REVIEWS OF

MODERN PHYSICS

VOLUME 7 JULY, 1935 NUMBER 3

The Quantum Theory of Valence

J. H. VAN VLECK, *Harvard University*, AND ALBERT SHERMAN,* *University of Wisconsin*

TABLE OF CONTENTS

---

* Fellow of the National Research Council.

CHAPTER I. GENERAL FEATURES

1. Introduction

THE valence concept was originally introduced into chemistry to account for certain whole number relationships in the combining ratios of atoms and radicals. It is hardly necessary here to mention how fruitful the idea proved to be, particularly in organic chemistry, where the structural formulae, based primarily on the quadrivalence of carbon, have served so well. As the structure and dynamical fabrication of the atom became known, the physicist and physical chemist have sought to understand the empirical rules of valence of atoms and radicals in terms of their electronic structure. Only since 1926 has the proper tool, quantum mechanics, been available. The nature, extent and success of these attempts, will form the subject matter of this review.

The first serious attempt to formulate a theory of valence in terms of atomic structure was made by G. N. Lewis[1] in 1916. Lewis' theory, based primarily on two ideas,—the idea that each nucleus tends to become surrounded by a closed shell of electrons corresponding to that present in an inert gas atom, and the idea that a pair of electrons shared between two nuclei constitutes the homopolar bond—made an instant appeal to chemists because it was able to correlate and predict in a simple fashion an enormous number of previously unrelated facts.

There are many objections to Lewis' theory, apart from its empirical nature. In considering the shortcomings of the theory one must realize that it was put forth in pre-quantum-mechanical days, before the advent of the spinning electron and of Pauli's exclusion principle. According to Lewis' theory one would expect NO_4^{---}, FO_4^-, but not PCl_5, SF_6. The first two are unknown; however, the last two are well known. Also, since in BH_3 all the valence electrons take part in forming bonds one would not expect it to be associated. However, B_2H_6 exists, while BH_3 is unknown. Lewis, of course, realized these deficiencies.

There were also many known anomalous valences of atoms. Thus, the carbylamines or isocyanides are known, in which carbon is apparently divalent. Trivalent carbon is also well known in, for example, the free radicals of Gomberg. A familiar example is tribiphenylmethyl. Also, many atoms have several valences, as, for example: $BiCl_2$, $BiCl_3$; $TlBr$, $TlBr_2$, $TlBr_3$; VCl_2, VCl_3, VCl_4, VF_5; BrF, BrF_3, BrF_5, etc.

Lewis' theory did not concern itself with the nature of the forces constituting the homopolar bond, nor was it capable of explaining directed valence,—e.g. the tetrahedral character of CH_4. The paramagnetism of O_2 was of course unintelligible, as well as the structure of tri-iodide ion.

The material in the following sections will show how present day theory enables one to understand many of these facts as well as facts considered normal in terms of Lewis' theory.

The subject of valence is really concerned with energy relations. If we knew the energies of all the possible different kinds of electron orbits in molecules, and also in the atoms out of which the molecule is formed, the rules of valence would automatically follow.

Now the principles of quantum mechanics enable one to write down an equation for any system of nuclei and electrons, the solution of which would provide us with complete information concerning the stability of the system, spatial arrangement of the nuclei, etc. To quote some now classic sentences of Dirac's:[2]

> The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions. . . . The underlying physical laws necessary for the mathematical theory of a large part of physics and *the whole of chemistry* are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. . . .

The complexities of the n-body problem are, alas, so great that only for the very simplest molecule, namely H_2, has it yet proved possible to integrate the Schrödinger wave equation with any real quantitative accuracy. Hence to date, anyone is doomed to disappointment who is looking in Diogenes-like fashion for honest,

---

[1] G. N. Lewis, J. Am. Chem. Soc. **38**, 762 (1916); cf. also I. Langmuir, J. Am. Chem. Soc. **41**, 868 (1919).

[2] P. A. M. Dirac, Proc. Roy. Soc. **A123**, 714 (1929). (The italics are ours.)

straightforward calculations of heats of dissociation from the basic postulates of quantum mechanics. How, then, can it be said that we have a quantum theory of valence? The answer is that to be satisfied one must adopt the mental attitude and procedure of an optimist rather than a pessimist. The latter demands a rigorous postulational theory, and calculations devoid of any questionable approximations or of empirical appeals to known facts. The optimist, on the other hand, is satisfied with approximate solutions of the wave equation. If they favor, say, tetrahedral and plane hexagonal models of methane and benzene, respectively, or a certain order of sequence among activation energies, or a paramagnetic oxygen molecule, he is content that these same properties will be possessed by more accurate solutions. He appeals freely to experiment to determine constants, the direct calculation of which would be too difficult. The pessimist, on the other hand, is eternally worried because the omitted terms in the approximations are usually rather large, so that any pretense of rigor should be lacking. The optimist replies that the approximate calculations do nevertheless give one an excellent "steer" and a very good idea of "how things go," permitting the systematization and understanding of what would otherwise be a maze of experimental data codified by purely empirical valence rules. In particular, he finds that a mechanism is really provided by quantum mechanics for the Lewis electron pair bond, and for the stereochemistry of complicated organic compounds. It is, of course, futile to argue whether the optimist or pessimist is right. In the present article we try to adopt a middle ground between the two extreme points of view, —a hope perhaps not realized. One thing is clear. In the absence of rigorous computations, it is obviously advantageous to use as many methods of approximation as possible. If they agree in predicting some property (for instance, the tetrahedral structure of methane) we can feel some confidence that the same property would be exhibited by a more rigorous solution—otherwise none. Consequently we shall discuss both of the two main methods of approximation which have been used; namely the method of molecular orbitals, developed by Lennard-Jones, Hund, Herzberg and Mulliken,[3] and the strictly homopolar method of Heitler, London, Slater and Pauling.[4]

2. Some definitions

A *molecular orbital*[5] is defined as a wave function which is a function of the coordinates of only one electron, and which is, at least hypothetically, a solution of a dynamical problem involving only one electron. The method of molecular orbitals seeks to approximate the wave function of a molecule containing n electrons as the product of n molecular orbitals, so that.

$$\Psi=\psi_1(x_1, y_1, z_1)\psi_2(x_2, y_2, z_2)\cdots\psi_n(x_n, y_n, z_n). \quad (1)$$

Throughout the article we shall use a capital Ψ to denote the wave function for the entire system, and small ψ for the wave function of one electron. In the method of molecular orbitals it is convenient, but fortunately not a necessary feature of the method, to express a molecular orbital as a linear combination of atomic orbitals. By an *atomic orbital* is meant a one-electron wave function for an electron moving in a field of only one atom. Then for a diatomic molecule AB with two chemically important electrons in equivalent states, the expression (1) becomes

$$\Psi=[a\psi_{\mathrm{A}}(x_1, y_1, z_1)+b\psi_{\mathrm{B}}(x_1, y_1, z_1)] \times[a\psi_{\mathrm{A}}(x_2, y_2, z_2)+b\psi_{\mathrm{B}}(x_2, y_2, z_2)], \quad (2)$$

where ψ_{A} and ψ_{B} are atomic orbitals referring to atoms A and B respectively. If the atomic orbitals be normalized to unity; i.e., if

$$\iiint\psi_{\mathrm{A}}^2dv=\iiint\psi_{\mathrm{B}}^2dv=1, \quad (3)$$

---

[3] J. E. Lennard-Jones, Trans. Faraday Soc. **25**, 668 (1929); F. Hund, Zeits. f. Physik **51**, 759 (1928); **63**, 719 (1930); G. Herzberg, Zeits. f. Physik **57**, 601 (1929); R. S. Mulliken, Phys. Rev. **32**, 186, 761 (1928); **33**, 730 (1929); Chem. Rev. **9**, 347 (1931); Rev. Mod. Phys. **4**, 1 (1932) (all primarily diatomic molecules). M. Dunkel, Zeits. f. physik. Chemie **7B**, 81; **10B**, 434 (1930); F. Hund, Zeits. f. Physik **73** 1, 565; **74**, 429 (1931–2); R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751; **43**, 279 (1932–3); J. Chem. Phys. **1**, 492 (1933) (polyatomic molecules).

[4] Heitler and F. London, Zeits. f. Physik **44**, 455 (1927); W. Heitler, Zeits. f. Physik **46**, 47; **47**, 836 (1928); **51**, 805 (1929); F. London, Zeits. f. Physik **46**, 455 (1928); **50**, 24 (1928); R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930); J. C. Slater, Phys. Rev. **37**, 481; **38**, 1109 (1931); L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[5] The "orbital" terminology is due to Mulliken, Phys. Rev. **41**, 49 (1932).

then for ψ_1, ψ_2 to be similarly normalized, the coefficients a and b must obey the relation

$$a^2+b^2+2abT=1,$$

where

$$T=\int\int\int \psi_A\psi_B dv. \tag{4}$$

If the wave functions of the two atoms overlap but little, the value of T is nearly zero, so that approximately

$$a^2=1-b^2. \tag{5}$$

In the various normalization relations, etc., throughout the article we assume the wave functions to be real. Otherwise the first integrand of (3) would be $|\psi_A|^2$, and that of (4) $\psi_A{}^*\psi_B$. This convention saves the repeated introduction of conjugate imaginaries, and is allowable since all the wave functions which we shall use are real (except those for $p\pi_+$ and $p\pi_-$ states). When we multiply out the right side of (1) explicitly and use obvious simplifications in notation, Eq. (1) becomes

$$\Psi=a^2\psi_A(1)\psi_A(2)+b^2\psi_B(1)\psi_B(2) \\ +ab[\psi_A(1)\psi_B(2)+\psi_A(2)\psi_B(1)]. \tag{6}$$

In (6), a term such as $\psi_A(1)\psi_A(2)$ implies that electrons 1 and 2 are both on atoms A, while $\psi_B(1)\psi_B(2)$ implies both electrons on atom B, and $\psi_A(1)\psi_B(2)$ means one electron on each atom.[6] Terms of the first two types we shall call *ionic* terms, as they require that instantaneously the molecule has an ionic structure. This is not the same as saying that the molecule is polar in the dielectric sense, for the mean moment will be zero if the two electrons have an equal tendency to congregate together on atom A or atom B, for then the molecule spends equal amounts of time in the configurations A^+B^- and A^-B^+. This will be the case if $a^2=b^2$ in (6). If on the other hand, a and b are unequal, there really is a polar structure and we then say that there are *polar* terms in the wave function. The word "homopolar" is to be construed as meaning that both polar and ionic terms are wanting.

3. Preliminary contrast of the two main methods

Because of the term e^2/r_{12} in the Hamiltonian function, which represents the familiar Coulomb repulsion, two electrons dislike being close together. Here r_{12} denotes the distance between electrons 1 and 2, and the action of repulsions of this character we shall often allude to as the r_{12} effect. The great failing of the method of molecular orbitals is the excessive presence of ionic terms, due to inadequate allowance for the r_{12} repulsion. Consider, for instance, the case of a symmetrical molecule, where $a=\pm b$, as will be proved in section 7. Then all coefficients in (6) become equal in absolute value, and this situation demands that the molecule spend as much time in the configurations A^+B^- and A^-B^+, taken together, as in the neutral condition AB. Actually there is much less A^+B^- or A^-B^+ than AB at any rate in symmetrical molecules, since ionization potentials are much larger than electron affinities, because of the r_{12} effect (e.g. 13.5 *vs.* 0.7 volts in hydrogen, a rather extreme example). Similarly, in a molecule composed of more than two atoms the method of molecular orbitals is characterized by a superfluity of ionic terms. The maximum number of superfluous electrons which can instantaneously accumulate on one atom equals its valence. Thus in CH_4 the method of molecular orbitals leads to no instantaneous structures involving H^{--} or H^{---} as this would violate the Pauli principle[7] but there can be momentary configurations involving C^{----} or H^-. If one assumes that the ionization potentials of H and of C are equal, one calculates that CH_4 spends the following amounts of time in various configurations:[7] $C^\circ(H_4)^\circ$, 27 percent; $C^+(H_4)^-$, 22 percent; $C^-(H_4)^+$, 22 percent; $C^{++}(H_4)^{--}$, 11 percent; $C^{--}(H_4)^{++}$, 11 percent; $C^{3+}(H_4)^{3-}$, 3 percent; $C^{3-}(H_4)^{3+}$, 3 percent; $C^{4+}(H_4)^{4-}$, $\frac{1}{2}$ percent; $C^{4-}(H_4)^{4+}$, $\frac{1}{2}$ percent. Again the ionic effect is clearly too large.

To avoid this difficulty of inadequate recognition of the r_{12} effect, the Heitler-London method goes to the other extreme, and assumes as its

---

[6] It is not entirely rigorous to say, as we do for our qualitative purposes, that ψ_A represents an electron entirely on atom A and ψ_B one entirely on atom B, as the wave function of atom B overlaps that of atom A, and *vice versa*, and actually there is no sharp dividing line between whether an electron is on one atom or the other. Mulliken notes that because of the overlapping of ψ_A and ψ_B it is possible to obtain a small electric moment and hence some polarity even when $a=b$.

[7] For details see J. H. Van Vleck, J. Chem. Phys. **1**, 181 (1933).

defining characteristic that all ionic terms are completely wanting. Thus in our two-electron example it uses approximate wave functions obtained by deleting the first two terms in (6).

It is hard to say categorically whether the method of molecular orbitals or the Heitler-London method is the better. The latter undoubtedly is much preferable at very large distances of separation of the atoms, at least in symmetrical molecules, for then the continual transfer of electronic charge from one atom to another demanded by the ionic terms surely scarcely occurs at all. On the other hand, at small distances, the Heitler-London method probably represents excessive fear of the r_{12} effect, and the factorization into n one-electron problems presupposed by the method of molecular orbitals may sometimes be quite a good approximation. The molecular orbitals are often the more convenient for purposes of qualitative discussion, whereas the H-L method has been used the more frequently for purposes of quantitative calculation, partly, but by no means entirely, because of habit. One nice feature of the method of molecular orbitals is the ease with which it takes cognizance of polar terms. Namely, in the example (2) or (6), simply by varying the coefficient a from zero to $\sqrt{\frac{1}{2}}$ to 1, one passes through all gradations of polarity from A^+B^- to AB to A^-B^+. For instance, if in (6), $a^2=0.9$ and $b^2=0.1$, then the molecule is dominantly A^-B^+. The importance of polar effects has been somewhat overlooked in recent days, due in large part to the homopolar influence of Heitler-London calculations. There are elements of truth in the old-fashioned chemistry that HCl has the structure H^+Cl^-, as the true wave function of HCl is expressible as a linear combination of various idealized types, and certainly H^+Cl^- must be given some representation. In the present article we shall slide rather lightly over polar effects, not because they are not important, but simply because they do not present any particular quantum mechanical features. One great service of quantum mechanics is to show very explicitly that all gradations of polarity are possible, so that in a certain sense it is meaningless to talk of such idealizations as homopolar bond, heteropolar bond, covalent bond, dative bond, etc. For a further discussion of this subject the reader is referred to Pauling's interesting paper,[8] "The transition from one extreme bond type to another." He shows from empirical evidence that the polarity of halogen compounds decreases as the mass or radius increases. Fluorine compounds are the example *par excellence* of polar valence. The reason that one does not have NeH probably lies fully as much in the old fashioned idea that the low electron affinity of Ne due to its completed inert gas shell, makes Ne^-H^+ an unstable configuration as in the more recent explanations in terms of exchange integrals, electron pairs, and a neutral structure.

The objections to either of the two methods can be obviated by adding extra terms to the wave functions. For instance, ionic and polar terms can be added in the Heitler-London method. However, we then have what we shall call refined procedures in distinction from the more naïve forms of the methods, for which our usual terminology is intended. As an example of a somewhat refined wave function we might use (6) modified by making the coefficients of the first two terms arbitrary, rather than zero as in the H-L method, or with their product equal to the square of the third coefficient as in the method of molecular orbitals. Since polar terms are so easily added in the Heitler-London method, at least in principle, its advocates often object to our stressing, as in the preceding paragraph, the simple fashion in which the molecular orbitals include polarity as in any sense a characteristic feature of the latter. However, the polar terms do seem more indigenous to molecular orbitals, since the arbitrary constant a governing the amount of polarity appears of necessity at the very beginning, whereas the corresponding polarity correction, likewise a one constant affair, is more or less optional in the Heitler-London theory.

Clearly, it becomes meaningless quibbling to argue which of the two methods is the better in refined forms since they ultimately merge. In fact, they may be regarded as simply two different starting points of a perturbation calculation, corresponding to different choices of unperturbed wave functions. The perturbation

---

[8] L. Pauling, J. Am. Chem. Soc. 54, 988, 3570 (1932).

development does not, however, take the same succinct form as in atomic problems, where the wave functions are orthogonal and where one may conveniently use power series in a parameter.

Chapter II. Diatomic Molecules

4. Relation to the Hartree field in atomic spectra

We shall now consider the various methods in some detail as applied to diatomic molecules. Consideration of polyatomic molecules will be deferred until Chapters III–IV. We shall begin with the molecular orbital procedure, as it is the simplest. It may be described as in principle the molecular analogue of Hartree's familiar method of the self-consistent field in atomic spectra.[9] We insert the words "in principle" because elaborate quantitative calculations based on the Hartree method have really been consummated in atoms, whereas the corresponding method in the molecular case is commonly used mainly for purposes of qualitative discussion, without any attempt at quantitative evaluation of the fields or wave functions.

The essence of the Hartree method is that any given electron is imagined to move in the "time exposure" rather than in the instantaneous field of the other electrons. In other words, we replace the momentary positions of the other electrons by their averaged positions in computing the force which they exert upon the given electron. The force-field then obtained is, of course, the same as one would compute from an electrostatic distribution of charge whose density in any region is proportional to the total fraction of the time which the charges responsible for the field spend in this particular region. The great advantage of the Hartree method is that it reduces the actual n-body problem to n one-body problems, since the averaging process has made the force on one charge independent of the position of the other charges. It is clear that, in consequence, inadequate cognizance is taken of the fact that two electrons are seldom close together because of the large repulsive force between them. Thus, as we have already mentioned in section 3, and as we shall analyze more fully in section 11, the method of molecular orbitals gives too large ionic terms,—for instance too much probability that the ground state of H_2 be instantaneously in a condition such as H^+H^- or H^-H^+. Trouble of this sort is obviously to be expected, since, with the type of approximation made, one of the electrons in H_2 has no way of knowing where the other is, and so the two may inadvertently, as it were, find themselves on the same atom.

5. Quantum numbers in a field of axial symmetry[10]

In atoms in S states, the charge distribution possesses central symmetry on the average so that any given electron may be considered as moving in a field of central symmetry. In a diatomic molecule things are not quite so simple. Here the "time exposure" field will at best be one of axial symmetry. We must therefore examine the quantization characteristic of the motion of an electron in an electric field of axial symmetry. In any field not departing greatly from central character an electron is described by four quantum numbers, three of which are associated with the orbit, and one of which determines the orientation of the spin of the electron. First let us assume that the field has only axial symmetry, but that the departures from central symmetry are not too large. It is well known that in a field of central symmetry the three orbital quantum numbers are the principal quantum number n, the azimuthal quantum number l, and the axial quantum number λ. The latter is really m_l, the projection of l upon the electric axis. In the diatomic molecule this axis is the line joining the two nuclei, and then, for some reason, it is customary to replace m_l by a new symbol, λ. Only the absolute value of λ is usually of interest because the state with $\lambda=+1$, for instance, is of the same energy as that for which $\lambda=-1$. The possible values of n are 1, 2, $\cdots$, while l can assume any value in the range 0, $\cdots$ $n-1$. The range for λ is $-l$, $-l+1$, $\cdots$ $+l$. The quantum number m_s, which space quantizes the

---

[9] For an excellent syllabus on the Hartree method see L. Brillouin, *La Méthode du Champ Self-Consistent* (Actualites Scientifiques, Hermann, Paris, 1933–4, Nos. 71 and 159).

[10] For a fuller account of approved notation in molecular spectra see R. S. Mulliken, Phys. Rev. **36**, 611 (1930).

spin, can only take on the values $\pm\frac{1}{2}$ since the spin quantum number for an individual electron is always $\frac{1}{2}$.

