cdab) + (abcd/H/dcba))\\
&+ ((abcd/H/cdba) + (abcd/H/dcab))\\
&- \tfrac{1}{2}((abcd/H/bcda) + (abcd/H/bdac) + (abcd/H/cadb) + (abcd/H/dabc))
\end{aligned}$$

$$\begin{aligned}
R = {} & (abcd/H/abcd) + (abcd/H/dbca) + (abcd/H/acbd)\\
&- \tfrac{1}{2}((abcd/H/cbad) + (abcd/H/adcb) + (abcd/H/bacd) + (abcd/H/abdc))\\
&- \tfrac{1}{2}((abcd/H/cabd) + (abcd/H/bdca) + (abcd/H/dbac) + (abcd/H/acdb)\\
&+ (abcd/H/bcad) + (abcd/H/dacb) + (abcd/H/cbda) + (abcd/H/adbc))\\
&+ ((abcd/H/badc) + (abcd/H/cdab) + (abcd/H/dcba))\\
&+ ((abcd/H/bdac) + (abcd/H/cadb))\\
&- \tfrac{1}{2}((abcd/H/bcda) + (abcd/H/dabc) + (abcd/H/cdba) + (abcd/H/dcab)).
\end{aligned}$$

The values of p, q, and r are just the same, with unity in place of H.

On account of the rather formidable nature of these formulas, it is worth while describing the physical nature of the terms. First in each case comes the Coulomb interaction $(abcd/H/abcd)$. Next come six terms connected with the six possible resonance interchanges of pairs of electrons. These six terms alone are large and important. Two of them in each case have positive coefficients, and hence produce binding, since the integrals themselves are generally negative. They correspond to valence bonds between two pairs of electrons: the pairs *ac* and *bd* in state A, *ab* and *cd* in B, *ad* and *bc* in C. Thus as with the three electron case we may say that each of our three states corresponds to one of the three possible ways of drawing the valence bonds, and the leading terms in the energies P, Q, R give just the sum of the binding energies for the two bonds, in each case. The remaining four resonance terms are for the other four possible bonds, and they come with coefficients $-1/2$, showing that the other pairs repel, but only half as strongly as if they were by themselves. The next group of eight terms come from cyclic permutations of three electrons, and the last nine come from permutations in which all four electrons change. Thus these last terms are all small, and we need not consider them in detail. As far as the broad outlines are concerned, we see that the diagonal energies follow the same principles as with three electrons. The solutions as well follow the same general lines. The real wave functions are combinations of A, B, and C, so that they do not correspond exactly to any one way of drawing the valence bonds. Nevertheless, in many cases one way will be much nearer the truth than any other, and in such cases one of these three functions will be a good approximation, and we may use the corresponding diagonal energy, as for example P/p, as a good approximation to the truth. It is worth while noticing how the wave function corresponding to a given way of drawing the valence bonds is constructed. Let us take, for instance, the function B, where the bonds are between a and b, and between c and d. Then in the first place the function is made up of the separate functions VII, VIII, IX, and X, in each of which a and b have spins opposite to each other, and similarly c and d have spins opposite to each other. Then these four functions are combined with such coefficients ± 1 that whenever we go from one function to another by interchanging the spins of a and b, or of c and d, we go to a function of opposite sign. This description proves to be a general one for the correct function to use in a case where there are definite valence bonds drawn in a certain way.

(d) More than four electrons, with only spin degeneracy

With more than four electrons, we cannot solve the problem of spin degeneracy, even to the extent of obtaining the levels of lowest multiplicity. For example, with five electrons, there are five doublet levels, and with six electrons there are five singlets. The energies would then be roots of an equation of the fifth degree, and it is useless even to set it up. On the other hand, we have noted in the case of four electrons that there can be cases (very important ones in actual practice), where the energy of the lowest state can be found as the mean energy of a wave function connected with one definite way of drawing valence bonds. And this can be done in general: whenever one method of drawing the bonds is very much more likely than any other, we can use this method for writing the energy in terms of the exchange integrals, to a good approximation. To set up the wave function, we proceed as follows: First, we draw the valence bonds, between definite pairs of electrons. All electrons are understood to be paired off, if the molecule has an even number of electrons, and all but one if it has an odd number. Then we take all the 2^N wave functions (if N is the number of complete pairs) for which the two electrons of any pair have opposite spins. We combine these functions with coefficients ± 1, such that when we pass from one function to another by interchanging the spins of a pair of electrons, we go to a function of opposite sign. This sum, divided by the square root of the number of terms for convenience in normalization, is the required function expressing the valence binding. The energy connected with the state is the ratio of the mean value of H over the state to the mean value of unity. Each of these quantities involves integrals connected with all sorts of permutations of the electrons. But if we confine ourselves to the most important terms, namely those in which no electrons change, or in which only a pair of electrons is interchanged, then the mean values are easily described. First there is the Coulomb term in the energy, or the term 1 in the matrix of unity. Then there are the interchange terms, with coefficients $+1$, between all the various pairs (N such terms) of electrons bound together. As far as these terms go, then, it is just as if all thepairs were independent of each other, and as if the energy required to dissociate the whole molecule were the sum of the energies required to dissociate its various bonds if they were by themselves. But the other possible interchange terms, between all other pairs of electrons, come in with coefficients $-1/2$, so that we interpret it as saying that all other pairs which are not definitely bound by valence forces repel each other, but by only half the amount they would exert if they were by themselves in the repulsive configuration. The further terms, in cyclic and other interchanges, come in with smaller coefficients, in different ways depending on the number of electrons.