In molecular spectra it is customary to use such a notation as

$$1s\sigma^2 2s\sigma^2 2p\sigma^2 2p\pi^3 \; {}^2\Pi \qquad (7)$$

to designate a state of the molecule. Here the numbers in front of the small letters denote the principal quantum numbers, the small Roman letters supply the values of the azimuthal quantum number ($l=0, 1, 2, 3 \cdots$ for $s, p, d, f \cdots$ respectively). The small Greek letters yield the values of the axial quantum number λ according to the rule that $\lambda=0, 1, 2, 3 \cdots$ for $\sigma, \pi, \delta, \varphi \cdots$ respectively. It will usually not be necessary to specify the sign of λ, or whether m_s is $+\frac{1}{2}$ or $-\frac{1}{2}$. The capital letter gives the value of the total or collective orbital angular momentum about the figure axis, which is denoted by the letter Λ, and is the algebraic sum of the individual components of angular momentum about this axis, so that $\Lambda=\Sigma\lambda$. (Here attention must be paid to the sign of λ.) The superscript preceding the capital Greek letter gives the value of the multiplicity, which is the same as $2S+1$, where S is the total spin quantum number for the molecule. The superscripts following the small letters give the number of electrons inhabiting the corresponding individual states. Thus in example (7), which happens to be the ground state of the OH molecule, there are two $1s\sigma$ electrons, two $2s\sigma$ electrons, etc.

In assigning electrons to the different states we must always bear in mind the limitations imposed by the Pauli exclusion principle. This principle requires that no two electrons can have all four quantum numbers the same. At first sight such a restriction might seem to require that none of the superscripts could be greater than unity. However, this is not really the case, for we have not specified the sign of λ or of m_s. Since there are two sign choices for each of the quantities λ, m_s we see that the Pauli rule allows four electrons to a given assignment of l, $|\lambda|$ except in the special case of a σ state, where λ vanishes and where hence there is no alternative in sign except for m_s. Thus, there can be at most four electrons, for example, of any one of the following types: $2p\pi$, $3d\pi$, $3d\delta$, etc., and at most two $1s\sigma$, or two $2p\sigma$ electrons.

The Pauli exclusion principle is the cornerstone of the entire science of chemistry, for without it one would not have an understanding of the Mendeléef periodic table and the like. The reader will recall that it, together with a knowledge of the relative order of binding of the various electronic orbits, yields the characteristic structure of the periodic table.[11] There are two electrons absorbed in the elements of the first period because the only two possible one quantum electrons are those embodied in the formula $1s\sigma^2$. The eight electrons of the next period are given by $2s\sigma^2 2p\sigma^2 2p\pi^4$. The third period might at first sight seem to require eighteen electrons rather than the eight found experimentally because there are eighteen possible 3-quantum electrons. However, the s and p electrons are considerably lower in energy than the d electrons, so that a break comes after the addition of $2s^2 2p\sigma^2 2p\pi^4$. The ten $3d$ electrons are assimulated in the midst of the acquisition of the $4s$ and $4p$ electrons. This interruption gives rise to the characteristic phenomena of the transition group, and swells the fourth period from eight to eighteen.

It may be well to contrast the notation (7) with that used for Russell-Saunders coupling, which is characteristic of free atoms not disturbed by external fields or by excessively strong spin-orbit interactions. Here the angular momentum of a given electron is not individually space quantized. Instead the l's of the atom are compounded vectorally and quantized to a resultant L. Similarly, the spins are compounded to a resultant S. (The latter quantization takes place even in molecules.) Then L and S are quantized to a resultant J. When the system has a quantized "collective" resultant angular momentum L (not to be confused with the axial component Λ of collective angular momentum quantized in Eq. (7)), of course all vestiges of individual space quantization are lost. In place of (1) one employs a notation such as

$$1s^2 2s^2 2p^6 \; {}^2P_{3/2}. \qquad (8)$$

Here the capital letter gives the value of L ($L=0, 1, 2, 3 \cdots$ for S, P, D, F, respectively), the superscript the value of $2S+1$, and the subscript the value of the inner quantum number J.

In molecules one uses the notation (7) rather than (8) because ordinarily molecular forces are strong enough to break down the L, S coupling. The J coupling is broken

---

[11] For instance, Pauling and Goudsmit, *The Structure of Line Spectra*, Chap. IX.

down by external fields even before the L, S is.[12] If the J, but not the L, S coupling, were broken down one would space quantize separately the collective (but not the individual) spin and orbital angular momenta. Capital Greek letters would then have a meaning and in place of $P_{3/2}$ in (8) one would use a notation such as $P\Pi_{3/2}$. The subscript gives the value of $\Lambda+M_S$.

The quantum numbers n and l have a direct significance only if the departure of the field from central character is not too great. If most of the vestiges of central symmetry are lost, only those orbital quantum numbers which are specified by Greek letters are relevant, since only the component of angular momentum parallel to the figure axis is constant in the arbitrary field of only axial symmetry. The various spin quantum numbers retain their validity since the spin is rather insensitive to electrical forces; in particular, one can still speak of the total spin S of the molecule. Of course, when n and l lose their meaning other quantum numbers take their place since four numbers are always associated with an electron, but the precise kinematical significance of these other quantum numbers will be complicated and depend upon the particular characteristics of the field. For instance, quantum numbers associated with the separation of variables in elliptic coordinates are appropriate if the axial field is one of two attracting Coulomb centers (e.g., H_2^+), but in other more complicated axial fields not even a separation of variables appears possible. To show that quantum numbers still exist, although of unknown kinematical nature, Mulliken uses a letter near the end of the alphabet, thus introducing terminology such as $u\pi$, $v\pi$, $w\pi$, $w\sigma$, etc., with the convention that the energy decreases as one progresses further in the alphabet. Thus u, v, w each really stand for two quantum numbers, and a $v\pi$ electron is more firmly bound than a $u\pi$ one.

6. *u* and *g* states

In symmetrical molecules such as H_2, N_2, etc., there is a division of orbits into two categories which is particularly helpful. An orbit is called g or u ("gerade" or "ungerade") according to whether its orbital wave function ψ is even or odd under the operation which the crystallographer calls inversion, i.e., reflection of all the coordinates in the molecular midpoint (i.e., the point equidistant from the two nuclei). If the midpoint is, as usual, chosen as origin of the coordinate system, one thus has

$$g:\ \psi(x, y, z)=+\psi(-x, -y, -z),$$
$$u:\ \psi(x, y, z)=-\psi(-x, -y, -z).$$

One might, perchance, inquire why wave functions are necessarily g or u. The proof that they must be is quite simple. Suppose one had a solution which did not possess the u or g property, say $\psi(x, y, z)$. Then since in a symmetrical molecule the wave equation is invariant under inversion in the midpoint, $\psi(-x, -y, -z)$ would also be a solution of the wave equation, or, equally well, linear combinations of $\psi(x, y, z)$ and $\psi(-x, -y, -z)$. The particular linear combinations

$$\psi(x, y, z)\pm\psi(-x, -y, -z)$$

represent two wave functions which are respectively even and odd under reflection in the nuclear midpoint. The states corresponding to these functions would both have the same energy so that the system would be degenerate, unless the wave function were already even or odd, in which case one of the combinations is identically zero. Hence either the wave functions are necessarily even or odd, or they are not already so but can be made so without loss of generality. In the latter case there is a twofold degeneracy (not to be confused with other twofold degeneracies such, for instance, as that regarding the sign of λ or of m_s). Actually this degeneracy does not occur, and so the wave functions are inescapably even or odd.

It is clearly to be understood that in this discussion we are reflecting only electronic coordinates, since the nuclei are throughout regarded as fixed attracting centers so that their coordinates do not enter. Symmetry properties when nuclear coordinates are reflected as well, are another matter, involving consideration of molecular rotation.

7. The united and separated atom parentages of a state

At intermediate, i.e., actual, inter-nuclear distances, the self-consistent fields appropriate to an atom do not show much semblance of central character, so it is best to use the $u, v, w\cdots$ notation. However, one can imagine the nuclei to be gradually hypothetically drawn closer and closer together. After a certain point in this process the field will surely become more and more nearly central in character, and is accurately central when the nuclei are made to coincide, thus forming what Mulliken calls the "united atom". Then notation of the type outlined in section 5 is clearly in order. It is, of course, possible to correlate the quantum numbers appropriate to actual inter-nuclear distances

---

[12] For unusual cases where J coupling still persists in molecules see Mulliken, Phys. Rev. **46**, 549 (1934).

with those appropriate to the united atom. The Greek letters must be the same in both cases since the component of angular momentum parallel to the figure axis remains invariant when the nuclear distance is varied. Also the orbit preserves its u or g character. For the united atom, an orbit is u or g according to whether l is odd or even. In other words, p and f states are u, while s and d states are g. This is simply a statement that spherical harmonics of odd and even degree are respectively odd and even with respect to reflection in the origin. (Thus, for example, $P_1{}^0=\cos\theta$ changes sign under the substitution $\theta\rightarrow\pi-\theta$ and $\varphi\rightarrow\varphi+\pi$, while $P_2{}^0=\frac{1}{2}(3\cos^2\theta-1)$ remains invariant.

Instead of examining what happens to an orbit when the nuclei are made to coincide one may equally well inquire what happens when the atoms are instead infinitely separated. Here again the identity of the Greek letters must be preserved. When one gives the quantum numbers n, l of the "separated" atomic orbit with which a given molecular state is genealogically related it is customary to write the Greek letter before the two other letters so as to avoid confusion with notation appropriate to the united atom. Furthermore in a molecule composed of two unlike atoms (e.g., HCl) one should also specify which atom is the source, and so use notation such as $\sigma 1s_{\mathrm{H}}$, $\pi 2p_{\mathrm{Cl}}$, etc. In molecules composed of like atoms A and B, the energy levels of the two separated atoms are the same, and to every wave function ψ_{A} of atom A, there is a corresponding wave function ψ_{B} relating to atom B and involving the same energy. Hence any linear combination of ψ_{A} and ψ_{B} is a solution when the atoms are completely separated. When the separation is very large, but not infinite, the degeneracy is removed and the appropriate linear combinations to use are the sum and difference. This follows from the fact that these combinations have the u and g property, so we may write

$$\psi_{g,\,u}=[1/2(1\pm T)]^{\frac{1}{2}}(\psi_{\mathrm{A}}\pm\psi_{\mathrm{B}}). \tag{9}$$

Here T is defined as in (4), and the radical factor has been inserted to preserve the normalization. Eq. (9) is an illustration of the fact that a molecular orbital can always be expressed as a linear combination of atomic orbitals. However, only at large inter-nuclear separations is a molecular orbital at all accurately described as a linear combination of a *few* atomic orbitals. Since the totality of atomic orbitals form what mathematicians term a "complete" set of functions, one can describe a molecular orbital appropriate to an arbitrary distance of separation as a linear combination of atomic orbitals if one uses an infinite number of terms in the sum, but such a development is obviously not very practical. In quantitative rather than qualitative work it is usually inadvisable to express the molecular orbital as a linear combination of atomic orbitals; in fact, the best feature of the method of molecular orbitals from the quantitative side is that such an expansion is not inherent in its use.

One is now in a position to construct diagrams correlating the states of the separated atoms with those of the actual molecule and of the united atom. Here the key to the construction is that the quantum number λ remains invariant, and that the u, g property is always preserved in molecules composed of like atoms. Furthermore, curves associated with like values of λ, and of similar u, g symmetry, should not intersect, in accordance with a well-known "non-crossing" rule of quantum mechanics for states which are capable of perturbing each other.[13] Namely, the interaction between two states tends to spread them apart and so the potential curves of two interacting states cannot cross. Thus one arrives at a correlation diagram such as is given in Fig. 1, which is reproduced from one of Professor Mulliken's papers[14] with his kind permission.

The reader will do well to study this figure, for it is the essence of the "*Aufbauprinzip*" or "configuration theory" of Hund, Mulliken, Lennard-Jones and others.[3] This diagram might well be on the walls of chemistry buildings, being almost worthy to occupy a position beside the Mendeléef periodic table so frequently found thereon. Just as the latter affords an understanding of the structure of *atoms* so does the former afford an understanding of the structure of *molecules*, with which the chemist is often concerned.

From Fig. 1, such correlation formulas as

$$2s\rightarrow\sigma_g 2s\rightarrow z\sigma\rightarrow 2s\sigma\rightarrow 2s;\ 2s\rightarrow\sigma_u 2s\rightarrow y\sigma\rightarrow 3p\sigma \tag{10}$$

should become apparent. (A correlation such as

---

[13] See F. Hund, Zeits. f. Physik **52**, 601 (1928).

[14] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932).

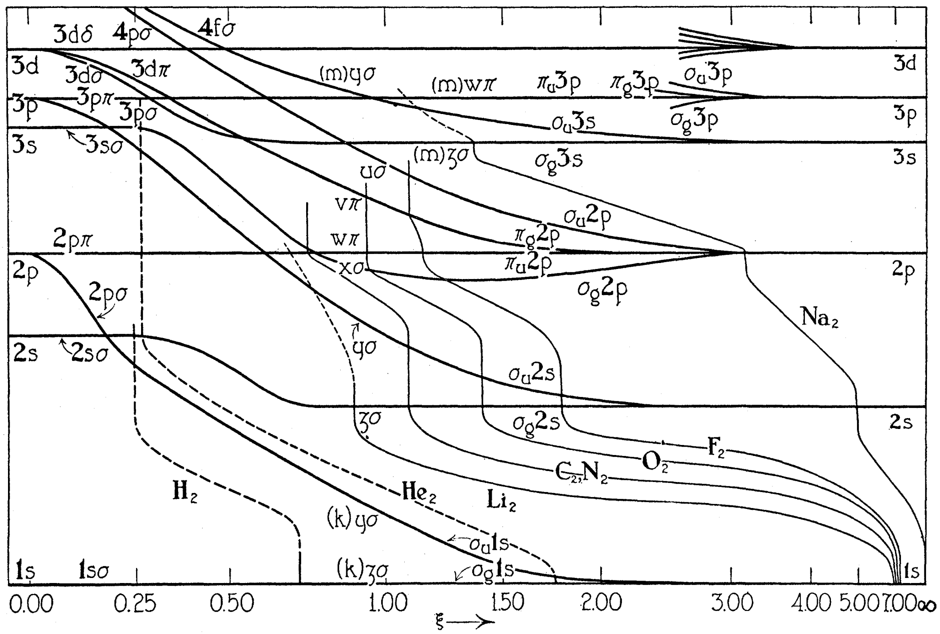


FIG. 1. Correlation between states of the united atom (left) and separated atoms (right), for molecules composed of two like atoms. The clue to the construction of the figure is the Pauli principle and the nonintersection of levels which have the same symmetry (i.e., which have the same value of λ and the same *u* or *g* property). A state of the united atom is *u* or *g* according as *l* is odd or even. The abscissa is the ratio of the inter-nuclear distance to orbital diameter. The guide lines emanating from the lower right corner are included to indicate the approximate position of some simple molecules in the diagram. A uniform scale has not been used for either asbcissae or ordinates.

$\sigma_g 2s \to 2p\sigma$, for instance, would be impossible since $2p$ is u rather than g; the correlation $\sigma_g 2p \to 2s$ does not occur as $2s$ has been pre-empted by $\sigma_g 2s$.)

Fig. 2 gives an analogous diagram for a molecule composed of two unlike atoms. Here the two combinations formed from two atomic orbitals cannot be described as *u* or *g*, and instead an asterisk is used to distinguish one of them.

Of course the correlation rules which we have discussed in some detail determine only where the curves "join on" at the extreme left and extreme right of the figure, and do not determine, except very roughly by interpolation the behavior of the curves between the two extremes. In sketching these curves, Mulliken has drawn to a considerable extent upon empirical information afforded by band spectra. The configuration theory by itself, for instance, does not tell us that $\sigma_g 2p$ is below $\pi_u 2p$ at large inter-nuclear distances. Indeed we have mentioned that the Heitler-London theory is a better approximation than molecular orbitals for large separations, and so this theory should be appealed to where possible in drawing the extreme right portion of the figures. No attempt should be made to deduce absolute energies from the figures. In fact, a different energy scale has been used for the united atom than for the dissociation products. For example, a $2p$ state of the united atom is clearly more firmly bound, and so represents a deeper energy level, than a $2p$ state of a completely dissociated atom, since the former has a greater nuclear charge than the latter. However, in the figures, the same height has been assigned to both levels. To illustrate the bonding effect of nonpromoted orbits, the figures should be bent downwards on the left side.

One thing should become apparent by now, from Fig. 1 or otherwise. The quantum numbers n, l for the orbit of the united atom which is associated with a given molecular orbital are not necessarily the same as those of the atomic orbitals for the separated atoms from which the given molecular state is derived. For example, in Fig. 1, the state $y\sigma$ is derived from the state $2s$ of the separated atom, but passes over into the state $3p$ for the united atom. Orbits for which the quantum number n has a larger value for the united atom than for the separated atoms are termed "promoted" orbits. Promoted orbits usually are a hindrance rather than an asset as far as molecule formation is concerned, since the energy increases when the principal quantum number n is increased. In other words, because of the Pauli principle, such electrons can be accommodated in the united atom only if they are housed in states of comparatively high energy, so that they have higher energy in the united atom than in the molecule. It is clear that many of the electrons must be promoted in passing to the united atom since here only one housing structure is available for the electrons, whereas two such structures are available for the separate atoms. Electrons which are not promoted are believed to be in general bonding electrons, unless they are sheltered in inner shells, since they lead to lower energy for the united atom than for the separate atoms on account of the higher effective nuclear charge for the former. Besides bonding and anti-bonding electrons there are nonbonding electrons, *viz.* the inner electrons whose wave functions do not appreciably overlap two atoms at a time (before linear combinations are taken) and for which the u, v, . . . nomenclature is not used. A nonbonding electron is always potentially either a bonding or anti-bonding one. The point is that its wave function is built out of atomic orbitals from the two atoms which do not overlap each other appreciably at the actual inter-nuclear distance, so that promotion has not yet become much of a draw-back, or nonpromotion an advantage. At smaller distances of separation, the bonding or nonbonding effects would begin to manifest themselves. Clearly K electrons are to be considered nonbonding electrons except in compounds containing hydrogen.

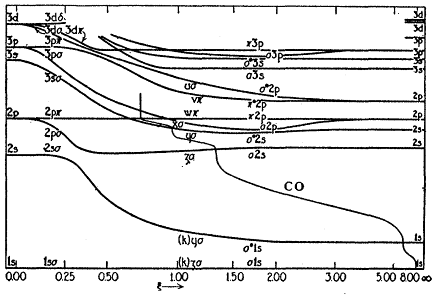


FIG. 2. Similar ,to Fig. 1 except that the constituent atoms are unlike. States of like λ cannot cross, but the u, g property is lost.

Thus in the examples taken from Mulliken given at the beginning of the next section he does not even deign to give a Greek nomenclature to the four electrons contributed to each by the K shells of the two atoms. Instead they are collectively simply labelled KK in Table I. One should not, however, form the impression that the energetic effect of the so-called "non-bonding" or "inner shell" electrons is entirely negligible. Instead we shall see in the appropriately numbered section 13, that it is large enough to render void all attempts at *quantitative* calculations of heats of dissociation in which inner shells are neglected.

Herzberg[3] defines the number of bonds as equal to half the difference between the number of bonding and anti-bonding electrons. In many ways this definition leads to a helpful concept of what is meant by a bond, but at the same time it is a little artificial, as there can be varying

TABLE I. *Molecular orbital nomenclature for some simple molecules.*

$$C[1s^22s^22p^2\ {}^3P]+N[1s^22s^22p^3\ {}^4S]\rightarrow CN[KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)\ {}^2\Sigma]$$
$$N[1s^22s^22p^3\ {}^4S]+N[1s^22s^22p^3\ {}^4S]\rightarrow N_2[KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2\ {}^1\Sigma_g]$$
$$C[1s^22s^22p^2\ {}^3P]+O[1s^22s^22p^4\ {}^3P]\rightarrow CO[KK(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2\ {}^1\Sigma]$$
$$N[1s^22s^22p^3\ {}^4S]+O[1s^22s^22p^4\ {}^3P]\rightarrow NO[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)\ {}^2\Pi]$$
$$O[1s^22s^22p^4\ {}^3P]+O[1s^22s^22p^4\ {}^3P]\rightarrow O_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^2\ {}^3\Sigma_g]$$
$$F[1s^22s^22p^5\ {}^2P]+F[1s^22s^22p^5\ {}^2P]\rightarrow F_2[KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^4\ {}^1\Sigma_g]$$

degrees of promotion and varying amounts of energy decrease for the non-promoted electrons. Thus in reality there is no hard and fast distinction between bonding, nonbonding, and anti-bonding electrons.

8. Structure of some simple molecules

It is interesting at this point to sketch in Table I the formation of some diatomic molecules.

The electron orbits are written in order of decreasing firmness of binding. This order, for most of the molecules, can be seen from Fig. 1.