In the general case, we can go even further than setting up these linear expressions for energy. We can work out a case where the valence bonds are not definite, but where they are intermediate between two of the definite cases we have considered. For them the correct wave function is a combination of two of these approximate functions, and we have only a quadratic equation for the energy. The simplest case is that where four electrons, a, b, c, d, are bound in some way intermediate between our three possible cases ab cd, ac bd, ad bc, but in which there are also many other electrons, which however are bound to each other in perfectly definite ways. This is the problem which we should meet in a rather general case of a chemical reaction, where two molecules approach, each one breaks into two halves by the parting of a single valence bond, and the parts recombine in either of the two possible ways. Here, just as with the four electron problem, we can set up three functions A, B, and C, corresponding to these three ways of drawing the bonds. These functions are set up, and their energies computed, according to the rules we have just described. But now, just as with four electrons, we find that these functions are not independent, but rather that $A+B+C=0$. Thus all the calculation of the preceding sections can be applied to this case, we obtain the energy as the root of the same quadratic, and the only difference is in the value of the diagonal energy values P, Q, and R. When we substitute in the correct values, we find that only those terms involving interchanges between the four electrons a, b, c, d remain inside the radical, so that this looks just as in the four electron problem. Outside the square root sign come the interchange integrals between other pairs of electrons, just as if we were using a linear solution rather than a quadratic one.

(e) Two electrons, one s and one p

The problem of two atoms, one containing an s and one a p electron, involves orbital as well as spin degeneracy. There are three possible p wave functions, and we must consider how this affects the energy levels. Further, we have a choice as to what three functions to take. For on account of the degeneracy, we may take any three linear combinations of the functions with which we start. First, however, we shall choose the conventional p functions. These may be denoted as p_+, p_0, p_-, having respectively the components 1, 0, 1− of angular momentum along the fixed axis. We naturally choose this axis as the line on which the nuclei are placed. Then we have twelve unperturbed functions: for p_+s we have four on account of spin degeneracy, for p_0s four, and for p_-s four more. But now there is a fortunate fact: just as with atoms, the component of orbital angular momentum about the axis of figure is a constant of the motion, and the matrix components of energy, and of unity, between two states with different values of this quantity, are zero. In other words, the matrix components vanish between states in different groups of four, and the secular equation automatically factors into three factors, each involving four states. Each of these yields a problem exactly like that without orbital degeneracy which we have considered before, and therefore results in a singlet and a triplet, the formulas being as before. As a matter of fact, however, we shall not have three singlets and three triplets, but only two of each, for the states p_+s and p_-s will yield the same energies, although different wave functions. Thus these will result in an orbital degeneracy which persists, at least until further perturbations are taken into account, and the states are Π states. The final conclusion, then, is that we will have from p_+s and p_-s a$^1\Pi$ and a$^3\Pi$, and from p_0s a$^1\Sigma$ and a$^3\Sigma$. To tell which of these is the lowest state, we must consider the magnitudes of the exchange integrals, for the energies of the singlet states are essentially given by these exchange integrals, and the one which has the largest negative value will correspond to the most stable level. But now these exchange integrals are such things as $\int a(1)b(2)$-$Hb(1)a(2)dv$. That is, they involve in their integrands the quantities $a(1)b(1)$ and $a(2)b(2)$, as if they were charge densities. Now if the functions a and b do not overlap at all—that is, if there is no region of space where they are simultaneously of considerable size—the integrand will be everywhere small, and the integral will be small. In general, the more they overlap, other things being equal, the larger will they be. But now the functions p_0 and s will overlap far more than p_+ and s, or $p-$ and s. The reason is found in the spatial arrangement of the functions, as has been described in an earlier paper. p_0 is concentrated along the axis joining the p and the s electron, so that it has its maximum intensity in just the place where it can overlap the s. On the other hand, p_+ and p_- have their concentration along the plane normal to the axis, and they are zero right on the axis. Thus we see that the $^1\Sigma$ state will be the most tightly bound, and will be the normal state. And in the course of our discussion, we have seen that the p electron will tend to take up that particular degenerate state which points out along the direction toward the other electron with which it is in valence binding. To get the actual energy, we have the formula, from our discussion of the two electron problem.

(f) Two atoms, each with a p electron

Here we have more degeneracy than before. Both electrons can be in p_+, or both in p_-. These will yield $^1\Delta$ and $^3\Delta$, with very weak binding. Then either one can be in p_+ and the other p_0, or either one in p_- and the other in p_0. This degeneracy would result in two $^1\Pi$, and two $^3\Pi$, and we should have to solve quadratics to determine the energy, were it not for the symmetry of the problem, by which we can actually separate into functions symmetric and antisymmetric in the nuclei. Finally we have the problem of no component of orbital angular momentum, with three possible orbital arrangements: p_+p_-, p_0p_0, or p_-p_+. As a result of this we should have three $^1\Sigma$ and three $^3\Sigma$. We should have to solve a cubic to get either of these, except that symmetry in the nuclei permits factoring into a linear and quadratic term. But the states p_+ and p_- have very little overlapping, while p_0 and p_0 overlap a great deal. Thus the latter state corresponds to a much lower energy, and we may anticipate that one of the wave functions, the one connected with the lowest energy, will correspond very closely to this particular orbital arrangement. We should be able therefore to obtain a fairly good approximation by taking just the singlet and triplet coming from p_0p_0 alone, getting strong binding for the singlet. Here again, then, we can say that for the valence bond the correct p electrons are those which point in the direction of the other electron.