Let us consider the case of N_2 in more detail. From Fig. 1, and the above definition of bonding and anti-bonding electrons, it is clear that the two $z\sigma$ electrons are bonding since they are not promoted and move in the field of two nuclei. The two $y\sigma$ electrons are promoted and anti-bonding. (The $2s$ electrons in the separate atoms are promoted to $3p$ states in the united atom, and this promotion is already well under way in N_2, as can be seen from the figure.) The four $w\pi$ and two $x\sigma$ electrons are bonding. The $x\sigma$ electrons are, to be sure, ultimately promoted, but at the actual inter-nuclear distance the resulting anti-bonding effect has not begun to enter, and instead one has the bonding action due to the dip in the $\sigma_g 2p$ curve on the right side of Fig. 1. Thus there are altogether eight bonding and two anti-bonding electrons. Since the bonding electrons are in excess the molecule will be stable, and by Herzberg's definition the number of bonds present is $\frac{1}{2}(8-2)=3$, in agreement with the usual chemical version. But the difference between the present interpretation of N_2 and the ordinary chemical concept of the structure of the molecule is to be noticed. A chemist would say that the valence of a nitrogen atom is usually three, and that therefore N_2 is $N\equiv N$. Since each bond is an ordinary electron-pair bond there are six electrons holding the molecule together. It is clear from the above discussion, however, that ten rather than six electrons are vitally concerned in the formation of N_2. The bonding action of the two $z\sigma$ electrons probably roughly cancels the anti-bonding action of the two $y\sigma$ electrons, so that the net bonding effect is approximately zero, but this is far different from saying that these four electrons do not play any part in the formation of N_2, and that hence their bonding action is zero.

With the aid of the configuration diagram one can immediately see why such molecules as H_2, Li_2, etc., are stable, while He_2 and Ne_2 are unstable. In H_2 there are two electrons. They can both be housed in the state $\sigma_g 1s \rightarrow 1s\sigma$ and are therefore both bonding electrons. In He_2 four electrons must be accommodated. Because of the Pauli principle only two electrons can be housed in the deepest state. The next two electrons must therefore settle in the next higher state, namely $\sigma_u 1s \rightarrow 2p\sigma$, which is decidedly anti-bonding in character, so that all told there are as many anti-bonding as bonding electrons, and the resultant bonding effect is nil.

In F_2 it is clear from Table I and Fig. 1 that there are six bonding ($x\sigma$ and $w\pi$) and four anti-bonding ($v\pi$) electrons, giving an excess of bonding electrons, hence stable F_2. (The $z\sigma$ and $y\sigma$ electrons are here essentially nonbonding.) On the other hand when we come to Ne_2 there are two more electrons which must be housed as compared to F_2. These can only be accommodated in the strongly anti-bonding state $\sigma_u 2p$. The presence of these last two electrons is such a drawback that Ne_2 is unstable. Similarly, turning to Fig. 2, we see that we can have a stable molecule of the type OF but not of the form NeF because the extra electron of Ne would be housed in the strongly anti-bonding state $u\sigma$ or $\sigma^* 2p$.

Perhaps the reaction of the reader at this stage is that the above is all very well, but that after all this configuration theory does not predict so very much more than the old octet theory of Lewis,[1] etc. The idea that any electrons present beyond a closed shell for the united atom are really a drawback to the molecule is, of course, implicit in the old theory of Lewis and Langmuir.[1] The answer to this objection is fourfold: (a) The configuration theory puts the old ideas of forming closed shells on a more tangible and definite quantum mechanical basis than hitherto. (b) The configuration theory yields useful information in intermediate cases in which the united atom does not have either just the right number of electrons for a closed shell, or one or two more. For example, BeH is a molecule which is not understandable in terms of the old valence theory, but is in terms of molecular orbital theory.

(c) The configuration theory is very useful in correlating the excited states of the molecule with dissociation products. For instance, it shows in the $(1s\sigma)(3p\sigma)\ {}^1\Sigma_u$ state of H_2 the molecule dissociates into one normal and one excited (2-quantum) atom. A correlation of this character is not, however, of interest to our immediate purpose of formulating a theory of valence, which is concerned obviously only with the normal state of the molecule. (d) The configuration theory shows in an easy way why it is that most stable diatomic molecules are diamagnetic, but that O_2 is paramagnetic, being abnormal among molecules with an even number of electrons in this respect. This must be regarded as one of the triumphs of configuration theory, for the explanation[15] with the alternative Heitler-London theory is somewhat less elementary. When two electrons have their three orbital quantum numbers the same, the spin quantum number m_s must have the opposite sign for the two. One can show that then the spins of the two electrons cancel, so that the resultant spin of the two electrons is zero. On the other hand, when two electrons are in different states the resultant spin can be either zero or one. Hence there should be neither a spin nor an orbital moment associated with groups such as σ^2, π^4 or δ^4, which may be regarded as closed shells. A group such as π^4 may be considered as two pairs of the form $\pi_+{}^2$, $\pi_-{}^2$, where we have added subscripts to give the sign of λ. There is no orbital moment because λ has the opposite sign for π_+ and π_- states, so that the moments associated with π_+ and π_- cancel each other. On the other hand, configurations such as π^2 do not represent closed shells. The three types of molecular states which can arise from π^2 are $\pi_+\pi_-\ {}^3\Sigma$, $\pi^2\ {}^1\Delta$, $\pi_+\pi_-\ {}^1\Sigma$. All but the last of these should be paramagnetic as they have non-vanishing values of S or Λ. In the first case the moment is due to the spin, in the second to the orbit. One can show that, all other things being equal, spins like to be parallel (this is the common Hund rule that the normal state is that of greatest multiplicity consistent with the Pauli principle[16]). Hence ${}^3\Sigma$ is the deepest of the three states arising from π^2. Consequently molecules of a structure consisting of closed groups (σ^2, π^4, etc.) plus π^2 have an incomplete outer shell, should be normally in a ${}^3\Sigma$ state, and should be paramagnetic. Reference to Table I shows that O_2 has such a structure, whereas C_2, N_2 and F_2 involve only closed groups. Therefore O_2 should be paramagnetic and indeed the susceptibility found experimentally corresponds precisely to the value which one calculates for a ${}^3\Sigma$ state from the quantum theory of magnetism, of which we shall not give the details.[17] Also S_2 should be paramagnetic and there is evidence that it indeed is.[17]

The existence of the B_2H_6 molecule is nicely interpreted by molecular orbitals on the ground that BH_3 is isoelectronic with O, so that if one uses the united atom approximation B_2H_6 is similar to O_2 in structure.[18] However indirect magnetic measurements indicate that B_2H_6 is diamagnetic[19] rather than paramagnetic. The explanation of this surprizing fact is at present not clear. A plane rather than the usually assumed trigonal structure for B_2H_6 would lift the $\pi_+\pi_-$ degeneracy and destroy the paramagnetism, but a plane model might be inadmissible on other grounds.

Clearly, all molecules with an odd number of electrons (e.g., NO_2, NO, ClO_2) should be paramagnetic, as there is at least one uncompensated spin. The molar susceptibilities of a large number of odd molecules and free radicals[20] have experimentally the value 1.27×10^{-3} which one calculates on the assumption that only the spin contributes to the susceptibility, and that there is one free spin. One can show that in molecules with more than two atoms all the susceptibility should arise from the spin. The diatomic odd molecule NO is normally in a ${}^2\Pi$ state. Quite irrespective of the experimental evidence, this state could be predicted from configuration theory, as in Table I. From a ${}^2\Pi$ state the moment arises both from the spin and the orbit, the orbital moment being required because $\Lambda\neq0$. The observed susceptibility checks nicely with the calculated value.[17]

---

[15] W. Heitler and J. Poschl, Nature **133**, 833 (1933).

[16] See p. 165 of reference 11.

[17] For details see Van Vleck, *Electric and Magnetic Susceptibilities*, Chap. X.

[18] Cf. R. S. Mulliken, Phys. Rev. **43**, 765 (1933); cf. also L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

[19] L. Farkas and H. Sachsee, Trans. Faraday Soc. **30**, 331 (1934). (Diamagnetism deduced from inability to produce para-ortho conversion in hydrogen.)

[20] N. W. Taylor, J. Am. Chem. Soc. **48**, 854 (1926); S. Sugden, Trans. Faraday Soc. **30**, 18 (1934); H. Katz, Zeits. f. Physik **87**, 238 (1934).

9. The method of Heitler and London

The H-L method[4] goes to the other extreme from molecular orbitals and assumes that ionic terms are completely wanting. For a molecule composed of two atoms A and B, each having one electron, an allowable structure from the H-L viewpoint is that represented by the product $\psi_A(1)\psi_B(2)$ of atomic orbitals relating to atoms A and B respectively, as then electron 1 is identified with atom A and electron 2 with atom B.[6] Another possibility is $\psi_A(2)\psi_B(1)$ wherein the electrons have traded places as compared with the preceding product. The proper linear combinations of the two possible products are, as one might expect, the sum and difference combinations

$$\Psi_{HL}({}^{1,\,3}\Sigma_{g,\,u})=C[\psi_A(1)\psi_B(2)\pm\psi_B(1)\psi_A(2)], \quad (11)$$

since the Hamiltonian function **H** will possess no matrix elements connecting them, i.e. since

$$\int\cdots\int\Psi_{HL}({}^1\Sigma_g)\mathbf{H}\Psi_{HL}({}^3\Sigma_u)dv_1dv_2=0. \quad (12)$$

The upper and lower sign choices in (11) give states which are respectively *g* and *u* as regards inversion in the molecular center. Further the orbital wave function (11) is either symmetric (upper sign) or anti-symmetric (lower sign) as regards permutation of the two electrons. Since **H** is symmetrical in the two electrons, the integrand of (12) is anti-symmetric, and hence the integral (12) is indeed zero.[21] If ψ_A, ψ_B are each normalized to unity (Eq. 3), the normalization factor C has the value

$$C=(2\pm 2T^2)^{-\frac{1}{2}}, \qquad \text{with } T=\iiint\psi_A(1)\psi_B(1)dv_1. \quad (13)$$

The upper and lower choices of sign in (11) give respectively singlet and triplet states. This is because the complete wave function is equal to a product of a spin and an orbital function. (This separability into spin and orbital factors is, incidentally, not in general possible when there are more than two electrons, nor is it rigorously true even with two electrons when we consider the effect of spin-orbit distortion, which is fortunately small except in heavy atoms.) Now the Pauli principle demands that the total wave function be anti-symmetric as regards electron interchange. Hence a symmetric orbital state demands an anti-symmetric, i.e., singlet spin factor, while an anti-symmetric orbital state requires a symmetric,[22] i.e., triplet spin part, as stated above.

The energy W associated with the two solutions given in (11) is obtained in the usual way by integrating them over the Hamiltonian operator **H**, i.e.

$$W=\int\cdots\int\Psi\mathbf{H}\Psi dv_1dv_2 \quad (14)$$

provided Ψ is normalized to unity. If our molecule is one of hydrogen, the Hamiltonian operator **H** has the form

$$\mathbf{H}=-(h^2/8\pi^2m)(\nabla_1{}^2+\nabla_2{}^2)+e^2/r_{AB}-e^2/r_{A1} -e^2/r_{A2}-e^2/r_{B1}-e^2/r_{B2}+e^2/r_{12}, \quad (15)$$

where $\nabla_1{}^2$ denotes the Laplacian operator for the coordinates of electron 1, r_{12} is the distance between electrons 1 and 2, r_{AB} is that between nucleus A and nucleus B, r_{A1} that between nucleus A and electron 1 and so on. We now substitute (15) in (14) and make use of the fact that $\psi_A(1)$ satisfies the equation

$$[(-h^2/8\pi^2m)\nabla_1{}^2-(e^2/r_{A1})-W_H]\psi_A(1)=0, \quad (16)$$

since $\psi_A(1)$ is an atomic orbital for a free hydrogen atom. Here W_H is the energy, -13.53 volts, of the ground state of the hydrogen atom. There are, of course, equations identical in type with (16) satisfied by the other atomic orbitals, except that the indices are different. One thus finds that (14) becomes

$$W=2W_H+(K\pm J)/(1\pm T^2), \quad (17)$$

where[23]

---

[21] When the integrand is anti-symmetric, the contributions of equal volume elements which differ only in the permutation of the electrons cancel each other, making the integral vanish. When the integrand is odd as regards inversion, the integral is likewise zero, due to cancelation of the contributions of volume elements at x_1, y_1, z_1, x_2, y_2, z_2 and $-x_1$, $-y_1$, $-z_1$, $-x_2$, $-y_2$, $-z_2$.

[22] For the symmetry properties of spin functions see, for instance, Sommerfeld, *Wellenmechanischer Ergänzungsband*, p. 275, or the chapter on helium in Pauling and Wilson's forthcoming book.

[23] The letters J,K have just the opposite significance with us than with Slater, reference 50.

$$
\begin{aligned}
K&=\int\cdots\int\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(2)(\mathbf{H}-2W_{\mathrm{H}})\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(2)dv_1dv_2\\
&=\frac{e^2}{r_{\mathrm{AB}}}-2e^2\int\int\int\frac{\psi_{\mathrm{A}}(1)^2}{r_{\mathrm{B}1}}dv_1+e^2\int\cdots\int\frac{\psi_{\mathrm{A}}(1)^2\psi_{\mathrm{B}}(1)^2}{r_{12}}dv_1dv_2,
\end{aligned}
\tag{18}
$$

$$
\begin{aligned}
J&=\int\cdots\int\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(2)(\mathbf{H}-2W_{\mathrm{H}})\psi_{\mathrm{A}}(2)\psi_{\mathrm{B}}(1)dv_1dv_2\\
&=\left\{\frac{e^2T^2}{r_{\mathrm{AB}}}-2T\int\int\int\frac{e^2}{r_{\mathrm{B}1}}\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(1)dv_1\right\}+\int\cdots\int\frac{\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(2)\psi_{\mathrm{A}}(2)\psi_{\mathrm{B}}(1)}{r_{12}}dv_1dv_2.
\end{aligned}
\tag{19}
$$

In writing (18) and (19) terms have been combined which are equal in virtue of the symmetry of the molecule or parity of the electrons. For instance, the integral given in (13) has the same value if 2 be substituted for 1. The expression T defined in (13) has been factored out where possible.

The expressions K and J defined in (18) and (19) are usually called, respectively, the Coulomb and exchange integrals. The word exchange is employed because electrons have traded places in $\psi_{\mathrm{A}}(1)\psi_{\mathrm{B}}(2)$ as compared with $\psi_{\mathrm{A}}(2)\psi_{\mathrm{B}}(1)$.

Evidently $|W-2W_{\mathrm{H}}|$ is the bonding energy of the molecule, since $2W_{\mathrm{H}}$ is the energy of two isolated hydrogen atoms. To compute this bonding energy it is, of course, necessary to evaluate the integrals in (18) and (19). To do this, use is made of the explicit form

$$\psi_{\mathrm{A}}(1)=(1/\pi a_0^3)^{\frac{1}{2}}e^{-r_{\mathrm{A}1}/a_0},\quad(a_0=h^2/4\pi^2e^2m)\tag{20}$$

of the normalized wave function for the ground state of the hydrogen atom. The integrals can all be evaluated in closed form except for the r_{12} term in (19), for which series expansions must be used.

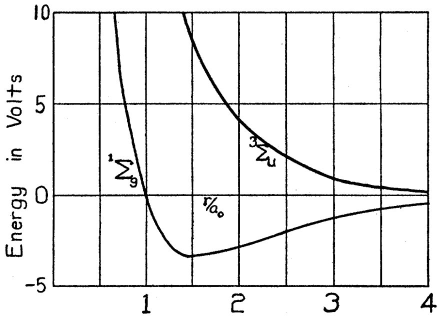


FIG. 3.

We illustrate in Fig. 3 the theoretical energy calculated from (17–18–19) for a system of two hydrogen atoms as a function of the distance between them. The discussion of the comparison of the attractive curve with experiment will be deferred until section 16. In spite of the fact that the $^3\Sigma_u$ state is repulsive, it is nevertheless to be considered as having physical reality. It is used to explain a certain continuous spectrum emitted by H_2, due to transitions from an excited triplet state, not shown in Fig. 3, down to the $^3\Sigma_u$ curve. Transitions down to this curve would obviously lead to a dissociation of the molecule, giving rise to a continuous spectrum.

10. Sign of the exchange integrals

Since the singlet state is computed to have a lower energy than the triplet, the plus sign choice in (17) gives a lower value of the energy than does the minus. Hence the exchange integral (19) is negative for a system composed of two hydrogen atoms. The conventional Heitler-London theory of valence, in its most elementary or naïve form, is based on the assumption that exchange integrals have negative signs in practically all cases, and in the absence of adequate computations for other molecules, is, in a certain sense, an extrapolation from hydrogen to the rest of the periodic table. Of course the fact that the great bulk of diatomic molecules are diamagnetic is empirical, but quite definite evidence that singlet states are usually deepest and exchange integrals therefore normally negative. In ferromagnetic materials, by exception, the exchange integrals are positive, as the basic idea of Heisenberg's theory[24] is that ferromagnetism arises because the exchange forces favor the parallel alignment of spins in ferromagnetic media.

In atoms, in distinction from molecules, the energy is lowest when the spins are parallel, or in other words, the exchange integral J is positive. This is, in fact, the essence of the Hund rule that the deepest state for a given configuration is that of highest multiplicity consistent with the Pauli principle.[16] That J is positive in atoms can be seen from Eq. (19), as in atoms one is able to make a perturbation calculation with wave functions which are orthogonal, and for which therefore the expression T defined in (13) vanishes. In such a calculation for a monatomic system containing two electrons, ψ_A and ψ_B would relate to two different states of the same atom, rather than to different atoms as in our molecular calculations. Now with $T=0$, all but the r_{12} or last part of (19) disappears, and so J is positive, as the last integral in (19) is positive. It is only because of the non-orthogonality, $T\neq 0$, i.e., because of the portion of (19) inclosed in parentheses, that exchange integrals are negative in molecular examples.

That the complete expression (19) must usually be negative can be seen by comparison with the method of molecular orbitals illustrated in Fig. 1. Usually a triplet state represents additional promotion as compared with the singlet state. For instance, if we consider the union of two $1s$ atoms in Fig. 1, the lowest possible triplet state involves the configuration $1s2p\sigma$ for the united atom, whereas there is only a singlet state leading to the united configuration $1s^2$, since spins must be anti-parallel when two electrons are housed in the same molecule orbital. According to (17) the excess of energy of the triplet over the singlet state is

$$W(^3\Sigma_u)-W(^1\Sigma_g)=\\ +(1-J)/(1-T^2)-(1+J)/(1+T^2)\sim -2J,$$

and hence J must be negative if there is even qualitative agreement with Fig. 1. The same result can also be seen graphically from Fig. 4 which is a contour map of charge density Ψ^2 computed from Eqs. (11) and (20). The contours near the nucleus are highest, i.e., represent the greatest charge density, which in general decreases as one recedes from the nucleus. Fig. 4 shows that there is more electronic charge density between the nuclei for the singlet than for the triplet, and so the nuclei tend to be drawn together in the singlet case due to the attraction of the electronic charge in the middle. This is the reason why the singlet state is stable, and the triplet state repulsive. At the same time the appreciable electronic charge in the center region means that the electrons are more often near each other in the singlet than in the triplet state, and so if the r_{12} effect alone were important, the triplet rather than singlet would be deepest. That the r_{12} effect always favors the high multiplicity is also in general apparent from the fact that in the triplet state for a two electron system, the orbital wave function is anti-symmetric and so has a node when the electrons coincide, thus reducing the influence of the repulsive r_{12} term.[25]

Of course there are cases where a two electron molecular system can have a triplet state without additional promotion. The behavior of the last two electrons bound in the oxygen molecule was a case in point, as we saw in section 8. In such instances J must be positive if the Heitler-London method is to yield a sensible result, and so here, were the exchange integrals really evaluated, it would presumably turn out that the part of J arising from the nonorthogonality fails to counterbalance the r_{12} part.

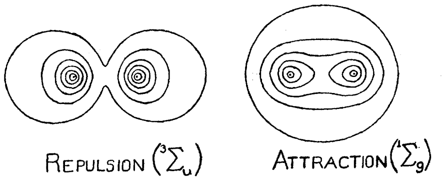


Fig. 4.

---

[24] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928) or Chap. XII of reference 17.

[25] For a more complete analysis and dissection of the various terms of the exchange integral see references 34 and 55.

11. Comparison of the states formed from two hydrogen atoms in the two methods[26]

At this stage, it is illuminating to compare the wave functions for a system formed by the union of two hydrogen atoms in their ground states when these functions are computed (a) by the method of molecular orbitals and (b) by the Heitler-London method. We have seen that with molecular orbitals, two possible one-electron wave functions $\psi_{g,u}$ are built upon the ground state of the hydrogen atom. These two states are represented by the two lowest curves in Fig. 1, and are given, respectively, by the upper and lower sign choice in Eq. (9) provided one makes the approximation, adequate for present purposes of qualitative comparison, that the molecular orbital can be represented as a linear combination of atomic orbitals. Since in all two electrons are available for a system composed of two hydrogen atoms, the complete wave function must be the product of two molecular orbitals. There are three possible situations,—(1) both electrons may be housed in the $\sigma 1s_g$ state, (2) they may both be in a $\sigma_u 1s$ state, or (3) there may be one in each. In the third case both a singlet and triplet are possible, in the other two evidently only a singlet. To form the singlet and triplet wave functions one must take the symmetric or antisymmetric combinations as regard electron permutation. Hence the four possible states are

$$\begin{gathered}\Psi_{\mathrm{MO}}({}^1\Sigma_g)=\psi_g(1)\psi_g(2), \quad \Psi_{\mathrm{MO}}({}^1\Sigma_g{}')=\psi_u(1)\psi_u(2), \\ \Psi_{\mathrm{MO}}({}^{1,3}\Sigma_u)=(1/\sqrt{2})[\psi_u(1)\psi_g(2)\pm\psi_u(2)\psi_g(1)].\end{gathered} \tag{21}$$

We have indexed each state according to its symmetry when the complete wave function is reflected in the molecular center. In this process the product of two u or of two g functions exhibits a g behavior, while the product of one u and one g is u. There are two ${}^1\Sigma_g$ states, and we distinguish the second of these by a prime.

At this point one is apt to be perplexed by the fact that there are four states in (21), whereas only two states are found in the usual Heitler-London approximation (11). This is because (11) is a purely homopolar structure, not ever allowing two electrons on the same atom. To round out the picture one should remember that another possibility besides (11) is a pure ionic structure wherein both electrons are always on the same atom. When we take linear combinations to give the proper u, g symmetry the pure ionic wave functions are

$$\Psi_{\mathrm{ION}}({}^{1,3}\Sigma_g)=C[\psi_{\mathrm{A}}(1)\psi_{\mathrm{A}}(2)\pm\psi_{\mathrm{B}}(1)\psi_{\mathrm{B}}(2)] \tag{22}$$

with C as in (13). Such wave functions are, of course, far indeed from physical reality, not only because the electrons are usually on different atoms, but also because the r_{12} effect makes the wave function of H^- quite different from the product of two wave functions for neutral H. By means of (9), (11), (13), (21) one finds the following relations between the molecular orbital wave functions, and those of the H-L method enriched by (22):

$$\Psi_{\mathrm{MO}}({}^1\Sigma_g)=[(1+T^2)/2(1+T)^2]^{\frac{1}{2}}[\Psi_{\mathrm{HL}}({}^1\Sigma_g)+\Psi_{\mathrm{ION}}({}^1\Sigma_g)], \tag{23}$$

$$\Psi_{\mathrm{MO}}({}^1\Sigma_g{}')=[(1+T^2)/2(1-T)^2]^{\frac{1}{2}}[-\Psi_{\mathrm{HL}}({}^1\Sigma_g)+\Psi_{\mathrm{ION}}({}^1\Sigma_g)], \tag{24}$$

$$\Psi_{\mathrm{MO}}({}^1\Sigma_u)=\Psi_{\mathrm{ION}}({}^1\Sigma_u), \quad \Psi_{\mathrm{MO}}({}^3\Sigma_u)=\Psi_{\mathrm{HL}}({}^3\Sigma_u). \tag{25}$$

The exact agreement in the two last cases could have been predicted, as there is only one possible ${}^1\Sigma_u$ or ${}^3\Sigma_u$ state in either form of approximation. That the ionic terms should be wanting for the triplet state even in the method of molecular orbitals is to be expected, as only singlet structures are possible when both electrons are in the same state on the same atom.

The excessive amount of ionic structure in $\Psi_{\mathrm{MO}}({}^1\Sigma_g)$ has already been commented upon in the introduction. Evidently the best results would be secured by a compromise

$$\Psi=A[\Psi_{\mathrm{HL}}({}^1\Sigma_g)+c\Psi_{\mathrm{ION}}({}^1\Sigma_g)] \tag{26}$$

---

[26] This type of comparison was first suggested by Hund, Zeits. f. Physik **73**, 1 (1932).

between the two methods. According to Slater,[27] the constant c has the value 0.13 at the equilibrium distance of separation. Weinbaum[28] obtains the slightly different value 0.16, which is perhaps more accurate. Thus the Heitler-London expression comprises the bulk of the wave function and the ionic correction is rather small. However, we must note that if we write (26) in the form

$$\Psi = B[\Psi_{\mathrm{MO}}({}^1\Sigma_g) + d\Psi_{\mathrm{MO}}({}^1\Sigma_g')], \tag{26a}$$

then it turns out that the coefficient d is also small, about 0.13.[29] This result is rather startling at first, and superficially interpreted, gives the impression that the molecular orbital approximation is as good as the H-L one. The only reason that d is so small is that the normalization factor is much larger in (24) than in (23), since T is about 0.4. If one omits this factor, i.e., deletes the radicals in defining the Ψ_{MO}, then the coefficient d is nearly unity. A similar sensitivity to the normalization does not exist in connection with (26), as the normalization factor is the same in Ψ_{HL} and Ψ_{ION} (cf. Eqs. (11) and (22)).

12. The Ritz or variational method[30]

This method is based on the fact that the accurate solution of the Schrödinger equation for the ground state is that which minimizes the expression

$$\int\cdots\int \Psi \mathbf{H} \Psi dv_1\cdots dv_f, \tag{27}$$

provided Ψ is normalized to unity. Also, the correct value of the energy is an extremum of (27).

As far as the calculation of bonding energies is concerned, the beauty of the Ritz method is that one can make an appreciable error in the wave functions, and still the error in the energy may be small, due to the fact that any expression is insensitive to errors in its argument near its extremum. Also one can be sure as to the sign of the error, as with approximate functions the calculated energy of the ground state is always greater than it should be.

One can apply the Ritz method in two fashions, (a) and (b), which are closely allied, respectively, to the method of molecular orbitals and to the Heitler-London method. In (a) one uses for Ψ an expression which is a linear combination of products of molecular orbitals (one-electron wave functions), while in (b) one uses linear combinations of the product of distorted or "flexible" atomic orbitals, each relating to a different atom so that there are no ionic terms. The linear combinations must be so chosen as to give the proper symmetry as regards electron interchange. The expressions thus tried will contain certain parameters which are chosen in such a way as to minimize (27). For instance, a typical choice of the type (a) for the ${}^1\Sigma_g$ state of H_2, is

$$\Psi = C_a[e^{\alpha r_{A1}} + e^{\alpha r_{B1}}][e^{\alpha r_{A2}} + e^{\alpha r_{B2}}], \tag{28}$$

while one of type (b), used by Wang in H_2,[31] is

$$\Psi = C_b[e^{\alpha(r_{A1}+r_{B2})} + e^{\alpha(r_{A2}+r_{B1})}], \tag{29}$$

where C_a, C_b are normalization constants and where α is to be so chosen as to make (27) a minimum. At finite distances of nuclear separation the parameter α will not have the value $-1/a_0$ (cf. 20) characteristic of infinite distances of separation, and so we have spoken above of distorted in distinction from true atomic orbitals. Better still one can, of course, use compromise wave functions such as (26), with c regarded as a variable parameter of which the optimum value is selected.[32] (This is how the previously given estimates of c were obtained.) Or one can add to (28) a term involving the argument r_{12} rather than just r_{A1}, r_{A2}, r_{B1}, r_{B2}. The inclusion of such a term can reduce the extent to which the electrons accumulate at the same position,

---

[27] Slater, quoted by Mulliken, Phys. Rev. **41**, 70 (1932).

[28] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

[29] See Mulliken, reference 27.

[30] Courant-Hilbert, *Methoden der Mathematischen Physik*, p. 157. We use the terms "Ritz" and "variational" as synonymous but originally Ritz varied only coefficients of a development in orthogonal functions, rather than arbitrary parameters, as in the modern quantum uses.

[31] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[32] The compromise wave functions give little improvement, however, unless they have a flexible rather than fixed screening parameter (cf. first and second Weinbaum entries in our Table II). When (26) is modified by introducing such flexibility, the value of c becomes 0.25.

and so at least partially counteract the excessive ionic tendency of the method of molecular orbitals. Furthermore, if desired, terms can be inserted which allow for the polarization of one atom by another. A good example is Rosen's trial functions[33]

$$\Psi = C_r[e^{-\alpha(r_{A1}+r_{B2})}(1+\sigma r_{A1}\cos\theta_{A1})(1+\sigma r_{B2}\cos\theta_{B2}) + e^{-\alpha(r_{B1}+r_{A2})}(1+\sigma r_{B1}\cos\theta_{B1})(1+\sigma r_{A2}\cos\theta_{A2})] \quad (30)$$

for H_2. Here θ_{A1} is the angle between r_{A1} and r_{AB}, and σ is a variable parameter, found to attain a value 0.1 for the equilibrium distance, and decreasing to zero for extreme values of r_{AB}. Naturally polarization corrections are not negligible. Mention of their existence is simply another language for saying that a development in terms of atomic orbitals is deficient if we include only the orbitals belonging to the ground state rather than also the many excited states necessary for development in terms of a complete orthogonal set.

Practically all attempts at quantitative calculation of heats of dissociation within the last two or three years are based on the variational method in some form or other. It is *the* method when more than a qualitative procedure is desired, and it is particularly convenient to have a scheme based on trial functions because the loss of the orthogonality in molecular problems means that systematic perturbation theory is much more difficult and less satisfying than in atomic problems.

13. The nightmare of inner shells

In the calculation of the heats of dissociation of molecules other than hydrogen, it has often been assumed that the only important forces are those between valence electrons not in closed shells. Unfortunately this pleasant state of affairs is actually not the case, as James[34] has shown most conclusively. He disquietingly shows, for instance, that the nice agreement that Bartlett and Furry[35] found between their calculated value 1.09 volts of the heat of dissociation of Li_2 by the Heitler-London method and the observed value 1.14 is completely destroyed when one includes the effect of the 1*s* electrons. The calculated value is then 0.3 volt. Consequently better wave functions are needed than those in the Heitler-London method. James finds that by using a variational method he can increase the calculated value to 0.7 volt.

The inner shells cause trouble not only because the forces from them are important but also for another reason. If one is using the Ritz method for an excited state, it is essential that the wave function be orthogonal to all the wave functions of lower states. Otherwise the computed wave function tends to become more and more like that of the lowest state, and the calculated energy creeps more and more towards that of the deepest level, so that it has no significance as the energy of an excited state. Consequently we cannot use the Ritz method to determine the wave functions of the valence electrons unless we are sure that they are orthogonal to all the wave functions of the inner electrons. This situation is most unfortunate, as unless great care is taken it prevents our using the variational method on a system composed of the valence electrons alone, moving in some sort of an assumed field, and some cruder nonvariational method for the inner shells. One could, of course, use the variational method with an anti-symmetric function (inclusive of spins) for the entire system of all electrons, but such a procedure is usually excessively laborious. Much of the literature on calculations of molecular energies by the variational method does not take cognizance of the fact that the wave functions of the excited states must be orthogonal to those of the inner shell. Those investigations which neglect the effect of inner shells are indicated by an *X* in Table III of section 16.

A procedure for avoiding the inner shell troubles has been proposed by Hellmann.[36] On the basis of an argument involving the Thomas-Fermi statistical method of treating

---

[33] N. Rosen, Phys. Rev. **38**, 2099 (1931).

[34] H. M. James, J. Chem. Phys. **2**, 794 (1934); Phys. Rev. **43**, 589 (1933).

[35] J. H. Bartlett and W. H. Furry, Phys. Rev. **38**, 1615 (1931).

[36] H. Hellmann, J. Chem. Phys. **3**, 61 (1935); Acta Physicochimica U. R. S. S. **1**, 913 (1935).

systems of many particles he suggests that the effect of the inner shells might be obtained by replacing them by a potential field which contains not only the usual electrostatic terms, but also a term designed to replace the exchange effects. Then the energy of a one-quantum orbit in this effective potential field would be the energy of the lowest quantum orbit not included in completed shells (e.g., in sodium a $1s$ state in Hellmann's potential field would correspond to the real $3s$ state). Since the Fermi-Thomas treatment gives in the case of the most favorable alkali atom, caesium, a result which is not entirely satisfactory, he proposes to find the best equivalent field by an empirical method based on observations of the atomic spectrum. Then by using this field the problem of finding the binding energy of the lowest state of Cs_2, for example, is reduced to that of finding the energy of a definite two-electron system. The present theoretical background for this procedure is not at all convincing, and the empirical evidence as to its value is still inadequate.

14. Interaction operators

Heats of dissociation are differential effects, i.e., energy differences between combined and separated atoms. For this reason they are difficult to compute accurately, and so the tables in section 16 should be viewed charitably. To make agreement between theory and experiment impressive, one should document the observed and calculated values of the energy required to blow a molecule to pieces into separated electrons and nuclei at infinity. On this basis, for instance, the observed energy of the hydrogen molecule becomes 31.80 volts, while the computed value for the Heitler-London method becomes 30.2 volts and James and Coolidge's result 31.77 instead of the values uniformly 27.07 volts smaller recorded on the differential or dissociation basis in section 16. However, the latter is what is of physical interest.

When we come to molecules formed out of other atoms than hydrogen, there is the obvious difficulty that the assumed atomic orbitals used in the actual variational procedures are not solutions of the dynamical problem for the separated atom, since only in hydrogen and helium are good wave functions available. The question immediately arises whether one should subtract the calculated or the actual energies of the separated atoms in order to make the fairest appraisal of what the calculation has done. In practise, one often uses a rather rough procedure in place even of either alternative. One often assumes in the Heitler-London method that the binding energy can be obtained by integrating in (14) over an "interaction" operator **H** which is only part of the complete Hamiltonian function. This interaction operator vanishes at infinite separation of the atoms, and so (14) is then assumed to give the heat of dissociation directly. For instance, one might try to obtain the heat of dissociation of say Li_2 regarded as a two electron system, by using (17–18–19) with $-e^2/r_{A1}$, etc., replaced by a potential V which is assumed to represent the effect of a nucleus screened by the K shell. The difficulty with this procedure is not merely that the Li_2 molecule cannot be treated as a two electron system, as we saw in section 13, but there is further trouble because of the fact that the assumed wave functions probably do not reduce at infinite separation to solutions of (16) (with of course $V(r_{A1})$ substituted for $-e^2/r_{A1}$). For further analysis of the difficulty arising from this cause the reader is referred to an article by James.[34] He shows that sometimes the approximation made in using interaction operators is so crude that the calculated heats of dissociation are rather meaningless. Computations open to this objection are labelled I in Table III, section 16. When a more accurate calculation is made, the purported agreement with experiment is usually lost, almost suggesting a theorem that in most so-called calculations of heats of dissociation, doubtless influenced by the answer to be desired, the nice agreement achieved at the nth approximation is usually lost at the $n+1$th stage!

15. Molecules with an odd number of electrons[37]

In odd molecules there is always one electron which has no partner in any scheme of electron pairing. The influence of this unmated electron in holding the molecule together is usually spoken of as a "one electron bond."[38] The method of molecular orbitals is at its best in the treatment of one-electron bonds, since these depend for their stability on the approximate symmetry of the potential field with respect to the atoms concerned. Even when the interaction of the bonding electron with all other electrons is considered there is no tendency for it to favor a particular atom and it may be regarded as

---

[37] Sections 15 and 16 have been written by Dr. H. M. James.

[38] Cf. Pauling, J. Am. Chem. Soc. 53, 3225 (1931).

flitting continually from one atom to another. The flitting effect, expressed analytically in the so-called resonance integral $\int\int\int\psi_A(1)\mathbf{H}\psi_B(1)dv_1$ is the major feature of the so-called "one electron bond." The Heitler-London method thus loses its advantages over the molecular orbital method; in fact, the crudest form of molecular orbital function may be identical with the approximate Heitler-London function.

The molecule H_2^+ gives us the example *par excellence* of the one-electron bond. In this case the complete program of the molecular orbital method can be carried through, and the energy may be determined with any desired precision. Complete agreement with the rather indirect determinations of the spectroscopist are thus obtained. The variational method has also been used in a number of attacks on this problem which have yielded surprisingly good results. Finkelstein and Horowitz[39] find, with the function $A(e^{-\alpha r_A}+e^{-\alpha r_B})$, a binding energy too small by only a fifth and an essentially correct equilibrium distance. Results accurate to less than 0.01 e.v. are found by Guillemin and Zener,[40] using the function $Ae^{-\alpha\lambda}(e^{-\beta\mu}+e^{\beta\mu})$, and by James,[41] using $Ae^{-\alpha\lambda}(1+\beta\mu^2\cdots)$. Here λ and μ are the elliptical coordinates

$$\lambda=(r_A+r_B)/r_{AB}, \quad \mu=(r_A-r_B)/r_{AB}. \qquad (31)$$

One may hope that these approximate molecular orbitals will prove to be useful in more complex problems.[42]

James[41] has treated Li_2^+ (not yet observed) in a similar manner, representing the inner shells by atomic orbitals, the binding electron by $e^{-\alpha\lambda}\Sigma_{mn}C_{mn}\lambda^m\mu^n$. He finds that the one-electron bond in Li_2^+ is stronger than the two-electron bond in Li_2, contrary to the usual assumption as to their relative strengths. The molecular orbital constructed as a sum of atomic orbitals, on the other hand, gives a binding which is only 1/5 that obtained by the more powerful method. This crudest form of the molecular orbital is thus of dubious value for quantitative considerations.

A closely related molecule, He_2^+, in which three electrons are actively engaged in the binding, has been considered by Pauling and by Weinbaum.[43]

16. Comparison with experiment for molecules with an even number of electrons[37]

The relative merits of the various methods of treating even molecules are best illustrated in the case of H_2. Here the simplicity of the problem has made convenient a large variety of attacks, and has made it possible to avoid the doubtful approximations which are so disturbing elsewhere. The results of nine computations on the ground state of this molecule are included in Table II. Comparisons are made throughout in terms of the maximum binding energy (i.e., binding energy for a hypothetical molecule without the actually unavoidable half-quantum of vibrational energy). The maximum binding energy differs from the dissociation energy by the zero-point vibration energy. This distinction has been ignored in some of the work on this subject, with the result that too favorable comparisons with experiment have been made. All the calculations in Table II except Sugiura's use the variational method in some form or other. In a few cases the vibration frequency has been computed; this is a difficult quantity to calculate theoretically as it involves the determination of the curvature of the potential curve at its minimum.

The binding energy given by the H-L method, too small by a third, is the poorest of the values given. As suggested in section 11, however, this is distinctly better than the crudest form of the method of molecular orbitals can do. The excessive equilibrium separation of the nuclei, as given in this computation, seems to be characteristic of the H-L method. Indeed, one must expect this, in view of fact that the virtues of the method lose significance as the nuclei

---

[39] B. N. Finkelstein and G. E. Horowitz, Zeits. f. Physik **48**, 118 (1928).

[40] V. Guillemin and C. Zener, Proc. Nat. Acad. Sci. **15**, 314 (1928).

[41] H. M. James, J. Chem. Phys. **3**, 9 (1935).

[42] For further references on H_2^+ see Hylleraas, Zeits. f. Physik **71**, 741 (1931); an interesting general article has been written by Pauling, Chem. Rev. **5**, 173 (1928).

[43] L. Pauling, J. Chem. Phys. **1**, 56 (1933). Calculations by Pauling's student, Dr. Weinbaum, which will appear shortly in J. Chem. Phys. will not assume the same screening constant for all three electrons and so are more rigorous than previous efforts. Weinbaum obtains a heat of dissociation of 2.2 volts, in good agreement with the experimental value 2.5. An early paper on He_2^+ was written by Majorana, Nuovo Cimento, 8, No. 1 (1930).

TABLE II. *Treatments of the ground state of H_2.*

	MAXIMUM BINDING ENERGY	EQUILIBRIUM SEPARATION	VIBRATION FREQUENCY
Heitler-London; done by Sugiura[45] (Eq. 11)	3.13e.v.	0.87A	4.8×10^3 cm^{-1}
Molecular Orbitals; Hylleraas[44]	3.6	.70	
Heitler-London with variable shielding; Wang[31] (Eq. 29)	3.77	.73	4.9
Wang+Polarization; Rosen[33] (Eq. 30)	4.02	.74	4.26
Heitler-London+Ionic Term; Weinbaum[28] (Eq. 26)	3.21	.90	
Wang+Ionic; Weinbaum[28]	4.00	.74	4.75
Wang+Ionic+Polarization; Weinbaum [28]	4.10	—	
James and Coolidge,[46] no r_{12} (Eq. 32)	4.27	—	
James and Coolidge,[46] with r_{12}	4.70	.74	
Experiment	4.725±.01	.74	4.38

approach; the rigidity of the wave function results in a rapidly increasing error in the computed energy, so that the integral (14) and hence the computed potential curve are too high at small distances. Accordingly, when a "Heitler-London" computation yields too small an equilibrium separation the auxiliary approximations must be questionable. (Compare, for instance, the results in the alkali metal molecules, which will be discussed later.)