Bartlett[11] has computed the integrals in this case of two p electrons, and in general finds verification of the statements of the preceding paragraph. In one respect his results are in extraordinary disagreement with what we should expect: he finds the exchange integral between the two p_0 states in the two atoms to be positive rather than negative, so that he finds the triplet, rather than the singlet, state to lie lower. This is so entirely in disagreement with expectation that we must question the result, and we cannot regard this question as being closed until further calculation is made. As a possible source of explanation of this discrepancy, however, we may note that Bartlett's calculation is for hydrogen, with nuclear charge 1, whereas in ordinary molecules the effective nuclear charge would be decidedly greater than 1. It seems altogether possible that the integral could depend enough on nuclear charge to change sign, and be negative with these larger charges.

(g) Two atoms, one with two equivalent p electrons, the other with an s electron

The atom with two equivalent p electrons furnishes an atomic problem, and we consider it first, assuming the atom with the s electron to be removed to infinity. This procedure is not necessary, but it is useful in that it suggests an improved method of dealing with the degeneracy of the p electrons, in this sort of problem. First we tabulate the various exchange integrals which we shall need. Being an atomic problem, we can go much further toward calculating them than we can without great difficulty in the molecular case. They can all be obtained from the tables in the paper on complex spectra, where they are given as combinations of certain integrals F^0 and F^2, integrals over the radial part of the wave functions of the electrons. The three degenerate functions in which we are interested may be symbolized in the interest of brevity by $+, 0, -$. Then from the paper mentioned we derive the values

$$(+\,+/H/+\,+) = F^0 + 1/25F^2, \text{ which we may symbolize } (1,\ 1/25)$$

$$(+\,0/H/+\,0) = (1,\ -2/25);\quad (+\,0/H/0\,+) = (0,\ 3/25)$$

$$(+\,-/H/+\,-) = (1, 1/25);\quad (+\,-/H/-\,+) = (0,\ 6/25)$$

$$(00/H/00) = (1,\ 4/25).$$

Now we may tabulate all the possible states we can set up, considering only the orbital degeneracy. These states may be tabulated as follows:

I	+	+
II	+	0
III	+	−
IV	0	0
V	−	0
VI	−	−

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[11] J. H. Bartlett, Phys. Rev. **37**, 507 (1931).

The state I is connected with $M_L=2$, II has it equal to 1, III and IV each have 0, V has -1, VI has -2. Hence all states may be considered separately, and have no matrix components of energy between them, except III and IV, which must be grouped together. When now we consider the spin degeneracy, I and VI will lead only to singlet levels, on account of the exclusion principle. The energy will be $(++/H/++)=(--/H/--)=(1, 1/25)$. The levels are two of the five sub-levels of ^1D, and this then is the energy of that state. II and V, being nondegenerate problems with nonequivalent electrons, will each give a singlet and a triplet, the singlet having energy$(+0/H/+0)+(+0/H/0+)=(1, 1/25)$, and accounting for two more of the sublevels of ^1D, and the triplets having energy $(+0/H/+0)-(+0/H/0+)=(1, -5/25)$, accounting for two sublevels of the ^3P. Finally III will lead to a singlet and a triplet, and IV to a singlet only, on account of the exclusion principle. But we cannot get these energies without solving a cubic between the states. One singlet is of course the remaining level of ^1D, the triplet is the remaining level of ^3P, and the other singlet is ^1S, so that as a matter of fact we can easily find the energy: we know the sum of roots, and also all the roots but one, so that we can subtract. Thus, considering only states of $M_S=0$, we have three states, of diagonal energies $(+-/H/+-)$, $(+-/H/+-)$, $(00/H/00)$. Adding, and subtracting the energies of ^1D and ^3P, we at once have for ^1S the energy $(1, 10/25)$. But this procedure, while feasible with the atomic problem, will not work with the molecular one. For there we cannot assume that the energy values will be repeated in problems with different values of M_L, and the device of subtraction is no longer open to us to any such extent as with atoms. Further, these very levels with $M_L=0$ are the ones that lead to stable molecular binding, and for that reason they are the most important ones for the molecular case. Thus if we retain the $+$, 0, $-$ p functions, we will meet real difficulty when we try to solve the molecular problem. Fortunately it is possible, however, to introduce other p functions which overcome this trouble, and which prove in general to be much more suited to calculation in molecular problems.

To set up these new functions, we start with the expression of p_+, p_0, p_- in rectangular coordinates. If the axis is chosen as the z axis, then these functions are

$$p_0 = zf(r)$$

$$p_+ = \frac{x+iy}{2^{1/2}}f(r)$$

$$p_- = \frac{x-iy}{2^{1/2}}f(r).$$

But now we can immediately introduce three linear combinations of these,

$$p_x = xf(r)$$

$$p_y = yf(r)$$

$$p_z = zf(r),$$

which prove to be the desired functions. We can obtain the exchange integrals with respect to them immediately, using their expression as combinations of the previous functions, and we find

$$\begin{aligned}(xx/H/xx) &= (yy/H/yy) = (zz/H/zz) = (1,\ 4/25)\\ (xy/H/xy) &= (yz/H/yz) = (zx/H/zx) = (1,\ -2/25)\\ (xy/H/yx) &= (yz/H/zy) = (zx/H/xz) = (xx/H/yy) = (yy/H/zz)\\ &= (zz/H/xx) = (0,\ 3/25).\end{aligned}$$

All other coefficients are zero, such as $(xx/H/xy)$, or $(xy/H/xz)$. Using these functions, we have the following states, considering only orbital degeneracy:

I	x	x
II	y	y
III	z	z
IV	x	y
V	y	z
VI	z	x.