Conversely, since the method of molecular orbitals is in error by an amount which increases as the nuclei are separated, the computed energy is too high at large separations and the equilibrium distance found from such computations may safely be considered a lower limit to the actual value. This is well illustrated by a result of Hylleraas,[44] who constructed his wave function from molecular orbitals which were solutions of the H_2^+ problem and of the related problem with nuclear charges $\frac{1}{2}e$. Essentially his assumption was that one of the electrons would go into the lowest state of H_2^+, the second moving in the field of the nuclei half shielded by the first. This gives a distinct improvement over the cruder forms of the method, in which the same orbital is used for both electrons. He thus found an equilibrium distance too small by 6 percent, associated with a distinctly better binding energy than that obtained by the Heitler and London method.

The other computations represented in the table use the variational principle, but differ markedly in the method of approach. We consider first those using orbitals of atomic type. Wang made the Heitler-London function flexible by introducing the variable parameter α in the fashion (29). The best value of α was found to correspond to an effective nuclear charge $Z=1.16$ for the equilibrium distance. The error in the binding energy was thus reduced by 40 percent. Rosen has amplified Wang's treatment by using wave functions of the form (30) and thus introducing into the atomic orbitals a term intended to represent the polarization due to the neighboring atom. Finally, Weinbaum[28] has further extended this method of attack by adding ionic terms to the Wang and Rosen functions.

A quite different form

$$\Psi=\Sigma_{mnjk}C_{mnjk}e^{-\alpha(\lambda_1+\lambda_2)} \times(\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k+\lambda_1{}^n\lambda_2{}^m\mu_1{}^k\mu_2{}^j) \quad (32)$$

for the function to be varied has been used by James and Coolidge.[46] Here λ, μ are elliptical coordinates defined as in (31). It is to be noted that such a function can be constructed from molecular orbitals in the usual manner only if certain relations exist between the C_{mnjk}. The greater flexibility of these functions corresponds to the abandonment of the self-consistent field approximation, and makes it possible to obtain the advantages of the Heitler-London method without sacrifice of the virtues of the molecular orbitals. For instance, the function $e^{-\alpha\lambda}(1-c\mu_1\mu_2)$ is large when the electrons are near different nuclei (the μ's have different signs) and small when they are near the same nucleus. By adjustment of the constant c one can strike the happy medium between the two extreme methods.

With a single term from (32), *viz.* $e^{-\alpha(\lambda_1+\lambda_2)}$, it is possible to obtain results comparable to

---

[44] E. A. Hylleraas, Zeits. f. Physik **71**, 741 (1931).

[45] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[46] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

TABLE III.[49]

		MAXIMUM BINDING ENERGY		EQUILIBRIUM SEPARATION	
		COMPUTED	OBSERVED	COMPUTED	OBSERVED
Li_2	Heitler-London,[35] I,X.	1.09e.v.	1.14e.v.	2.4 A	2.67A
	Heitler-London[34] I	.33		3.07	
	Heitler-London[34]	.28		3.18	
	Variational[34]	.62		—	
LiH	Heitler-London[47] I,X	2.30	2.56	1.44	1.6
Na_2	Heitler-London[48] I,X	.81	.76	2.83	3.08
K_2	Heitler-London[48] I,X	.55	.51	4.18	3.91
	Semi-empirical,[36] with H-L method	.19		4.0	
KH	Semi-empirical,[36] with H-L and Ionic terms	.8	2.06	2.0	

X denotes neglect of inner shells (cf. section 13); I signifies use of interaction operator (section 14).

those of the Heitler-London method. With a much more complicated function James and Coolidge have obtained a binding energy of 4.27 e.v., and there is reason to believe that this is about the best that can be done with a function of this form. The approximation inherent in this method, as well as all others we have mentioned, is that the trial wave functions depend on only four coordinates, while the energy, and hence the correct wave function, must contain five. None of these functions has depended directly on r_{12}, though the importance of the electronic interaction makes it clear that they should. This does not mean, of course, that the character of these wave functions was not affected in an important manner by the presence of the term e^2/r_{12} in the energy. Each of the functions takes account of the electronic repulsion in its own way—the molecular orbital method (in the more accurate forms) by tending to prevent large accumulations of charge anywhere, the Heitler-London method by tending to keep the electrons near different nuclei, the function (32) by doing both. What all these functions fail to do is to take account of the effects of the electronic repulsion in a *detailed* manner, rather than an averaged one. In order to eliminate this remaining error James and Coolidge have finally added r_{12} terms by regarding the coefficients C in (32) as polynomials in r_{12}.

Other Molecules. In the study of more complicated molecules only the Heitler-London method and its simplest derivatives have found extensive application. A considerable portion of this work has been concerned with excited or ionized states of the molecules, and so does not concern us here. The only results, however, which might lead one to be optimistic concerning the possibility of accurate predictions in this field are concerned with one-electron bonds (section 15), and with the basic states of molecules homologous to H_2 —Li_2, LiH, Na_2, etc. Results on the latter molecules are summarized in Table III. The most impressive of these, it will be noted, are characterized by the presence of approximations which reduce the problem to a H_2-like one, except that instead of hydrogenic wave functions for the electronic orbitals, there were used orbitals supposed to represent the valence electrons of the respective atoms. The choice of such orbitals is highly arbitrary, but in these investigations the simplest orbital to use turns out to give remarkably good results. Apparently, however, because of difficulties mentioned in sections 13 and 14, we must ascribe the satisfactory character of these results to a good fortune, as to the continuance of which we can obtain no assurance.

An attempt to improve these results by a straightforward variational treatment involves one in serious computational difficulties. The most obvious improvement would involve the use of a function of the sort indicated in (32) to describe the valence electrons, while the inner shells are introduced by means of simple atomic orbitals. The molecular energy thus computed

---

[47] E. Hutchisson and M. Muskat, Phys. Rev. **40**, 340 (1932). Calculations on LiH by the variational method, inclusive of inner shells, will be published shortly by J. Knipp. His computed heat of dissociation differs from the observed by a little less than a volt.

[48] N. Rosen and S. Ikehara, Phys. Rev. **43**, 5 (1933); N. Rosen, Phys. Rev. **38**, 255 (1931).

[49] Additional calculations on the ground states of diatomic molecules include Gentile, Zeits. f. Physik **63**, 795 (1930) (He H, He_2); Furry and Bartlett, Phys. Rev. **39**, 210 (1932) (Be_2); C. Ireland, Phys. Rev. **43**, 329 (1933) (BeH).

would then be compared with the energy of the separated atoms, computed with the same inner shell functions, to determine the binding energy. James has found that with Li_2 such a procedure gives a binding energy some 0.5 e.v. too low; the omission of r_{12} terms here thus introduces approximately the same error as in H_2. The difficulties involved in the introduction of these terms, due to the presence of other electrons, seem to be an effective check to further improvements in the calculations. In principle, then, we appear to have a way in which to treat diatomic molecules with any desired precision. Unfortunately, the limits of human patience restrict the usefulness of the complete method.

CHAPTER III. POLYATOMIC MOLECULES TREATED BY THE HEITLER-LONDON-PAULING-SLATER METHOD

We shall now turn to molecules composed of more than two atoms, and shall, for the present, employ entirely homopolar approximations of essentially the Heitler-London type, deferring the method of molecular orbitals until Chapter IV. We do this mainly because much of the literature has been dominated by the homopolar approach, and the two methods are not as easily handled simultaneously as in the diatomic case. To be sure, we have seen in Chapter II that the Heitler-London method was somewhat of a disappointment from a quantitative standpoint in diatomic molecules. However, there are features of interest even in a qualitative theory when we come to complicated molecules, as there are all the various general questions of the spatial arrangement of the atoms, bond structures, modes of vibration, etc. Hence information of value can be obtained even though the quantitative accuracy may not be sufficient to permit reliable calculations of heats of dissociation which, as we have emphasized in section 14, are sensitive differential effects.

17. The Dirac vector model

If the complete wave function is expressible as a product of individual wave functions, then

$$\Psi=\psi_1(1)\psi_2(2)\psi_3(3)\cdots\psi_n(n), \qquad (33)$$

where in the Heitler-London method the ψ's must be taken to be atomic rather than molecular orbitals. Here and elsewhere $\psi_1(1)$ is an abbreviation for $\psi_1(x_1, y_1, z_1)$, etc. However, along with (33), owing to the fact that one electron is indistinguishable from another, there are obviously $n!-1$ other products which are equally good and which differ from (33) only in that the arguments of the various ψ's have been permuted, or in other words, the electrons interchanged. For instance, instead of (33) an equally good product is $\psi_1(2)\psi_2(3)\psi_3(1)\cdots\psi_n(n)$. The question immediately arises as to what are the proper linear combinations of the $n!$ products to use. The situation is far more complicated than in a two electron system, where there are only two rather than $n!$ products, and where one is led immediately to the symmetric or antisymmetric combinations (11). There are three ways of answering this question.

(a) One procedure is to use group theory without including spin factors in the ψ's, so that we deal entirely with orbital wave functions. However, the technique of the permutation group is complicated, and more general than needed for practical purposes because the Pauli principle must be satisfied after addition of the spin. In the language of group theory, many "characters" for the orbital permutation group are not compatible with the Pauli principle, i.e., are not capable of extension into an antisymmetric representation when spin as well as orbital arguments are permuted. Thus the character theory is too general. Hence it is simpler to include the spin at the outset. This is the essence of

(b) Slater's method.[50] This utilizes the fact that if spin factors are already included in the ψ's, only the antisymmetric combination of the various products should be used. This is an excellent method and furnishes a straightforward way of making perturbation calculations. We pass over it rather lightly, partly because it is so frequently described in the literature, and partly because we do not pretend to enter on any detailed calculations. A particular form of Slater's method commonly employed in chemical problems is the so-called method of bond eigen-

---

[50] J. C. Slater, Phys. Rev. **34**, 1293 (1929); cf. also M. Born, Zeits. f. Physik **54**, 729; **65**, 718 (1930).

functions.[51] A third procedure is that furnished by

(c) The vector model. This is the method which we shall employ, as it is particularly "*anschaulich*," and enables one to visualize the various bonding situations in terms of spin alignment.

We saw in section 9 that the exchange energy, i.e., the part of the energy involving the exchange integral J defined in (19), depended on the way the spin was aligned. In this respect it differed from the "Coulomb" energy. Namely, if we neglect products of the order JT, the exchange energy was $-J$ when the spins were parallel, and $+J$ when they were anti-parallel. The answer was thus similar to that which would be obtained were there a large amount of spin-spin coupling. Actually, the only forces between spins are magnetic forces which are exceedingly small, and the only reason that the spin figures in the answer is that the constraints imposed by the Pauli principle correlate different spin alignments with different electrostatic exchange energies. Thus the spin is only an "indicator," and the physical situation is different than in the old theories of Parsons, Lewis and others, where magnetic forces between spins or magnetons were held responsible for chemical bonds. However, the formal results are in a certain sense rather similar.

The query immediately arises as to whether this correlation of spin alignment with exchange energy carries over to systems of more than two electrons. The answer is in the affirmative, as Dirac has shown,[52] but the mathematical proof will be deferred until the appendix. It will there be shown that the solution of the problem of the exchange or permutation degeneracy, subject to the constraints of Pauli principle, is formally equivalent to solution of a problem in spin-spin coupling with the Hamiltonian function

$$\mathbf{H}=Q-\tfrac{1}{2}\Sigma_{j>i}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)J_{ij}. \tag{34}$$

Here $\mathbf{s}_i\cdot\mathbf{s}_j$ denotes the scalar product of the spin $\mathbf{s}_i$ of the electron in orbit i and that $\mathbf{s}_j$ of the electron in orbit j. Angular momentum is throughout to be measured in multiples of $h/2\pi$, and J_{ij} is the exchange integral[53]

$$J_{ij}=\int\cdots\int\psi_i(1)\psi_j(2)\mathbf{H}\psi_j(1)\psi_i(2)dv_1dv_2 \tag{35}$$

connecting states i and j. The additive constant Q in (34) is the "Coulomb" energy. The expressions $\mathbf{s}_i$, $\mathbf{s}_j$ appearing in (34) are really vector matrices, and they will be discussed more completely in the appendix. For the present purposes of qualitative discussion, no particular harm will be done, if they are regarded as ordinary algebraic vectors by readers not familiar with angular momentum matrices.

In (34) we have supposed that no two electrons describe the same orbit. Such electrons we shall say inhabit "free" orbitals. In addition there may be what we shall term "filled orbitals" which occur twice and so have the full quota 2 of electrons allowed them by the Pauli principle. We shall use Greek letters for filled orbitals. We obviously do not have exchange energy connecting two identical filled orbitals, as one must not talk of a trade of places when the places are the same, and all the necessary energy has already been included in the Coulomb portion. There is, however, exchange energy connecting members of different filled orbitals or connecting filled orbitals with free ones. This part of the energy has the value

$$-\tfrac{1}{2}\Sigma_{i,\mu}J_{i\mu}-\tfrac{1}{2}\Sigma_{\nu>\mu}J_{\mu\nu} \tag{36}$$

and should be added to (34). Then Q in (34) is to be understood to denote the Coulomb energy of the entire system, including both free and filled orbitals.

To see that (36) is the proper value for the part of the exchange energy involving filled states let $\mathbf{s}_\mu$, $\mathbf{s}_{\mu'}$ be the two spins associated with a given pair of filled orbitals μ, μ' and $\mathbf{s}_j$ be any other spin, which may be associated with either a free or filled orbital. Then the exchange energy connecting μ, μ' with j is

---

[51] G. E. Kimball and H. Eyring, J. Am. Chem. Soc. **54**, 3876 (1932); L. Pauling, J. Chem. Phys. **1**, 280 (1933); Eyring and Kimball, J. Chem. Phys. **1**, 239, 626 (1933); Eyring and Sun, J. Chem. Phys. **2**, 299 (1934); Bear and Eyring, J. Chem. Phys. **3**, 98 (1935); Eyring and Gershinowitz, J. Chem. Phys. **3**, 224 (1935); G. W. Wheland, J. Chem. Phys. **3**, 230 (1935).

[52] P. A. M. Dirac, Proc. Roy. Soc. **A123**, 714 (1929); cf. also applications of J. H. Van Vleck, Phys. Rev. **45**, 405 and R. Serber, Phys. Rev. **45**, 461 (1934).

[53] The reason that the term $-2W_H$ appears in the integrand of (19) but not in (35) is simply that a different origin for the energy has been used in the two cases. Unfortunately the exchange integral is not invariant of the origin when the wave functions are not orthogonal.

$$-\tfrac{1}{2}J_{j\mu}(1+4\mathbf{s}_j\cdot\mathbf{s}_\mu)-\tfrac{1}{2}J_{j\mu'}(1+4\mathbf{s}_j\cdot\mathbf{s}_{\mu'}) = -J_{j\mu}[1+2\mathbf{s}_j\cdot(\mathbf{s}_\mu+\mathbf{s}_{\mu'})] = -J_{j\mu}, \quad (37)$$

since $J_{j\mu}=J_{j\mu'}$ in virtue of the identity of μ and μ' and since $\mathbf{s}_\mu+\mathbf{s}_{\mu'}=0$ inasmuch as the Pauli principle requires zero spin for two particles in the same orbital. The factor $\frac{1}{2}$ enters in (36) since we have included both the filled obritals in (37), so that (37) comprises the results of two terms in a sum such as (36).

We are now in a position to enumerate how many states of a given spin can arise from a system involving n free orbitals. There can in addition be any number of filled orbitals as they do not affect the multiplicity. We first note that if S_1, S_2 be two spin (or more generally, angular momentum) quantum numbers, the spin quantum number S_{1+2} associated with the resultant of the two parts 1, 2 can have the values

$$S_{1+2}=|S_1-S_2|,\ |S_1-S_2|+1,\ \cdots,\ S_1+S_2. \quad (38)$$

The two extremes correspond classically to the vectors being parallel and anti-parallel. Of course if parts 1 and 2 are each one electron, then $S_1=S_2=\frac{1}{2}$ and the resultant can only be 0 or 1. However, the parts compounded may already be the resultant contribution of several electrons. For instance, if a third electron is added, then we must compound $\frac{1}{2}$ with 0 or 1 thus obtaining for the resultant of all three the values $\frac{1}{2}$ (twice) and 3/2. In this fashion one obtains the "branching diagram" given in Fig. 5, which is more or less self-explanatory. It shows that the permutation problem for a system of six electrons is such that there are 5 states with spin quantum number $S=0$, nine with $S=1$, five with $S=2$ and one with $S=3$. An analytical formula

$$N=\binom{n}{k}-\binom{n}{k-1} \qquad (k=\tfrac{1}{2}n-S) \quad (39)$$

is available for the number of states N in the general case, but the branching diagram is more instructive. It will be noted that the number of states, after summing over S is still considerably less than the number $n!$ of possible permutations. For instance with 4 electrons, there are by Fig. 5 only six states in all whereas $4!=24$. This is mainly because the Pauli principle limits the number of possible combinations, as already mentioned on p. 190. In the perturbation problems connected with the lifting of the exchange degeneracy, the secular equation is readily factored according to the value of the spin S. Thus in a system with eight electrons available for bonding and with zero total spin, one is confronted with a secular equation of degree 14, as one sees by extending Fig. 5 or using (39). Further factorization is possible if the molecule has elements of symmetry. Thus methane, which is a system involving eight valence electrons, the equation of 14 splits into factors all of degree 3 or lower because of the tetrahedral symmetry. The factorization is achieved by means of group theory, and for an account of how it is down, the reader is referred to the original articles.[54]

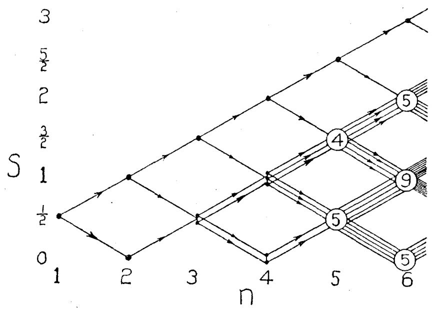


FIG. 5.

18. Troubles with higher order permutations and nonorthogonality

It is to be emphasized that (34) is not a rigorous formula even were the Heitler-London method adequate. Namely (34) neglects nonorthogonality in certain places, though not in others. It is the generalization to the n electron problem of replacing the denominator $1\pm T^2$ by 1 in (17). Here T denotes the overlap or nonorthogonality integral, as in (13). Use of (34) does not require that $T=0$ in (19). It would be a much worse approximation to set $T=0$ in (19) than in (17), since we have seen in section 10, that without the terms involving T the expression (19) would have the wrong sign. Thus the denominator effect of T in (17) is one of higher order. Eq. (34) also neglects higher order per-

---

[54] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933); F. Seitz and A. Sherman, J. Chem. Phys. **2**, 11 (1934); A. E. Stearn, C. H. Lindsley and H. Eyring, J. Chem. Phys. **2**, 410 (1934); R. Serber, J. Chem. Phys. **2**, 697 (1934).

mutations, i.e., assumes that $\int\cdot\cdot\int\Psi'\mathbf{H}\Psi dv_1\cdot\cdot dv_f$ if Ψ' and Ψ are products analogous to (33) which differ from each other by more than a simple permutation. The neglect of these integrals involving higher order permutations is closely related to the neglect of nonorthogonality. Since no term in $\mathbf{H}$ contains the coordinates of more than two electrons such integrals always involve T as a factor and so would vanish were there complete orthogonality.

The approximations mentioned in the preceding paragraph would be warranted were the inter-nuclear distance very large, but the trouble is that (34), or equivalent formulas in the Slater method, are actually used at distances for which the approximation is not a good one. For instance, the value of T at the equilibrium distance in H_2 is 0.42, and so T is not negligible in comparison with unity. This point has been stressed particularly by Coolidge and James.[55] who show that Eyring's calculations of the activation energy for the process $H+H_2\rightarrow H_2+H$ are radically changed when corrections are made for higher-order permutations and nonorthogonality. However, good qualitative results are obtained from (34), and the quantitative agreement with experiment is better than one would expect. Because ionic effects are not negligible, the Heitler-London approximation is not an accurate one even when one takes higher order permutations and nonorthogonality into account, and it is quite conceivable the computed energies are not improved when these factors are considered. Empirically, this seems to be the case, and of course in any case Eq. (34) should give the qualitative trend of the energy with directional arrangement when the latter is varied, thereby changing the J_{ij}.

It should not be inferred that the troubles with nonorthogonality and higher order permutations are peculiar to the vector model. Similar approximations are usually made with the Slater method, as without them the calculations either become excessively laborious, if the integrals are really reckoned out, or involve too many undetermined constants to be significant, if the integrals are regarded as parameters to be evaluated by comparison with experiment. Unless otherwise stated, it will be supposed that all calculations quoted in the present chapter do not include the effect of nonorthogonality and higher order permutations, so that we do not need to allude again to this omission.