When we investigate the matrix of the energy, we see that I, II, III must all be considered together as a group, since the matrix components between them do not vanish. On the other hand, each of the states IV, V, and VI forms a separate group by itself, without components to any other states. On account of the exclusion principle, I, II, III will between them yield three singlets, and examination shows that these are the ^1S, and two sublevels of ^1D. IV, V, and VI give each a singlet and a triplet, each leading to one of the levels of ^1D and one of ^3P. Thus we have for ^1D the energy $(xy/H/xy)+(xy/H/yx) = (1,\ 1/25)$, and for ^3P $(xy/H/xy)-(xy/H/yx) = (1,\ -5/25)$. Finally by subtraction we find $^1S{:}\,^1S+2\,^1D = 3(1,\ 4/25)$, $^1S = (1,\ 10/25)$. Since we must use subtraction here as before, it would seem at first sight as if we should be no better off then we were before. But this is not true, for it appears that the states xy, yz, zx are the ones concerned in the lowest states of the molecule, and the orbital degeneracy is entirely removed from these states.

We may now pass to the molecular problem, using the $x\ y\ z$ functions. We assume the other atom to be located along the x axis, and denote its wave function by X. Again considering only orbital degeneracy at first, we have the following table of functions:

I	x	x	X
II	y	y	X
III	z	z	X
IV	x	y	X
V	y	z	X
VI	z	x	X

Now when we investigate the matrix of the energy, we still find, as we did before, that IV, V, and VI may be considered by themselves, although I, II, and III must be grouped together. The reason is a very general one of symmetry. Let us for instance take the substates of IV and V for which all spins are parallel, so that we need not consider them. Then

$$H_{\mathrm{IV},\mathrm{V}} = (xyX/H/yzX) - (xyX/H/zyX) - (xyX/H/Xzy) - (xyX/H/yXz) + (xyX/H/Xyz).$$

The terms most likely to give something different from zero will be those in $1/r_{ij}$ in H. Take these for example in the first integral. This is $\int x(1)y(1)y(2)z(2)X(3)X(3)(1/r_{12}+1r_{23}+1/r_{31})dv_1dv_2dv_3$. But now the first integral is zero, because interchanging the z coordinates of both electrons 1 and 2 changes the sign of the function $z(2)$, leaving everything else unchanged, so that each contribution to the integral is balanced by an equal and opposite one. The second term is zero for the same reason, and the third on account of the possibility of interchanging the y coordinates. We note that this argument is dependent on having the function X symmetrical with respect both to y and z, so that this electron must be on the x axis.

As with the atom, then, we have three states, IV, V, and VI, without orbital degeneracy, and three others, I, II, and III, which must be considered together. These last three give rise to three doublet levels, which prove to be $\mathrm{a}^2\Sigma$, and the two sublevels of $\mathrm{a}^2\Delta$. On account of the fact that two roots coincide, we can solve the cubic equation, and it proves to be the case that these levels are high up, as we would expect from the fact that they come from the higher atomic levels. Thus if we are interested only in the lower molecular levels, we may confine ourselves to the states IV, V, VI. Each of these is a problem of three electrons with spin degeneracy, but without orbital degeneracy. The solution, then, can be carried out as in section (b), and we obtain in each case a quartet and two doublets, the latter as the two roots of a quadratic. The problems IV and VI lead evidently to the same energy levels, and examination shows them to be Π levels, while V yields Σ levels. A simple discussion shows that the Π levels will be lower than the Σ ones, the lower $^2\Pi$ being the lowest level of all. For illustration, let us take assumed values for the exchange integrals, and actually work out the energies.

As an example, we choose OH, for which some of the quantities are approximately known. The O atom, of course, has four p electrons rather than two, but the energy formulas for the case where two are lacking from the closed shell should be the same as when only two are present. It is known that the heat of dissociation of OH into O and H is of the neighborhood of 5.4 volts.[12] Further, the energy difference between the ^3P and ^1D of the O atom is about 2 volts.[13] Let us now make most crude assumptions, merely to get orders of magnitude. We shall suppose that we can neglect all lack of orthogonality, that the energy comes entirely from resonance terms, so that we can

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[12] R. S. Mulliken, Phys. Rev. **33**, 739 (1929).

[13] R. Frerichs, Phys. Rev. **36**, 398 (1930).

neglect Coulomb interactions, and that we can neglect exchange terms from cyclic permutations of electrons. We shall need, then, values for a number of exchange integrals. First, we can derive the value of $(xyX/H/yxX) = (yzX/H/zyX) = (zxX/H/xzX)$ from the 2 volt separation between the terms of the atom. For this separation should be twice the integral, which is therefore about 1 volt. Next, we note that the other exchange integrals fall into two classes: $(xyX/H/Xyz)$ and $(xzX/H/Xzx)$, in which X and x electrons are in resonance, and $(xzX/H/xXy)$, $(xzX/H/xzX)$, $(yzX/H/yXz)$, etc., in which an X and either a y or z electron are in resonance. Now the X and x electrons overlap greatly, while the X and y or z overlap much less. Thus the integrals of the first group are large numerically, those of the second group small. Both are negative, presumably. In the absence of calculation, we make the rough approximation that the second is 1/5 of the first. Then to get the correct heat of dissociation we may take the integrals of the first sort to be about -5 volts, and those of the second sort -1 volt, for the value of distance of separation which gives the minimum of energy. Having values for our integrals, we may now use our solutions of the three electron problem to find the approximate energies, for the assumed distance of separation. From states IV or VI, we have a $^4\Pi$ and two $^2\Pi$'s. The energy of the first should be $-(xyX/H/yxX) - (xyX/H/Xyx) - (xyX/H/xXy) = -(1) - (-5) - (-1) = 5$ volts, corresponding to large repulsion. For the doublet states, we must solve a quadratic: the energies are

$$\pm \left\{\tfrac{1}{2}(((xyX/H/yxX) - (xyX/H/Xyx))^2 + ((xyX/H/Xyx) - (xyX/H/xXy))^2 + ((xyX/H/xXy) - (xyX/H/yxX))^2)\right\}^{1/2}$$

$$= \pm \left\{\tfrac{1}{2}[(1 + 5)^2 + (-5 + 1)^2 + (-1 - 1)^2]\right\}^{1/2} = \pm 28^{1/2} = \pm 5.3 \text{ volts.}$$