Inglis[56] gives a calculation which apparently shows that in a system composed of n electrons, the error factor due to nonorthogonality is of the order $(1-\frac{1}{2}nT^2)$ rather than $1-T^2$ as in (17) for a two electron system. In this event, Heisenberg's calculations on ferromagnetism would be devoid of all meaning, as here n is an enormous number, *viz.* the number of electrons in the micro-crystal. However, as one of us will show elsewhere, there is a counterbalancing correction from the higher order permutations, so that the error factor is probably always of the order $1-T^2$ rather than $1-\frac{1}{2}nT^2$.

19. Electron pair bonds

The extreme values which can be assumed by any given term in (34) are $+J_{ij}$, $-J_{ij}$. This result is fairly apparent from examination of the two electron problem (cf. Eq. (17) with $T=0$) and is also proved in the appendix, where it is shown that the eigen-values of $-\frac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)$ are ± 1. The two extremes $+J_{ij}$, $-J_{ij}$ correspond to the spins being respectively anti-parallel and parallel. Since the exchange integrals are usually negative (cf. section 10), the extreme $+J_{ij}$ is the desirable state of lowest energy. An electron pair bond may be described as two electrons in different atoms whose spins are anti-parallel, so that their resultant is zero, and the corresponding exchange term $-\frac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)J_{ij}$ has its extreme value J_{ij}. It is impossible for all terms to realize their minimum values simultaneously, as not all of the spin vectors can be mutually anti-parallel at once. It is obviously desirable to minimize the large terms in (34) even at the expense of unfavorable values for the small terms. This is the state of affairs envisaged in what may be called the approximation of electron pair bonds. Electrons may be paired for either of two reasons: (a) they may be electrons of the same atom in identical orbits, in which case the Pauli principle requires their

---

[55] A. S. Coolidge and H. M. James, J. Chem. Phys. **2**, 811 (1934).

[56] D. R. Inglis, Phys. Rev. **46**, 135 (1934).

resultant spin to be zero, or (b) the exchange or apparent spin-spin coupling between them may be much larger than the corresponding coupling of either of the two with other spins, so that the two are determined to be partners at all costs. Usually electron-pair bonds are achieved in virtue of directional valence, to be discussed in section 22, wherein individual wave functions project out in particular directions from the central atom, and so have an especial affinity for the particular attached atom which is located along this direction. It is to be understood that any electron already paired because of (a) is unable to participate in any pairing of the type (b) of the chemical bond type. For instance, an atom in a configuration $2s^2 2p^2$ is unable to form more than two electron-pair bonds with outside atoms because the two $2s$ electrons are already paired with each other because of (a). On the other hand, the Pauli principle (effect a) does not require that the two $2p$ electrons be paired with each other, as the spatial quantum number (Greek letter) may be different for the two electrons, so that each $2p$ electron is able to form an electron-pair bond of the form (b).

Of course, electron-pairing often may not be a good assumption since the molecular arrangement may be such that there are not any naturally designated couples (e.g., four monovalent atoms at the corners of a square, or six monovalent atoms forming a regular plane hexagon, or eight such atoms at cube corners). However, when electron-pairing is a good approximation the expression for the exchange energy takes a particularly simple form, being a linear function of the various exchange integrals. Let us denote by i, i' two electrons which are paired, and let J_{ij} be the exchange integral connecting two electrons i, j. Then the exchange energy is

$$W=\Sigma_{i'>i}J_{ii'}-\tfrac{1}{2}\Sigma_{j>i(j\neq i')}J_{ij}. \qquad (40)$$

Do not confuse the Hamiltonian (34) which is a matrix, and the energy value (40), which is a number and is an approximation to the lowest eigenvalue of (34) (with $Q=0$) if the assumption of electron pairing is nearly correct. We shall call the coefficients of the exchange integrals in the expression for the energy the "exchange coefficients." We see according to (40) that *within a pair the exchange coefficient is* $+1$, *while it is* $-\tfrac{1}{2}$ *between two electrons not belonging to the same pair.*

To prove that the exchange coefficient is $-\tfrac{1}{2}$ for two electrons not in the same pair we have to show that in $-\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)$ the term $\mathbf{s}_i\cdot\mathbf{s}_j$ effectively vanishes if $\mathbf{s}_i$ is paired to a spin other than $\mathbf{s}_j$. Let $\mathbf{s}_{i'}$ be the partner of $\mathbf{s}_i$ in the spin pairing. Then on the average only the component of $\mathbf{s}_i$ parallel to $\mathbf{s}_i+\mathbf{s}_{i'}$ is effective,[57] as $\mathbf{s}_i$, $\mathbf{s}_{i'}$ precess around their resultant $\mathbf{s}_i+\mathbf{s}_{i'}$. Furthermore this component is $\tfrac{1}{2}(\mathbf{s}_i+\mathbf{s}_{i'})$ inasmuch as $\mathbf{s}_i$ and $\mathbf{s}_{i'}$ are equal in absolute magnitude. Hence

$$\overline{\mathbf{s}_i\cdot\mathbf{s}_j}=\tfrac{1}{2}\overline{(\mathbf{s}_i+\mathbf{s}_{i'})\cdot\mathbf{s}_j}=0$$

since $\mathbf{s}_i+\mathbf{s}_{i'}=0$. This derivation involves retention of only the average value, i.e., of the diagonal matrix element in a system of representation in which $\mathbf{s}_i+\mathbf{s}_{i'}$ is diagonal. This is allowable only if electron pairing is a good approximation, and for this reason (40) is not an exact expression. However, all our discussion will be based, at least implicitly, on formula (40), unless otherwise stated, until we come to section 27.

Since the exchange integrals are assumed negative in the Heitler-London theory, the exchange energy will be positive for transpositions involving electrons already paired with other atoms, inasmuch as their exchange coefficients in (40) are $-\tfrac{1}{2}$. Hence already paired electrons tend to repel other electrons.

We may illustrate (40) by the case of CH_4. As we will later see, there are four tetrahedral carbon wave functions which project out towards the four hydrogen atoms. Let J_{CH} be the exchange integral connecting a tetrahedral wave function and the nearest H atom, and let J_{CH}' be the integral connecting it with any of the other H atoms, which are equidistant in virtue of the tetrahedral symmetry. Let J_{HH} be the exchange integral connecting two hydrogen atoms, and let J_{CC} be that between the tetrahedral orbitals of carbon. Then, according to (40), on counting the number of exchanges of various types, we have

$$W=4J_{CH}-12\times\tfrac{1}{2}J_{CH}'-6\times\tfrac{1}{2}J_{HH}-6\times\tfrac{1}{2}J_{CC}. \qquad (41)$$

Since J_{HH} is negative and has a minus coefficient in (41), we see that the exchange energy connecting the H atoms is repulsive.

Very generally, according to (40), "corner" atoms attached by bonds to a central atom will

---

[57] This retention of only average values is analogous to that in the well-known calculation of the Landé g-factor; cf. p. 68 of reference 11.

tend to repel each other, as presumably exchange integrals decrease in absolute magnitude with increasing separation, making

$$-\tfrac{1}{2}\partial J_{ij}/\partial r_{ij}<0 \quad \text{if} \quad -\tfrac{1}{2}J_{ij}>0.$$

Repulsions due to this cause are subordinate to the effects of true directional valence as we shall see later. However these exchange repulsions between distant atoms may be connected with the fact that dielectric constant measurements show us that there is not completely free rotation in a molecule such as C_2H_6. Since the $C-C$ bond is here only a single one, the effects of directional valence do not interfere with the rotation of either H_3 group about the $C-C$ axis, and so the "exchange repulsions" between the two H_3 groups may be the main cause hindering the rotation.[58] The energy will be lowest when the azimuthal angles of one group of H atoms differ by 60° from those of the other set of H atoms. One should not expect this exchange repulsion to be large, inasmuch as the two sets of hydrogen atoms are so far removed from each other. Indeed the potential hills interfering with free rotation are known experimentally to be small, amounting to about 0.015 volt.[59, 60]

20. The valence state of the carbon atom

The carbon atom is known from spectroscopic data to be normally in the state $2s^22p^2\ {}^3P$. As we have already seen, it is then only able to form two bonds. To form four bonds it is necessary to excite the atom to the configuration sp^3. Since there are three types of p wave functions (*viz.* $p\sigma$, $p\pi_+$, $p\pi_-$) there are no constraints on the electrons in an sp^3 configuration because of electron-pairing of type (a). Until recently it was thought that such an excitation required only about 1.7 volts,[61] and clearly the carbon atom is willing to sacrifice this much internal energy in order to form two additional bonds, each of which involve an energy increment of 4 or 5 volts or so. However, the actual energy increment is now known from spectroscopic data to amount to 7 volts[62] instead of 1.7 volts. In this connection we must mention that the configuration of the carbon atom appropriate to forming four electron-pair bonds is not the same as the ${}^5S$ state, as has commonly been supposed. This point has caused considerable confusion in the literature. If the ${}^5S$ state of C were that concerned the energy of excitation necessary to form tetravalent compounds would be somewhat lower,[62] about 4.3 instead of 7 volts, but would still be higher than usually believed hitherto. The fact that the excitation energy is 7 volts does not mean that the activation energy necessary to form a quadrivalent carbon compound is 7 volts, as when one brings up the hydrogen atom and so begins gradually to lift the carbon atom out of the s^2p^2 configuration and place it partially in sp^3 (an intermediate zone in which electron pairing is not a valid approximation) the increase in internal energy of the carbon atom would be at least partially offset by the energy of the incipient $C-H$ bonds formed.

If the promotional energy required for a carbon atom to form four tetrahedral bonds is 7 volts, and R is the repulsive energy between the hydrogen atoms, the gross strength of a $C-H$ bond is $\frac{1}{4}(7+R)$ volts greater than the net strength obtained by taking one-fourth the heat of formation of CH_4 from normal atoms, since the gross binding energy is partly counterbalanced by the increased internal energy of the carbon atom and repulsion of the hydrogen atoms. The distance between hydrogen atoms can readily be calculated in CH_4, since the $C-H$ distance is known. If we use a Morse potential energy curve for H_2, R can be roughly evaluated and is about 3 volts.[63] Therefore, $E_{\mathrm{CH}}=17.3/4+(7+3)/4=4.3+2.5$, i.e., the real strength of a $C-H$ bond is 2.5 volts greater than the net strength and is 6.8 volts instead of 4.3 volts.

If there are any chemical data incompatible with a difference between the gross and net

---

[58] H. Eyring, J. Am. Chem. Soc. **54**, 3201 (1932).

[59] A. Eucken and K. Weigert, Zeits. f. physik. Chemie **B23**, 265 (1933).

[60] In C_2H_4, on the other hand, there is no "free rotation," and both theoretically and experimentally there is a quite appreciable "twisting frequency"; cf. W. G. Penney, Proc. Phys. Soc. London **46**, 333 (1934).

[61] W. Heitler and G. Herzberg, Zeits. f. Physik **53**, 52 (1929); cf. also Pauling, reference 4.

[62] J. H. Van Vleck, J. Chem. Phys. **2**, 20 and especially 297 (1934).

[63] In this calculation one uses about 35 percent of a Morse function, assuming the Morse curve to be 90 percent exchange, 10 percent Coulomb. This is because the "exchange coefficient" between already paired electrons is $-\frac{1}{2}$ rather than 2. See section 19 or references 70 and 62.

C−H bond energies amounting to as much as 2.5 volts the cause for the discrepancy may be that in tetravalent carbon compounds electron-pairing is not a perfect approximation, and especially that part of the time the carbon atom may be in the s^2p^2 configuration. In other words, the wave function of the carbon atom may be a linear combination of s^2p^2 and sp^3 wave functions so that, in Pauling's language, the carbon atom resonates between the two configurations. For this reason the increase in the internal energy of the carbon atom may not be as high as 7 volts.

Further calculations are really necessary before it can be said that it is at all obvious from quantum mechanics why carbon should usually be in a quadrivalent rather than divalent condition. Calculations being made by H. Voge on the relative percentages of s^2p^2 and sp^3 should throw some light on this point.

21. Some simple valence rules[64]

Since there are four possible two-quantum orbital types (*viz.* $2s$, $2p\sigma$, $2p\pi_+$, $2p\pi_-$), it is clear that if there are more than four electrons outside the K shell of an atom, they will not all be able to form electron-pair bonds. Instead, some of the electrons will have to "double up" by occupying the same orbit. When this is the case, electrons occupying identical orbits will have their spins paired to each other (pairing of type (a) in section 19), and so will be unable to form electron-pair bonds with outside atoms. Since four kinds of orbits are available it is clear that if there are 5, 6, 7, 8 electrons available, the number which can have a private orbit is respectively 3, 2, 1, 0. Hence the maximum possible number of electron-pair bonds for N, O, F, Ne should be respectively 3, 2, 1, 0. This agrees with experiment. Pentavalent nitrogen is of course well known (e.g., NH_4Cl) but only four of the five bonds are presumably of the electron-pair type (arising from N^+ which is isoelectronic with the carbon atom), the fifth bond being ionic,—i.e., NH_4Cl should be written $(NH_4)^+Cl^-$. The difficulty of housing congestion does not arise when there are four electrons or less, and so the number of electron-pair bonds for Li, Be, B, C equals 1, 2, 3, 4, respectively, or, in other words, the number of electrons outside the K shell.

When we come to consider the chemistry of the elements beyond the first two periods of the Mendeléef table, the housing problem is less acute. There are, in fact, no less than nine different kinds of 3-quantum orbits, *viz.*, one s, three p, and five d orbits. (There were only four kinds of 2-quantum orbits since a $2d$ orbit is impossible inasmuch as one must have $n>l$.) Hence, as long as there are no more than nine electrons outside the preceding inert shell, the number of maximum possible valences should be equal to the number of such electrons. However, when there are eight electrons, filling twice each the s and p orbits, they apparently do not like to form valences presumably because the energy of excitation to a d orbit is so large. This point does appear to be passed over a little glibly in most of the accounts of the quantum theory of valence, as the necessary energetic calculations have not been carried out. It is assumed throughout that it is too big a sacrifice to excite states of higher principal quantum number (otherwise we would have such things as pentavalent nitrogen in which all the bonds were of the electron-pair type, due to excitation of N to say the configuration $2s2p^33d$). We now see that there are cases where even an increase in l is too big a sacrifice in order to form bonds. For example, argon does not exhibit valences despite the fact only a promotion in l is required to convert its outer shell from $3s^23p^6$ to $3s^23p^{6-x}3d^x$, giving a valence $2x$. Apparently this stage is reached by the time we reach a group of eight electrons of the form s^2p^6, but not at seven as septivalent chlorine is known. Assuming this dividing, we see that

Cl, Br, I, should exhibit valences of 1, 3, 5, 7 but F only 1;

S, Se, Te should exhibit valences of 2, 4, 6 but O only 2;

P, As, Sb, Bi should exhibit valences of 3, 5, 7 but N only 3.

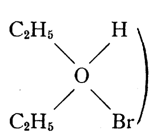
We have listed several possible valences for one atom because it may not be willing to advance the value of l for more than one or two electrons in order to form valences. For example, to form septivalent chlorine three electrons have to be

---

[64] The valence rules given in the present section were, for the most part, first derived by London by a somewhat different method Zeits. f. Physik **46**, 455 (1927).

excited to *3d* states. The possible valences increase two units at a time because for every electron excited to a *d* state, one frees both members of a pair of type (a), section 19.

Not all the valences predicted in the above table are found experimentally. For instance, septivalent Br, P, As, Sb, or Bi are not known. It is customary to dismiss this difficulty by saying that the valences given in the table are "possible valences," and some of them may not be realized for energetic reasons. For example, the atom may be willing to forego its normal configuration only if it forms quite a few valences. It is not clear, however, why both Cl and I exhibit a valence of seven while Br does not.

Also, valences are found which are not given in the above table,—e.g., ClO_2, ClO_3, NH_4Cl, $(CH_3)_4NOH$, $(C_2H_5)_2 \cdot O \cdot HBr$, $(C_2H_5)_2OCH_3MgI$. The first two molecules are all "odd molecules," —i.e., contain an odd number of electrons, and hence should all be paramagnetic. They really do not constitute exceptions to the above scheme if we consider the odd electron to be a free bond. The two nitrogen molecules apparently contain pentavalent nitrogen. The last two molecules are examples of the "oxonium" compounds of organic chemistry in which oxygen is supposed to be tetravalent (e.g., ). The customary and rather naïve explanation of these discrepancies is that the Heitler-London theory is one of homopolar valences, and that any valence which it does not explain is of the heteropolar type (cf. pentavalent nitrogen, discussed above). However, things are probably not quite so simple as this, and so many approximations are made in the Heitler-London theory besides the omission of ionic terms that it does not appear necessary to blame all exceptions on polar effects, although they are doubtless very often the major contributing factor. The approximation of assuming electron-pairing is one that might well be questioned, and in some of the compounds not explained by the simple rules, quite possibly no description in terms of electron-pairs may be allowable, and the role of Coulomb forces may be more important than they are usually given credit for being.

Although there are exceptions to the rules, one must admit that the simple model based on Eq. (40), or its equivalent, enables one to understand the main experimental valences much better than any preceding theory. It accounts especially nicely for the fact that atoms of the second period (Li to F) cannot exhibit as many valences as those of later periods.

22. Theories of directed valence based on electron-pairing—*s* and *p* valences

It is a matter of common knowledge that certain directional arrangements are characteristic of valences. For instance, in methane the four C−H directions are tetrahedrally arranged and so make angles of 109.5° with each other. There are clearly two possible ways of accounting for these arrangements. One way is to assume that one direction is as good as another as far as the central atom is concerned, and suppose that the forces between the attached atoms are responsible for the way the atoms are grouped. If the electron-pair bonds connect the attached atoms only with the central atom, and not with each other, then clearly the forces between the attached atoms will be repulsive in virtue of what we have previously said in section 19. Attempts to explain directional effects in this general way have been made by Heitler and Rumer[65] (see section 27), but soon encounter difficulties. For instance, if repulsions between attached atoms are the all important factor one would predict tetrahedral methane, to be sure, but one would also expect ammonia to be plane, and water to be linear, as then the hydrogen atoms are as far apart as possible. Instead, the nature of the central atom has the dominating part in determining how the attached atoms are situated. Theories which take this into account we may call theories of directional valence. In such theories the exchange integrals connecting an attached atom with a central atom will not be a function solely of the distance between the two atoms, but in addition will depend upon the direction of the line joining the two atoms. Thus $J_{ij} = J_{ij}(r, \theta, \varphi)$ whereas in what may be termed

---

[65] W. Heitler and G. Rumer, Zeits. f. Physik **68**, 12 (1931); W. Heitler, Phys. Rev. **38**, 243 (1931).

the non-directional theory of valence one assumes $J_{ij}=J_{ij}(r)$.

s valences. If an electron of a central atom is in an s state, clearly this particular electron can give rise to no directional effects since its charge cloud is centro-symmetric, and we actually have here the case $J_{ij}=J_{ij}(r)$. In the Heitler-Rumer theory of valence all valences of the central atom are treated as effectively in s states, even though really they are in p or d states. A gross error is thereby made as far as directional effects are concerned.

p valences. For a p electron there are three kinds of wave functions,—$p\sigma$, $p\pi_+$, $p\pi_-$ corresponding to different spatial orientations. All three depend markedly on angle so that strong directional effects are to be expected with p valences. Since the solution of the Schrödinger equation in a central field is of the form $f(r)$, $P_l^m(\cos\theta)e^{im\varphi}$, the three p functions are

$$\psi_{p\sigma}=f(r)\cos\theta, \tag{42}$$

$$\psi_{p\pi_+}=f(r)\sin\theta\, e^{i\varphi}/\sqrt{2}, \tag{43}$$

$$\psi_{p\pi_-}=f(r)\sin\theta\, e^{-i\varphi}/\sqrt{2} \tag{44}$$

as one sees by substituting the values of the associated Legendre functions P appropriate to $l=1$, $m=1$, 0, -1, respectively. The factor $1/\sqrt{2}$ has been inserted in (43–44) for purposes of normalization.

In valence, in distinction from magnetic calculations, it is desirable to use sum and difference combinations of $\psi_{p\pi_+}$ and $\psi_{p\pi_-}$, thus making the wave functions real and the azimuth factors cosines or sines rather than exponentials. This is allowable since the solutions of the Schrödinger equation without loss of generality can be taken to be real in the absence of external fields, in fact are necessarily real if the degeneracies are removed. We thus obtain the three real orthogonal functions

$$\psi_{p\sigma x}=f(r)\sin\theta\cos\varphi=F(r)x, \tag{45}$$

$$\psi_{p\sigma y}=f(r)\sin\theta\sin\varphi=F(r)y, \tag{46}$$

$$\psi_{p\sigma z}=f(r)\cos\theta=F(r)z, \tag{47}$$

where $F=f/r$ and the Greek letters now refer to the axis of quantization indicated by the subscripts x, y, z.