Thus the one doublet lies as high as the quartet, but the other one corresponds to attraction, of about the right amount, and represents the normal state. In the same sort of way, the energy of the $^4\Sigma$ is $-1+1+1=1$ volt, and of the two $^2\Sigma$'s $\pm\left\{\tfrac{1}{2}[(1+1)^2+(-1+1)^2+(-1-1)^2]\right\}^{1/2} = \pm 2$ volts. One doublet is attractive, but not nearly as much so as the $^2\Pi$ state, so that it would correspond to an excited level.

The lowest state, then, comes from the problem in which we have a resonance interaction between the X electron of the one atom, and the x electron of the other, which can overlap with it a great deal. No such overlapping is possible in the other cases, and there is not nearly as tight binding. In this lowest state, the binding between X and x is so strong that we can speak of a definite valence bond between them, and it is interesting to see if the approximate formula for energy based on the assumption of a definite bond is applicable. This gave for the energy the interaction integral concerned in the bond, decreased by half the sum of all other interaction integrals. Thus in this case it would be $-5 - \tfrac{1}{2}(1-1) = -5$ volts, which is a fairly good approximation to the root of the quadratic, -5.3 volts. Thus in this case we should be justified, if we were not looking for very accurate values, in using this approximation, and saying that the valence bond was definitely between the electrons which have large overlapping, the X and x electrons.

It is interesting to consider what our Π levels do in the case of large internuclear separation. There the leading term in the energy is the atomic integral $(xyX/H/yxX)$, which is independent of distance. Noticing how this enters the expressions for energy, we see that the $^4\Pi$, and the lower $^2\Pi$, go to the lower, ^3P state of the atom, while the other $^2\Pi$ goes into the ^1D of the atom. At large distances, the energy is given to a next approximation by using our linear functions. Thus the energy of the lowest state is given by $-(xyX/H/yxX) + \frac{1}{2}((xyX/H/Xyx) + (xyX/H/xXy))$. The binding energy, $(xyX/H/Xyx)$, comes in only with a factor $\frac{1}{2}$. But more significant than this is the fact that the interaction energies between X and x and y both come in with the same sign, so that they both contribute to the binding. In the other limiting case, on the other hand, when the binding between X and x is the large term, these two interactions come in with opposite sign, so that while X is bound to x, it is in repulsive interaction with y. It is easy to see, therefore, that the qualitative nature of interactions can change depending on whether molecular interaction is large or small compared with atomic energy differences. The whole theory of directional valence, as developed by the present writer and by Pauling, is a phenomenon connected with strong valence binding. In that case, definite interaction energies come in with positive sign, and contribute to binding. Our object is then to adjust the orbital wave functions, by making concentrated bond functions, so as to make these interaction integrals as big as possible. On the other hand, all other interactions come in as repulsions, so that it is necessary to make them as small as possible. By applying these principles, we are led to the idea of sharply concentrated wave functions for valence binding, sticking out in definite directions in space. If the valence binding were weak compared with atomic energies, on the other hand, there would not be this necessity, for there are no definitely defined bonds which give attraction with others leading to repulsion. Thus in these cases we should not be led to concentrated wave functions, and to directional effects. Now it is very significant that Heitler in his discussion has always limited himself to consideration of a single atomic energy level. That means essentially that he assumes the atomic interactions to be so large that he need consider only the lowest state, as if the other atomic states lay much further up. In this case we would expect no such directional effects as with strong valence bonds, and it is interesting to note that Heitler has not inferred the existence of such effects from his calculations.

(h) Three atoms, one with two equivalent p electrons, the others with an s electron each

This problem could serve as a simplified model of the H_2O molecule, just as the preceding one resembled the OH. In general, we shall find the problem too difficult to get accurate solutions. There is a special case, however, in which we can carry through the calculations, and we assume that special case to start with. Fortunately it is not far from the truth. This is the case in which the lines joining the monovalent atoms to the divalent one make an angle of 90° with each other. Assuming this case, we let one s electron be along the x axis, the other along y, and we denote their functions by X and Y. We use the x, y, z p functions, as before. Then considering orbital degeneracy alone, we have just the same six functions as in the previous case. Moreover, the addition of the extra atom, so long as it is just on the y axis, does not interfere with the vanishing of matrix components between the groups of states IV, V, and VI. As before, then, I, II, and III lead to a group of high levels, which we must consider together. The problem is no longer linear, and we cannot use the notations Σ, Π, Δ, etc., but can denote states only by their multiplicities. We can thus only say that from these states we have three singlets and three triplets, and we can be quite sure that they will be high, repulsive levels. Next we consider the states IV, V, VI. The lowest level will come from state IV, with x and y, p electrons, for then we have the possibility of two strong bonds. The states V and VI allow only one strong bond each, and so must be much less strongly attractive levels, and we may neglect them. Now the problem of x, y, X, Y electrons is a four electron problem with only spin degeneracy, and therefore leads to two singlet states, three triplets, and a quintet, of which one singlet will be the lowest. The energy of this singlet comes as the solution of a quadratic, as we have already found, but just as with the preceding case, we can often use the linear approximation to the quadratic. To investigate this, we may put in rough approximate values for the integrals in H_2O, as we did for OH.

Neglecting the same terms that we did for OH, we need a number of exchange integrals to determine our energies. We will assume the same values of the integrals which have already occurred in OH, as follows:

$$(xyXY/H/yxXY) = 1$$

$$(xyXY/H/XyxY) = (xyXY/H/xYXy) = -5$$

$$(xyXY/H/YyXx) = (xyXY/H/xXyY) = -1.$$

The only other integral which we need is $(xyXY/H/xyYX)$, the exchange integral between the two hydrogen atoms. This we can get approximately from the band spectrum of hydrogen, for its energy is given directly in terms of this integral. To get the distance between the two hydrogens, we note that the OH distance in H_2O, according to all calculations, is about 1A, so that the distance between the hydrogens, assuming the right angled model, is 1.41A. This is about twice the distance of equilibrium for two hydrogens interacting with each other, and the exchange energy at this distance is about -0.8 volts.

We now have for our energy the value $-\{\frac{1}{2}((-5-5+1+1)^2+(-1-1-1+0.8)^2+(1-0.8+5+5)^2)\}^{1/2}=-9.3$ volts. This is not far from the energy indicated for dissociation of H_2O into H, H, and O. Thermochemical data would lead to a value of about 10 volts. Thus we see that our general calculation is fairly good, in spite of its many crude features. It is now interesting to note that here again the valence bonds are strong enough so that we can use our linear approximation. This would give for the energy $-5-5$

$-\frac{1}{2}(-1-1+1-0.8)=-9.1$ volts, quite a good approximation to the quadratic. This should be a fairly representative case for the magnitudes in actual compounds, so that it seems as if we were justified in using this approximation in general.

For angles other than 90° between the bonds, we can no longer get such a valid solution. For then our nondiagonal terms between states IV, V, and VI no longer vanish on account of symmetry, and we cannot consider the states as leading to independent problems. There is one other case which we can solve properly, however: that where the angle is 180°, the linear molecule. In that case we still can separate our problem, and states IV or VI lead to identical energy levels, and give the lowest state. Suppose our two s electrons are on the x axis, and denote them by X, $-X$. Then we have

$$(xyX-X/H/yxX-X)=1$$

$$(xyX-X/H/Xyx-X)=(xyX-X/H/-XyXx)=-5$$

$$(xyX-X/H/xXy-X)=(xyX-X/H/x-XyX)=-1$$

$$(xyX-X/H/xy-XX)=0 \text{ practically,}$$

the last because the H atoms are so far apart. Then the energy of the lowest singlet is $-\{\frac{1}{2}((-5-1+5+1)^2+(-5-1-1-0)^2+(1+0+5+1)^2)\}^{1/2}=-7$ volts. In other words, the right angled arrangement is decidedly more stable than the linear one. For this linear model, we cannot use our approximate method, for no one way of drawing the valence bonds is preferred over any other: we cannot say whether the X or the $-X$ hydrogen is bound to the x p function of the oxygen.

For angles near 90° we can have resort to an approximate method to indicate the general form of the curve of energy against angle. Even if the nondiagonal terms between our state IV and other states are no longer zero, they will still be small, for small deviations of the angle. Thus we may still use a first order calculation, taking the unperturbed wave function as formed in IV, and averaging the correct energy over it. To be more precise, we assume the functions X and Y to be located, not just on the x and y axes, but on axes in the same plane, but inclined by an angle ϕ to these axes, so that they make an angle of $90°+2\phi$ with each other. We still have the same six states, considering orbital degeneracy, and the lowest state will come from IV, but now with some contributions from the other state. We neglect these contributions, however, solving merely the problem of state IV by itself. The only difference from our previous calculation comes then in the values of the exchange integrals. If previously the integral $(xyXY/H/XyxY)$ was -5 volts, and $(xyXY/H/xXyY)$ was -1 volts, then we can easily show that in the present case, with the new definition of X, we have $(xyXY/H/XyxY)=-5\cos^2\phi-1\sin^2\phi$, and $(xyXY/H/xXyY)=-1\cos^2\phi-5\sin^2\phi$. We do this by noting, for example, that the function x can be written as a linear combination of two functions, one pointing along the direction at the angle ϕ, the other along the direction at right angles to it. Each of these functions is just like an ordinary p function, and has interaction integrals with the s electrons just as if the latter were along the x axis. When we put in these expansions, we at once get the expressions mentioned. Now we are ready to substitute in the energy formula. For convenience, we use only the linear formula, which we have already shown to be sufficient. We know all terms except the exchange integral between X and Y, which will depend on ϕ because that affects the distance between hydrogen atoms. We now have for our energy

$$2(-5\cos^2\phi - 1\sin^2\phi) - \tfrac{1}{2}(2(-1\cos^2\phi - 5\sin^2\phi) + 1 + (xyXY/H/xyYX)).$$

This can be put in the form $-9.5+12\sin^2\phi-\frac{1}{2}(xyXY/H/xyYX)$. Of course, it reduces properly for $\phi=0$. On the other hand, it is not correct for the linear model, which we get by putting $\phi=45°$; in this case it reduces to -3.5, rather than the correct value -7. Thus we see that it will give in general too high energy values, as of course we can see from general principles, for the mean value of the energy over an incorrect wave function always will give too high energy. Nevertheless, the general form of the variation with angle is certainly a suggestion of the correct law: surely the energy increases as the angle deviates from a right angle, and presumably the correct law could at least be well approximated by a $\sin^2$ law. We can then say at least qualitatively what to expect. If the hydrogen exchange integral $(xyXY/H/xyYX)$ could be neglected, the stable position of the molecule would be with the right angle form. But actually this integral decreases numerically as the hydrogens move farther apart, or as the angle increases. Since it appears in the form of a repulsion between the hydrogen atoms, we shall find equilibrium at an angle slightly larger than a right angle. The p valences by themselves have a definitely directional effect, but this is superposed on an ordinary repulsion of the atoms which are not bound by valence forces.