The charge cloud associated with $\psi_{p\sigma x}$ is a dumb-bell shaped affair, with the axis of the dumb-bell in the x direction, $\psi_{p\sigma y}$ and $\psi_{p\sigma z}$ are similar to $\psi_{p\sigma x}$ except that the axes are directed along the y and z directions respectively. On the other hand $\psi_{p\pi_-}$ and $\psi_{p\pi_+}$ have doughnut or ring shaped charged clouds, and correspond respectively to left and right-handed de Broglie waves describing a circular path. When we take the linear combinations

$$\psi_{p\sigma x} \text{ and } i\psi_{p\sigma y}=[\psi_{p\pi_+}\pm\psi_{p\pi_-}]/\sqrt{2}$$

the interference between the right and left-handed waves produces a node along the x axis in the case of $\psi_{p\sigma y}$ and along the y axis in the case of $\psi_{p\sigma x}$, thus producing a dumb-bell shaped structure. This is illustrated in Fig. 6. The wave functions $\psi_{p\pi_+}$, $\psi_{p\pi_-}$ carry a magnetic moment, while $\psi_{p\sigma x}$, $\psi_{p\sigma y}$ do not, as the latter are associated with standing rather than progressive waves traveling around a circle.

Slater[66] was the first to suggest that in the H-L method the dumb-bell shaped charge clouds in $\psi_{p\sigma x}$, $\psi_{p\sigma y}$ may be responsible for many phenomena of directional valence, especially those involving right angles. The same idea was also enunciated independently by Pauling.[67] These two authors were also the first to propose the tetrahedral wave functions to be discussed in section 24. Hence we usually speak of the "Heitler-London-Pauling-Slater" rather than Heitler-London theory when homopolar calculations are made in which the directional properties of the p or sp^3 wave functions play a major role.

It is to be understood that the whole procedure assumes that it is a good approximation to build the complete wave function out of atomic orbitals appropriate to a central field, as the expressions (42–47) inclusive are all solutions of

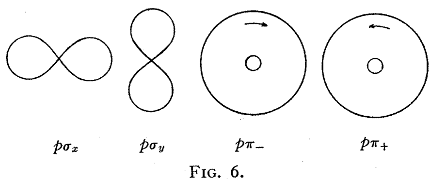


FIG. 6.

---

[66] J. C. Slater, Phys. Rev. **37**, 481; **38**, 1109 (1931).

[67] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); also reference 8 and Pauling and Huggins, Zeits. f. Krist. **87**, 205 (1934).

a one electron wave equation only if the potential has spherical symmetry. Actually this is somewhat of an idealization for three reasons. In the first place, an atomic wave function cannot really be factored into one electron functions. Secondly, the Hartree self-consistent field, which represents the best attempt at such factorization, is not centro-symmetric if the atom has other ingredients besides closed shells and s electrons. Thirdly, in any chemical combination there is always the distortion of the central symmetry due to the fields from adjacent atoms. The qualitative import of Eqs. (42–47) is, however, probably not voided. If the third difficulty is too serious, the method of molecular orbitals (Chap. IV) should be used instead, since its forte is use of a self-consistent field with the proper molecular rather than atomic symmetry.

Let us suppose there is an electron-pair bond between an s electron of some attached atom and the $p\sigma_x$ electron of the central atom. Then the exchange energy associated with this particular pair is greatest if the attached atom lies on the x axis, since the exchange integrals will clearly be largest in absolute value if the wave functions of the two atoms overlap as much as possible. This requirement clearly demands that the attached atom be located on the axis of the dumb-bell associated with the particular electron of the central atom with which it is paired.

If a second atom is brought up, and if the pairing between $\psi_{p\sigma x}$ and the first attached atom is not broken, then clearly the only possibility is for the second atom to pair with one of the other wave functions, $\psi_{p\sigma y}$ or $\psi_{p\sigma z}$, so that it will become located on the y or z axis. Hence in a molecule such as H_2O the angle between the two OH axes should be 90°. The experimental value is 106°. The departures from 90° are to be blamed upon repulsions between the attached atoms (cf. section 19) and upon sp^2 hybridization, to be discussed later.[68] Similarly, if the first two atoms have preempted the x and y directions a third atom tends to become located on the z axis, so that in a molecule like NH_3 the three NH axes should make angles of 90° with each other. The NH_3 molecule is then pyramidal in structure, each axis making an angle of 54.7° with the axis of the NH_3 pyramid. The experimental value is 67°, and the discrepancy is to be attributed to the same causes as in H_2O.

In connection with the above we may note that the tendency to acquire a 90° angle arises not alone because of the desire of the attached atom to be on as intimate terms as possible with the particular wave function of the central atom with which it is paired but also because it shuns being involved with the wave functions of the central atom with which it is not paired. This idea is expressed mathematically in the fact that the "exchange coefficient" between a paired electron and any electron not a member of a pair is $-\frac{1}{2}$ rather than $+1$. When the coefficient is $-\frac{1}{2}$ the corresponding term in the energy is minimized by taking the exchange integral to be as large as possible, i.e., of smallest possible absolute magnitude since, as we have already said, exchange integrals are usually negative.

Analytically the situation is formulated as follows. Since the three p wave functions (45–46–47) are of the form $F(r)x$, $F(r)y$, $F(r)z$, respectively, they transform like the components of a vector. Thus a wave function of the form $\psi_{p\sigma x}$ when referred to the x axis transforms according to the scheme

$$\psi_{p\sigma x}\rightarrow\cos\alpha\psi_{p\sigma}+\sin\alpha\psi_{p\pi} \qquad (48)$$

when referred to an axis of quantization making an angle α with the x axis. Here the $\psi_{p\pi}$ wave function is real and so of the dumb-bell rather than doughnut type, but with the axis of the dumb-bell perpendicular rather than parallel to the new axis of quantization, so that it must be classified as of the π (i.e., $|\Lambda|=1$) rather than σ type as far as this particular quantization is concerned.

It is convenient at this point to introduce the notation

$$N_{kl}=-\int\cdot\int\psi_{\mathrm{H}}(1)\psi_k(2)\mathbf{H}\psi_{\mathrm{H}}(2)\psi_l(1)dv_1dv_2, \qquad (49)$$

where ψ_{H} denotes a wave function of the attached atom (usually hydrogen) and ψ_k, ψ_l are wave functions of the central atom O. The subscripts k and l can assume the values s, $p\sigma$, $p\pi$ (which we often abbreviate to s, σ, π) with the understanding that the axis of quantization is relative

---

[68] See J. H. Van Vleck, J. Chem. Phys. **1**, 236 (1933) and reference 70.

to the O−H axis. The sign behavior can be shown to be as follows:[69]

$$N_{ss}>0,\quad N_{\sigma\sigma}>0,\quad N_{\sigma s}>0,$$
$$N_{\pi\pi}<0,\quad N_{\pi s}=N_{\pi\sigma}=0. \tag{50}$$

The vanishing of $N_{\pi s}$ or $N_{\pi\sigma}$ is readily established from the diagonality of $\mathbf{H}$ in Λ which makes it impossible for Σ and Π states to perturb each other, provided $\mathbf{H}$ has axial symmetry. The expressions N_{ss}, $N_{\pi\pi}$, $N_{\sigma\sigma}$ are negatives of exchange integrals while $N_{\sigma s}$, $N_{\pi s}$, $N_{\pi\sigma}$ are closely related "hybridization" integrals. The fact that $N_{\pi\pi}$ is negative (i.e., the corresponding integral positive) shows that it is too sweeping a generalization to say that exchange integrals are always negative. If we use the transformation property (48), and (49), (50), we see that if the O−H axis makes an angle α with the x axis, the exchange integral connecting $\psi_{\sigma x}$ and ψ_{H} is

$$J_{x\mathrm{H}}=\int\cdot\int\psi_{p\sigma x}(1)\psi_{\mathrm{H}}(2)\mathbf{H}\psi_{\mathrm{H}}(1)\psi_{p\sigma x}(2)dv_1dv_2$$
$$=-[N_{\sigma\sigma}\cos^2\alpha+N_{\pi\pi}\sin^2\alpha]. \tag{51}$$

This equation expresses the essence of directed valence for ordinary cases. It shows that the value of the exchange integral is a function of α, and for some value of α (viz. $\alpha=0$ or π) will be as large as possible in absolute value.

23. The water molecule

We shall now consider the H_2O molecule in a little detail, as it serves as a concrete illustration of the preceding assertions on directed valence, and as it has perhaps been the subject of more quantitative calculation than any other polyatomic molecule. The oxygen molecule has six two quantum electrons, but, as explained in section 21, four of them must "double up" in the orbitals which they inhabit. These four may be taken to be represented by $2s^22p\sigma_z^2$ as the $2s$ orbital is the deepest and so first to be completely filled, while the doubly filled $2p$ orbital may without loss of generality be taken to be $2p\sigma_z$. Then the two electrons of the oxygen atom with free spins are $2p\sigma_x$, $2p\sigma_y$ and the wave functions available for valence purposes are

$$\psi_1=\psi_{p\sigma x},\quad \psi_2=\psi_{p\sigma y},\quad \psi_3=\psi_{\mathrm{H}_a},\quad \psi_4=\psi_{\mathrm{H}_b},$$

where ψ_{H_a}, ψ_{H_b} are the wave functions of the two H atoms (cf. Fig. 7).

If one assumes electron pairing and uses Eq. (40), the exchange energy for H_2O becomes

$$W_{\mathrm{ex}}=J_{13}+J_{24}-\tfrac{1}{2}[J_{14}+J_{23}+J_{12}+J_{34}], \tag{52}$$

where J_{13} is the exchange integral connecting orbitals ψ_1 and ψ_3, etc. We shall now set $J_{34}=0$, i.e., neglect the "exchange repulsion" between the hydrogen atoms. This neglect is clearly desirable for present purposes as we are interested in exhibiting the directional effects of central valences irrespective of forces between corner atoms. We shall also take $J_{12}=0$, as study of atomic spectra shows that this integral, which is a purely internal property of the oxygen atom, is small. The most favorable locations for the H atoms are in the xy plane, as the "free" dumb-bells of the O atom have their axes in the plane. If the H atoms are in the xy plane and arranged as in Fig. 7 (where the prime on α' is rather indistinct), then in view of (51), Eq. (52) becomes

$$\begin{aligned}W_{\mathrm{ex}}=&-[N_{\sigma\sigma}\cos^2\alpha+N_{\pi\pi}\sin^2\alpha]\\&-[N_{\sigma\sigma}\cos^2\alpha'+N_{\pi\pi}\sin^2\alpha']\\&+\tfrac{1}{2}[N_{\sigma\sigma}\sin^2\alpha+N_{\pi\pi}\cos^2\alpha]\\&+\tfrac{1}{2}[N_{\sigma\sigma}\sin^2\alpha'+N_{\pi\pi}\cos^2\alpha'].\end{aligned} \tag{53}$$

Owing to (50), this expression obviously has a minimum at $\alpha=\alpha'=0$, giving us a right-angled model. It is significant that such a very simple skeleton calculation leads us to a geometrical

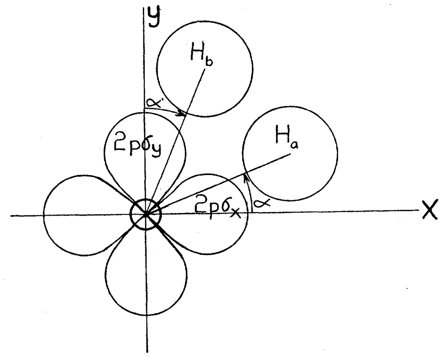


FIG. 7. The H_2O molecule.

---

[69] J. H. Van Vleck, J. Chem. Phys. 2, 27 (1934).

arrangement in approximate agreement with experiment. The experimental value is, to be sure, 106° rather than 90°, but the computed value is immediately increased to about 100° when a simple correction[70] is made for the effect of the repulsions between the hydrogen atoms.

Eq. (53) does not include the Coulomb energy connecting O and H, nor the exchange energy involving the electrons $2s$, $2p\sigma_z$ in filled orbits, but these portions of the energy give no directional effect. To prove this for the Coulomb portion, one first notes that the Coulomb integrals K have a transformation property similar to (51), so that

$$K_{x\mathrm{H}} = -M_{\sigma\sigma}\cos^2\alpha - M_{\pi\pi}\sin^2\alpha, \qquad (54)$$

where M_{kl} denotes a Coulomb expression analogous to N_{kl}, obtained by replacing $\psi_{\mathrm{H}}(2)\psi_l(1)$ by $\psi_{\mathrm{H}}(1)\psi_l(2)$ in the integrand of (49). The interatomic part of Coulomb energy involving $2p\sigma_x$, $2p\sigma_y$ is given by an expression similar to (53) except that M is substituted for N, and that the coefficients are all -1 rather than some of them $+\frac{1}{2}$. It is the latter circumstance that makes the Coulomb contributions impotent for directional effects as it converts (53) into an expression $-2M_{\sigma\sigma}-2M_{\pi\pi}$ independent of α. The part of the exchange energy involving $2s^22p\sigma_z^2$ is readily shown to be $(-\frac{1}{2})[-4N_{ss}-4N_{\pi\pi}]$ while the corresponding Coulomb portion is $-4M_{ss}-4M_{\pi\pi}$. Thus with our approximations, the total bonding energy in the equilibrium position $\alpha=\alpha'=0$ is

$$W = -2N_{\sigma\sigma}+3N_{\pi\pi}+2N_{ss} -2M_{\sigma\sigma}-6M_{\pi\pi}-4M_{ss}. \qquad (55)$$

At this point we may digress to remark that quite generally, in other valence calculations, the Coulomb in distinction from exchange terms linking the central and attached atoms usually prove to be independent of direction. Consequently, if in all our discussion of directional valence we seem to be talking always of exchange energy and saying little about the usual Coulomb type, this is not only because Coulomb integrals are often small compared to the exchange ones, but also because they are of less stereochemical interest and significance.

One easily finds that, with the various approximations which we have made, the energy of the OH radical should be half of (55).[71] This agrees with experiment, as the actual heat of dissociation of OH is approximately 4.9 volts, while that of H_2O into $O+2H$ is about 10 volts. However, the theory is less successful when one compares with experiment the energies themselves rather than the ratio of the values for OH and H_2O. What is particularly discouraging is that even the ratio comes out wrong when one abandons making rough approximations.

The corrections arising from the fact that electron pairing is not a perfect approximation even when (34) is granted are unimportant. Namely, one can use in place of (52) the more accurate formula (65) to be given later. The alteration as compared with (52) then amounts to only about 0.1 volt[72] if, say, we take $N_{\sigma\sigma}=2$, $N_{\pi\pi}=-0.6$ volts.

Much more serious is the neglect of nonorthogonality and higher order permutations inherent in (40) or (52). Coolidge,[73] taking them into account, finds as the result of a long calculation, a heat of formation of 3.5 volts for the H_2O molecule. He is able to raise this value to 5.7 volts by including polar terms, but even this result is about 4 volts too low. This remaining discrepancy is presumably to be attributed to omission of ionic (in distinction from polar) terms and perhaps to polarization effects. Also there may be some error because the assumed atomic orbitals are not accurate solutions of the wave equation of the oxygen atom.

Another thing which one can do is to try to compute the transverse vibration frequency of the H_2O molecule by means of (53), supplemented by a few easily made corrections for H−H repulsions. By the transverse vibration we mean the mode of oscillation wherein the angle HOH varies while the OH separations remain approximately stationary. This frequency is an easier quantity to calculate than a heat of dissociation since the former is not a differential

---

[70] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1934).

[71] See footnote 12 of the preceding reference.

[72] Cf. J. C. Slater, Phys. Rev. **38**, 1135 (1931). Slater was the first to note that electron-pairing makes little difference in H_2O. He assumed a somewhat different set of values for the N's than we give in section 24, but with either choice electron pairing is a good approximation.

[73] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

effect and is insensitive to errors in factors such as e.g. Coulomb energy which are largely independent of direction. Van Vleck and Cross[70] calculate a value 1660 cm^{-1}, differing from the experimental value by only 4 percent, but such close agreement is probably fortuitous in view of the approximations which must be made.

24. sp^3 hybridization and directed quadrivalence

As we have seen in the preceding section, carbon must be in the sp^3 state in order to exhibit its ordinary tetravalent behavior. Since it is a matter of indifference to an s state at what angle its partner is located, and since p valences tend to form at right angles to each other, it may at first sight seem strange that methane should be characterized by tetrahedral angles, unless perchance this state of affairs be blamed on repulsions between corner atoms which we have said are not a dominant factor. In the Heitler-London-Slater-Pauling theory the answer is found in the introduction of "sp^3 hybridization" as first suggested by Pauling.[74] If we disregard the difference in energy between the $2s$ and $2p$ states of carbon, any linear combination of the $2s$ and $2p$ wave functions may be regarded as a legitimate solution of the wave equation for the central atom. Of course in a truly central field it would be regarded as a very bad error to mix s and p wave functions, but if the separation between the $2s$ and $2p$ states is small compared with the bonding energy, then the ability to form the best possible bonds is the all-important consideration, and what would be the best solution for the central atom, considered alone, becomes comparatively unimportant.[75] In order to form four independent bonds from the central atom the four linear combinations which are selected must be mutually orthogonal. Now because the three wave functions resemble the components of a vector any linear combination of functions may be regarded as a $2p\sigma$ function referred to some direction. Hence any one of our four linear combinations may be regarded as of the form

$$\psi_i = a_i\psi_{2s} + b_i\psi_{2p\sigma_i}, \qquad (56)$$

where $2p\sigma_i$ means a $2p\sigma$ wave function referred to some direction $C-i$. We must form four orthogonal linear combinations of the form (56). The requirement[76] of orthogonality gives us immediately relations of the form

$$a_ia_j + b_ib_j \cos(i, j) = 0, \qquad (57)$$

as one sees from (48) and the fact that $\psi_{2p\sigma}$ and $\psi_{2p\pi}$ are mutually orthogonal when the space quantization is relative to the same axis. In addition, there is the requirement

$$a_i^2 + b_i^2 = 1 \qquad (58)$$

if the wave functions are to be normalized to unity. It is not possible to select the four valence directions at random, for there are eight quantities $a_1 \cdots a_4$, $b_1 \cdots b_4$ whereas there are six relations of the form (57) and four of the form (58). Eight unknowns cannot, of course, be made to satisfy ten independent equations for arbitrary values of $\cos(i, j)$. It is, however, possible to satisfy the ten equations if we make the simple assumption that the hybridization ratio is the same for all four linear combinations. This assumption is warranted for molecules such as CH_4, where all four attached atoms are identical. Then $a_i^2 = \frac{1}{4}$, as the single wave function ψ_{2s} is to be apportioned equally between the four wave functions $\psi_1 \cdots \psi_4$. From (58) we have $b_i^2 = \frac{3}{4}$. The condition (57) will now be satisfied if $\cos(i, j) = -\frac{1}{3}$, i.e., if each valence direction makes a tetrahedral angle with the other valence directions. Hence we are led to the tetrahedral model of CH_4, quite irrespective of the repulsions between the corner atoms, if we assume that the hybridization ratio is the same for all four bonds. It seems reasonable that in a molecule such as CH_4 the energy should then be lowest on symmetry grounds. Actual calculation[77] of the energy

---

[74] L. Pauling, Proc. Nat. Acad. Sci. **14**, 359 (1928).

[75] Actually the separation between $2s$ and $2p$ is not small in C, amounting to between 5 and 10 volts; cf. reference 62.

[76] The precise reason that they must be orthogonal is a little involved. If two electrons are in identical orbits they are not free to form other bonds, or in terms of the vector model, their spins cannot be aligned independently but must be anti-parallel to each other. If two wave functions are not orthogonal to each other in cases where they are built out of linear combinations of orthogonal functions one can say that one function contains part of another, or in other words that one has progressed a step towards the two electrons being in the same state, so that their spins are not free. If one makes a proper perturbation calculation one is, of course, finally led to the proper linear combinations, which are orthogonal.