(i) Four atoms, one with three equivalent p electrons, the others with an s electron each.

Here we have a model of the NH_3 molecule, for example. We shall not discuss it in as great detail as we have used in the preceding cases, for the principles are similar. Again the only cases which we can treat correctly are those in which the three monovalent atoms make angles of 90° with each other. But as before this is the stable position if we can neglect the repulsion of these atoms for each other, and if we consider the repulsions the angles are slightly increased. Taking account of orbital degeneracy, and taking the s atoms to have wave functions X, Y, and Z, we have the following states:

I $xxyXYZ$
II $xyyXYZ$
III $yyzXYZ$
IV $yzzXYZ$
V $zxxXYZ$

VI $zzxXYZ$

VII $xyzXYZ$

The states like $xxxXYZ$ are forbidden by the exclusion principle. Now as before, when the states XYZ are really along the axes, the state VII has vanishing matrix components to all other states. It is from this last state that we expect to get the lowest level of the molecule. It is the only one which allows strong bonds between X and x, between Y and y, and between Z and z. In this connection, we can use a principle which we did not mention with the other cases, but which was equally applicable there. In such a state as $xxyXYZ$, the two electrons x form essentially a closed subshell, and cannot take part in valence binding. Only the single electron y is free to form a bond, and naturally in these functions there can be no great binding energy, and they will lead to high and probably repulsive levels of the molecule. Thus we are led to the problem $xyzXYZ$, a six electron problem without orbital degeneracy. We cannot get its exact solution, but we can use our approximate method valid in cases of strong binding, and that should be satisfactory here. According to this, the energy is the sum of the exchange integrals between X and x, between Y and y, and between Z and z ,which are all large and negative, and diminished by half the sum of all other exchange integrals. Those between X and y and z and the other similar ones, will reduce the energy, as in the preceding problem. Those between X and Y, and the other similar ones, will represent the repulsion between the hydrogen atoms. There are, then, no essential differences between this problem and those we have already discussed.

(j) Five atoms, one with four s and p electrons, the others with an s electron each

This problem could represent the methane molecule, CH_4. A new situation enters here, in that we may not confine ourselves to p electrons only. For then we should have to have for the atom a combination, say, like $xxyz$, necessarily having two electrons in a closed group, and leaving only two free for forming bonds. We must then consider the possibility that some of the electrons in the large atom are in s orbits. Since two s electrons would again form a closed group, defeating our purpose, we have but one possibility, namely that there be one s electron and three p's. Then by analogy with our previous case we expect the lowest state to come from the configuration in which the four electrons in the large atom were all in different states, as $s\ x\ y\ z$, so that all could take part in binding. With our four other atoms, we then have an eight electron problem, in which we hope to be able to neglect orbital degeneracy. We cannot do this in general, however, any more than we could with the other problems except in special cases, for particular positions of the other atoms. For we have nondiagonal terms of the energy, between our function and others in which two s or p electrons are in the same wave function. Our object, then, is so to move around our other atoms, and also to make such linear combinations of the functions s, x, y, z, that these nondiagonal terms will become as small as possible, and the solutions of our problem without orbital degeneracy will approach as closely as possible to the real solution of the problem. Now we may regard this in either of two ways. First, if we can really make the nondiagonal terms zero by such manipulation, then when we have done it we shall be justified in neglecting orbital degeneracy, and the solution we get will be correct. But second, if we leave out of account these nondiagonal terms from the beginning, we can always solve for the lowest level coming from our one set of orbital functions. This energy level will vary as we manipulate the positions and orbital wave functions of the electrons, and by the general variation principle we know that the lowest possible energy which it can get will be the correct energy value. Thus we simply manipulate the orbital functions to make the energy a minimum, and use this minimum property as a criterion for the correctness of the functions. This process, to take care of spin degeneracy by exact or approximate solution of the perturbation problem, but to treat orbital degeneracy by a variation method, may be considered to be the real essence of the scheme suggested by the present writer and by Pauling for the treatment of molecular problems.

When now we try to make the energy of our lowest state a minimum, we have very definite information to assist us. First, the energy will surely be lower if we can form definite strong valence bonds than otherwise. If we can, then we know that the lowest state of the problem of spin degeneracy can be approximately set up, and that the energy will be a sum of the exchange integrals connected with the bonds, diminished by half the sum of all other exchange integrals. All these exchange integrals connected with molecular interactions are presumably negative. Then we have a perfectly definite way to make our energy low: We must manipulate the functions in such a way as to make the exchange integrals connected with our definite bonds as big numerically as possible, and to make all others as small as possible. But this is just what is accomplished by making the orbital functions as concentrated in space as possible, and by making the two functions involved in a bond overlap as much as possible. By this maximum overlapping and concentration, the desired integrals will be made large on account of their large integrand, and those which we wish to be small will do so, since the very concentrated orbital functions will keep out of the way of other functions, overlapping them very little, and not contributing greatly to other exchange integrals. Thus the requirement of concentrated bond functions, each strong in a restricted region but keeping out of the way of others, which has been emphasized by the writer and by Pauling, is just the requirement necessary to make our energy a minimum, and hence to result in an approximation near the true solution.

In particular, for four combinations of s and p functions, those which most nearly possess the desired property are the tetrahedral ones, described in the previous paper. Let us then introduce these functions, in place of $sxyz$. We must still move around the four univalent atoms, if we want to make the energy a minimum. They must be so placed that one overlaps each of the four tetrahedral functions. This definitely fixes them in a tetrahedral arrangement.

When we have done this, the energy will be made up of the attractive terms binding each hydrogen to its corresponding electron in the carbon; the repulsive term between each hydrogen and all the other carbon electrons; and the repulsions of the hydrogens for each other. Of course, we will also be interested in finding the energy of the molecule when the hydrogen atoms do not have just these positions, in order to investigate vibrational frequencies. Then we must simply move the hydrogens, and compute the energy by the same formulas for the different orbital functions. It is entirely likely, however, that if the hydrogens are slightly displaced, it would prove that a slight compensating displacement of the oxygen functions would reduce the energy. We can imagine that four functions could be set up, not pointing just to the corners of a regular tetrahedron, but in slightly different directions, which would be more advantageous in this case. In a detailed theory this possibility would have to be investigated, and in any case those orbital functions used which gave the lowest energy.

It is quite worth while considering what our lowest energy level will do as the hydrogen atoms are removed from the carbon. At first we should say that it would go into the ^5S level of the atom, the lowest level of the configuration $sxyz$. But this presumably will not be the case, for we have the possibility of a state of the same nature going into the ^3P level of the configuration s^2xy, a lower level, and we know that levels of the same character do not cross. Thus our lowest level will gradually change its properties, as the distance of separation is increased, until finally it will have the correct properties for this ^3P atomic state. Our method will not give a correct description of this whole process. Still, on account of the term in the Coulomb interaction energy which gives essentially the interaction within the atom, our solution will show the level built up as we have done it going to a high energy at large separation, and we should find that by changing the orbital functions by going to the s^2p^2 configuration we could reduce the energy. It is thus in the spirit of the variation method that at each distance of separation we should seek the compromise between these which gives the lowest energy, and treat that as giving the correct description of the state. It is worth while noting that this sort of situation is very common: very often the electronic configuration present in molecular binding at small distances of separation is not that characteristic of the atomic level into which the molecule would disintegrate adiabatically. Lack of knowledge of this fact has been the cause of much misunderstanding.

(6) General Methods for Valence Bonds

In the course of the illustrations in the last section, we have been developing several general principles for use in discussing molecular binding which are worth describing separately. By use of these methods, it is believed that approximate solutions for the lowest states of most molecules may be obtained, accurate enough for rough discussion of chemical problems and of band spectra. In the first place, we make in this method a characteristic difference in treatment between orbital and spin degeneracy. The treatment of spin degeneracy is based on an approximate solution of the perturbation problem in which we have spin degeneracy without orbital degeneracy. This solution is valid in cases where there are strong and unambiguous valence bonds; that is, where the electrons can be all divided into pairs, such that the exchange integral between the two electrons of a pair is large, but those between electrons not forming a pair are small. It states approximately that the energy is a sum first, of the Coulomb energy; then of the sum of the exchange integrals over all pairs forming bonds; finally of the sum, with coefficient $-\frac{1}{2}$, of all other exchange integrals. That is, the electrons very definitely form bonds from pairs of electrons, rather than just having bonds in an indefinite way between atoms, as Heitler has assumed. And the two electrons in a pair result in attraction, but each electron is in repulsive interaction with every other electron except the one with which it is paired, although these repulsions are diminished to half the value they would have had if the electron were not bound in a shared electron pair. It is worth while noting that, for use in problems of chemical reaction, we have a somewhat more general solution than this, in which we can follow through in detail the process of breaking apart of a single bond in each of two molecules, and of joining together the remaining parts in either of the two possible ways to form other molecules.

We have found it most practicable to treat orbital degeneracy, not by the perturbation method at all, but by the variation method. This rests essentially on the hypothesis that it is possible to find a set of orbital functions, one for each electron, such that the lowest energy level of the problem of spin degeneracy connected with these orbital functions is a good approximation to the lowest state of the problem. We have seen cases where we could find such functions, others where we could do it approximately, though perhaps not exactly. No doubt as more cases are examined in detail, many will be found where the hypothesis is justified, but also very probably some will be found where it is not, and where our method is not applicable. It seems likely that all simple problems of molecules with only single bonds will fall into this scheme, but probably at least some cases of double and triple bonds, as for example the rather anomalous case of the lowest state of O_2, will require special treatment. Other cases which we surely could not treat by the general method would be those like C_6H_6, the benzene ring, where an ambiguity between two ways of drawing the valence bonds seems to be an essential feature of the structure. But if our hypothesis is justified, then we may proceed by varying the orbital functions to try to find the lowest energy level. On account of the expression for energy in terms of exchange integrals mentioned above, the way to do this is very definitely to set up concentrated bond orbital functions, in order to make the desired exchange integrals large, and all others small. This in turn leads to functions very definitely localized in space, with definite directional properties. When we have found such functions, by the methods suggested by Pauling, or by straightforward variation of the energy, we may then use the formulas developed in the present paper to find the actual energy of the molecule, deriving the necessary exchange integrals either from calculation based on atomic models, or partly on experimental material from band spectra of simpler molecules. This method, which suggests a definite and quite feasible procedure for dealing with a great variety of molecules, should surely be applied to many cases, and should result in chemical and physical information of considerable value.