[77] J. H. Van Vleck, J. Chem. Phys. **1**, 230 (1933).

with the aid of (40) and (48) shows that in molecules of the type CH_4 the energy is indeed lowest when the hybridization ratios are equal and the configuration is tetrahedral. With this configuration the exchange energy connecting C with the H atoms is found by (41), (48) and (49) to be[78]

$$W_{\mathrm{ex}}=N_{ss}-2.5N_{\sigma\sigma}+4N_{\pi\pi}-3\sqrt{3}N_{\sigma s}. \quad (59)$$

It is interesting to note that in this calculation the directional effect favoring the tetrahedron results only in virtue of the "hybridization integral" $N_{\sigma s}$ defined in (49). It can be shown that were $N_{\sigma s}=0$, the matter of geometrical arrangement would be a matter of indifference as long as (57) is satisfied. From the difference between the bonding energies of CH and 4CH, and other empirical data, one concludes that N_{ss}, $N_{\pi\pi}$ are each about 2 volts, $N_{\sigma s}$ about 1 volt and $N_{\pi\pi}$ about -0.6 volt. This agrees in part with Coolidge's direct computation of the integrals for $H_2.O$[79] Of course the values for OH and CH need not be exactly the same. He obtained $N_{\sigma\sigma}=2.3$, $N_{\pi\pi}=-0.6$. However, all such computations are somewhat dependent on the precise form assumed for the atomic orbital of the O atoms, and in the present state of affairs, especially in view of the difficulties mentioned in section 18, it seems better not to attempt a program as ambitious as the direct computation of the heat of dissociation but rather to proceed in the converse direction and deduce approximate values of the N's from observed bonding energies.[80] Even this reverse procedure is open to question, but the observed data on simple C, N, O compounds involving hydrogen seem compatible with N's of the sizes estimated above, although it is still not clear why the potential hill to be surmounted in turning an NH_3 molecule inside out should be as low as it actually is ($\frac{1}{4}$ volt).

We have seen that CH_4 is characterized by equal hybridization ratios for all four bonds. On the other hand, with molecules such as $CHCl_3$ only three hybridization ratios need presumably be the same, while in CH_2Cl_2, one would expect these ratios to be equal only in pairs. Actual calculation[77] shows that in these cases one should use hybridization ratios equal only to this extent, and that the energy would be higher in $CHCl_3$ or CH_2Cl_2 were all four ratios equal. When all four ratios are not equal, Eq. (57) can no longer be satisfied with tetrahedral angles. Instead one can show that the $Cl-C-Cl$ angles in $CHCl_3$ and CH_2Cl_2 should be greater than 109.5°, the tetrahedral value. Incidentally the method of molecular orbitals leads to the same type of deviation, thereby showing that two entirely different methods often lead to the same result. Early x-ray data revealed the following $C-Cl$ angles: $CHCl_3$, 116.4°, CH_2Cl_2, 123.8°, CCl_4, 109.5°. One of the present writers[77] construed the departures from 109.5° found in $CHCl_3$ and CH_2Cl_2 as nice confirmations of the valence theory, but unfortunately, more recent electron diffraction measurements[81] show that in all three compounds the angles are substantially 109.5° (within 2 or 3 degrees the experimental error). However, Dr. Penney has recently shown[81a] that only very small deviations from 109.5° are to be expected when one examines the size rather than simply the sign of the deviation predicted by theory.

The original papers of Slater and Pauling perhaps give inadvertently the impression that with sp^3 hybridization the angles are necessarily tetrahedral. This is not at all true, as many different types of hybridization are possible, and exactly the tetrahedral angles are characteristic only of compounds such as CH_4 where all four attached atoms are identical. Fortunately, the deviations from the tetrahedral values are usually not large.

Many chemists still believe that tetrahedral angles are characteristic of the carbon atom's bonds, regardless of the nature of the attached atoms. Thus, to quote from a popular organic textbook, "According to the fundamental hypothesis of stereochemistry the four valency bonds of the carbon atom are imagined to be

---

[78] See the preceding reference for detailed proof of (59).

[79] Coolidge (private communication) obtained, however, a larger value of N_{ss}, about 3 volts. This value is probably reduced somewhat when allowance is made for the fact that the $2s$ wave functions are more tightly bound than $2p$. Dr. W. G. Penney informs the writers that $N_{\sigma s}$ may be somewhat larger than 1 volt.

[80] Cf., however, H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932) and reference 62.

[81] L. E. Sutton and L. O. Brockway, J. Am. Chem. Soc. **57**, 473 (1935).

[81a] W. G. Penney, Trans. Faraday Soc. **31**, 734 (1935).

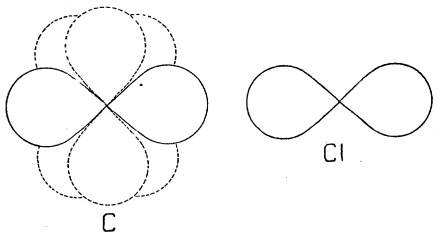


FIG. 8. $\sigma\sigma$ bond.

directed towards the summits of a regular tetrahedron, at the center of which lies the atom itself."

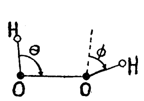
So far we have assumed that the atoms attached by the central atom are all univalent, and in an *s* state. The restriction to an *s* state is, however, not really necessary. If one of the univalent attached atoms is in a *p* state, the foregoing considerations all apply, with the understanding that the axis of the paired *p* orbit of the attached atom is directed toward the central atom, as shown in Fig. 8. Thus CCl_4 should have the same tetrahedral structure as CH_4.

Penney and Sutherland[82] have applied the method of electron pairs based essentially on Eqs. (34), (48), (51) to a theoretical calculation of the energy of H_2O_2 and NH_2-NH_2, and find the rather surprising result that free rotation cannot occur in either of these molecules at ordinary temperatures, and that the stable forms of these molecules are those in which the azimuth of one half of the molecule with respect to the other is about 100°. The H_2O_2 molecule would be as shown in Fig. 9, in which φ is the angle between the planes HOO and OOH. Here θ and φ are approximately 100°. This result is surprising because H_2O_2 and N_2H_4 have long been supposed to possess symmetrical structures. Both molecules are known to possess high dipole moments (H_2O_2, $2.06+10^{-18}$ e.s.u., N_2H_4, 1.84 10^{-18} e.s.u., each at 18°C), as one would expect from an unsymmetrical model such as Penney and Sutherland's.

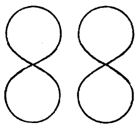
25. Double or $\pi\pi$ bonds—sp^2 and sp hybridization

The type of bond shown in Fig. 8 may be described as a $\sigma\sigma$ bond. There can only be one bond of this character connecting any two atoms. To account for double and triple bonds one introduces the concept of $\pi\pi$ bonds[83] (Fig. 10) wherein the axes of the dumb-bells of the two atoms are perpendicular to the line joining the two atoms. The amount of overlapping is altered when one of the dumb-bells is rotated about the horizontal axis in Fig. 10, and is a maximum when they are parallel, as in the $\pi\pi$ bond. This is the reason why free rotation is usually associated with single bonds but not with double bonds. Clearly, there is no change in bond energy for rotation about a horizontal axis in Fig. 8. Hence there is free rotation about a single bond insofar as the effects of directional valence are concerned, provided the attached atom is in an *s* or $p\sigma$ state. When the bond is of the $\pi\pi$ type, or is a hybrid affair involving a $p\pi$ ingredient, there may not be free rotation even though there is only a single bond. The molecules H_2O_2 and N_2H_4, also probably NH_2OH, are examples of the latter state of affairs. Besides the $\sigma\sigma$ and $\pi\pi$ bonds illustrated in Figs. 8 and 10, it is possible to have still a third bond by pairing two dumb-bells whose axes are perpendicular to the plane of the paper, and which thus form another $\pi\pi$ bond. This is the source of the triple bond.

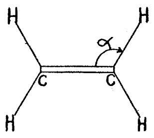
sp^2 hybridization. If we consider a compound such as C_2H_4 illustrated in Fig. 11, the second carbon bond is probably a pure $\pi\pi$ bond involving the two dumb-bells whose axes are perpendicular to the plane of the paper. The first carbon bond and the four C−H bonds are then in the plane of the paper. They are probably not of the pure *p* or pure *s* type, but instead



H_2O_2
FIG. 9.



$\pi\pi$ bond
FIG. 10.



C_2H_4
FIG. 11.

---

[82] W. G. Penney and G. B. B. M. Sutherland, J. Chem. Phys. **2**, 492 (1934); Trans. Faraday Soc. **30**, 898 (1934).

[83] This terminology is due to Hückel and Hund.

involve hybridization, which, following Pauling,[67] we may characterize as sp^2 rather than sp^3 hybridization, inasmuch as the third p function of each C atom has already been consumed in the $\pi\pi$ bond and so is not involved. The precise value of the angle α in Fig. 11 depends on the hybridization ratios. If they are the same for all three bonds H−C, H−C, C−C involving a given carbon atom, then the angle α is 120°, while it is 90° if two of the bonds are sp mixtures, and one, the C−C, bond is pure $\sigma\sigma$. Actually the angle α probably lies between these limits. Pauling[67] discussed C_2H_4 on the basis of sp^3 (tetrahedral) rather than sp^2 hybridization, thus making $\alpha = 109.5°$ and both carbon bonds share part of the s wave function but actual calculation[84] shows that the energy is lower with the sp^2 type.

sp hybridization. Besides sp^3 and sp^2, there can also be sp hybridization, as first shown by Pauling. The two sp functions which are mutually orthogonal and normalized to unity are

$$(\psi_{2s} \pm \psi_{2p\sigma})/\sqrt{2}. \tag{60}$$

These two functions correspond to dumb-bells which are heavy on one end and light on the other, due to the fact that $2p\sigma$ has the opposite sign or phase on the two ends of the dumb-bell and so reinforces $2s$ on end, but opposes it on the other. (This sign behavior can be seen by replacing x by $-x$ in Eq. (45).) The sp hybridization would enter in a model of CO_2 by the H-L-S-P method, shown in Fig. 12. The two shaded dumb-bells emanating from the O atom, the one hatched vertically, the other horizontally, are the two sp functions (60), and are paired with $p\sigma$ wave functions of O_b and O_a, respectively. The second $C-O_a$ bond is a $\pi\pi$ bond formed by pairing the two unshaded dumb-bells. The second $C-O_b$ bond is similar except that the two dumb-bells are perpendicular to the plane of the paper and so not shown in Fig. 12.[85]

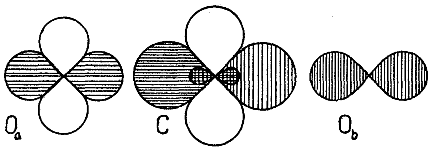


FIG. 12. The CO_2 molecule.

26. Transition elements— sp^3d^2 and sp^2d bonds

So far we have dealt with the chemistry of light atoms (or equally well with that of heavy atoms not in transition stages where inner groups are being augmented by the addition of d electrons). On the other hand in elements of the transition groups (Fe, Pd, Pt, etc.) there is additional latitude arising because there are d as well as s and p wave functions available for valence purposes. The principal quantum number of the d functions is one unit lower than that of the s or p ones (e.g., $3d$ *vs.* $4s$, $4p$ in Fe) in order to counterbalance the larger l-value for the d states and so give approximately the same firmness of binding, which is necessary if s, p, d all participate together in valence.[86] The increased complexity due to admission of d states enlarges the number of possible bonds and spatial arrangements. The five d wave functions are conveniently separated into the following two groups, which, following Bethe,[87] we shall call d_γ and d_ϵ

$$d_\gamma:\ \psi(d\gamma_1) = (1/12)^{\frac{1}{2}} f(r)(3z^2 - r^2),$$

$$\psi(d\gamma_2) = \tfrac{1}{2} f(r)(x^2 - y^2), \tag{61}$$

$$d_\epsilon:\ \psi(d\epsilon_1) = f(r)xy, \quad \psi(d\epsilon_2) = f(r)zx,$$

$$\psi(d\epsilon_3) = f(r)yz. \tag{62}$$

Pauling[67] shows that tetrahedral bonds can be formed by $sd_\epsilon{}^3$ as well as sp^3 hybridization. The strongest tetrahedral bonds are. as he shows, probably a mixture of the two types, sc that s, p, d_ϵ all contribute. What is more interesting is that he shows that by taking linear combinations of s, p, and d_γ wave functions he can form new "sp^3d^2" wave functions which are ideally suited for attaching six corner atoms octahedrically arranged (i.e., at the six face centers of a cube). With the ever present assumption of electron pairing, it was not possible to do this with only p and s wave functions, in nice

---

[84] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

[85] Actually, there is probably a "resonance" wherein the $\pi\pi$ bonds continually interchange between O_a and O_b. Then Fig. 12 applies only half the time. The other half, O_b has the vertical $\pi\pi$ bond, and O_a the one perpendicular to the plane of the paper.

[86] In Nickel, for instance, the separations between $3d$, $4s$, and $4p$ are only a matter of a volt or so; cf. Bacher and Goudsmit, *Atomic Energy States*, p. 323.

[87] H. Bethe, Ann. d. Physik 3, 133 (1929).

agreement with the experimental fact that coordination numbers of six, associated with octahedral arrangements, are particularly characteristic of transition groups. Pauling also shows that four bonds, all in a plane, and corresponding to the four corners of a square, can be formed by sp^2d_γ hybridization. The four wave functions involved are s, $p\sigma_x$, $p\sigma_y$, and $d\gamma_2$.[88] For the precise values of the hybridization ratios, also for information as to how one can form cylindrical prismatic arrangements, the reader is referred to the interesting papers of Pauling[67] and of Hultgren.[89] The latter shows that it is not possible to obtain more than six equivalent bonds with any arrangement.

Pauling [67] assumes that in an ion such as e.g. $\mathrm{Ni(CN)_4^{--}}$ or $\mathrm{Fe(CN)_6^{---}}$, the superfluity of negative electrons is to a large extent absorbed by the central atom, so that its structure is mainly $\mathrm{Ni^{--}(CN)_4}$ or $\mathrm{Fe^{---}(CN)_6}$ rather than the conventional ionic form $\mathrm{Ni^{++}(CN^-)_4}$ or $\mathrm{Fe^{+++}(CN^-)_6}$. In our opinion, this assumption is the greatest element of weakness in his theory, as each successive electron affinity is lower than the preceding, and the Ni or Fe atom presumably is not anxious to have two, three or in some cases proposed by Pauling, even four extra electrons. (The conventional form, on the other hand, probably transfers charge too far in the opposite direction.) However, we do not mean to imply that there are not elements of truth in his ideas, as a true wave function is a linear combination of wave functions representing different possible phases through which the system resonates. Surely the state of affairs assumed by Pauling is one possible phase, but the question is whether it is preponderant or even representative.

The case of $\mathrm{Ni(CN)_4^{--}}$ is particularly interesting. The $\mathrm{Ni^{--}}$ ion has 12 electrons to house (not counting inner closed shells), whereas there are only nine orbitals (sp^3d^5) available in all. Hence some of the electrons must "double up" and occupy the same orbital. As the $3d$ orbitals are known from spectroscopic data[86] to be lower than the $4p$ and $4s$, the d orbitals will be those filled twice. Thus in $\mathrm{Ni^{--}}$, the singly occupied orbitals available for valence purposes are s, p^3, d. Now with sp^3d at one's disposal one can form four sp^2d bonds in a plane, or form tetrahedral sp^3 bonds. With the latter, none of the d orbitals would be used for bonding purposes. Hence the eight electrons of the central ion which are not involved in bonds would have their choice of five different, about equally good d orbitals. They would not all have to "double up," and those having orbitals to themselves can have their spins parallel, which they prefer to do since by the Hund rule[16] the energy is then lowest. Then the $\mathrm{Ni^{--}}$ ion would be paramagnetic. Actually it is diamagnetic, as is shown, for instance, by susceptibility measurements on $\mathrm{K_2Ni(CN)_4}$. This fact indicates that the bonds are of the square sp^2d type. Indeed, if the sp^2d bonds are used, the eight unbonded electrons have at their disposal four d orbitals and one p orbital. The latter has higher energy, so that they all double up in d orbitals, with their spins hence necessarily anti-parallel, giving diamagnetism. Thus Pauling boldly predicted that $\mathrm{Ni(CN)_4}$ should be plane. No x-ray data on this ion were available when Pauling made this prediction. X-ray measurements did show[90] that $\mathrm{K_2PtCl_4}$ had a square configuration, and one would perhaps expect the $\mathrm{PtCl_4^{--}}$ and $\mathrm{Ni(CN)_4^{--}}$ ions to exhibit a similar structure. This similarity has been substantiated by subsequent x-ray measurements[91] on $\mathrm{BaNi(CN)_44H_2O}$. We must mention that a square configuration for the $\mathrm{Ni(CN)_4^{--}}$ ion, if diamagnetic, could also have been predicted by the method of molecular orbitals without the necessity of assuming a $\mathrm{N^{--}}$ ion, as we shall see in section 33. This alternative procedure was, however, not advanced until much later.

Pauling shows that magnetic data are in good agreement with his structure, and he was the first to interpret such phenomena as that the $\mathrm{Fe(CN)_6^{---}}$ ion is considerably less paramagnetic than the $\mathrm{FeF_6^{---}}$ ion. To suppress most of the magnetism, it is only necessary that the

---

[88] In place of s, a $d\gamma_1$ bond could be used, or a linear combination of s and $d\gamma_1$. The reason is that s and $d\gamma_1$ have the same tetragonal directional properties (i.e., belong to the same tetragonal representation in Table V, section 33). The s bond is probably stronger than the $d\gamma_1$, and it is so better not to utilize the latter for bonding purposes, especially since otherwise it can be filled twice.

[89] R. Hultgren, Phys. Rev. **40**, 891 (1932).

[90] R. G. Dickinson, J. Am. Chem. Soc. **44**, 2404 (1922).

[91] H. Brasseur, A. de Rassenfosse and J. Piérard, Zeits. f. Krist. **88**, 210 (1934).

inter-atomic forces be able to disrupt the Russell-Saunders coupling of the central atom. As one of us will show elsewhere, mechanisms for doing this are provided not only in Pauling's model but also in the method of molecular orbitals or even in the conventional polar structure $Fe^{+++}(CN^-)_6$. Hence, in our opinion, it cannot be inferred from the magnetic data whether a bond is of the Pauling covalent or the conventional polar structure unless these data are supplemented by a certain amount of empirical information. It is, however, found experimentally that covalent bonds are more effective than conventional polar ones in destroying magnetism, as it is known from other data[8] that the bonds in the fluoride are much more polar than in the cyanide. Once this fact is substantiated by measurements on a few compounds, one can presumably extrapolate to others and say that abnormally low magnetism in transition compounds of high magnetic dilution probably means that there are strong covalent bonds. Thus magnetism furnishes a useful criterion for determining the bond type. The covalency is doubtless not as extreme as $Fe^{---}(CN)_6$, but probably intermediate between this and $Fe^{+++}(CN^-)_6$, so that the Fe ion may well be nearly neutral. The intermediate stages are most easily interpreted by the method of molecular orbitals (section 33).

27. Abandonment of the restriction to electron-pairing—nondirectional theories of valence

In the remainder of the present chapter, we shall consider systems for which there are no naturally designated electron-pairs, and for which in consequence we can no longer use Eq. (34). One category of hypothetical systems of this type is provided by what may be termed the "nondirectional" theory of valence, in which all valence electrons of a given atom are treated as alike, and as effectively in S states, so that the directional properties of the wave functions are completely ignored. Obviously one must then abandon the approximation of electron pairing, as the partnership affiliations were due largely to directional properties. There exists a rather formidable literature largely on this nondirectional theory of valence.[92] In our opinion, much of the mathematics used in it is needlessly imposing, since most of the results can be obtained, as one of us showed elsewhere,[52] by means of the vector model rather than by group theory or even the Slater determinants.

In the nondirectional theory of valence the spin of each atom has its maximum possible value, as a simple calculation, given in the appendix by means of the vector model, shows that then the energy is lowest. Thus in NH_3, the spin of the N atom, which has three valence electrons, would be 3/2. The collective spin of the H atoms is likewise 3/2, since it must be equal and opposite to that of the N atom to give zero resultant spin for the complete molecule. This state of affairs is to be contrasted with that in the directional theory based on electron pairing, wherein it is meaningless to talk about the resultant spin of the N atom inasmuch as all collective quantization for the N atom has been disrupted by the pairing to the H atoms. Were the nondirectional theory applicable, tetravalent carbon compounds would be really built upon the ^5S state (spins of C electrons all mutually parallel) rather than the somewhat different valence state mentioned in section 20.

As far as explaining the spatial arrangements of molecules, we believe that the nondirectional theory commits a very gross error in attributing all directional effects to repulsions between corner atoms. For instance, it predicts plane NH_3. Consequently we shall not discuss this theory further (except in connection with activation). Of course it is not without its elements of truth because, as we have already said, nearly every type of theory is represented in the complicated linear combinations involved in true wave functions.

28. Activation energies

There is, however, one realm in which the nondirectional theory of valence has been very fruitful, and that is in the computation of activation energies. The form of theory here used differs slightly from that above in that one does

---

[92] W. Heitler, Zeits. f. Physik 79, 143 (1932); *Handbuch der Radiologie*, 2nd ed., vol. 6, part 2; W. Heitler and A. A. Schuchowitzki, Physik. Zeits. d. Sowjetunion 3, 241 (1933); M. Born, Ergebnisse der exakten Natur. 10, 387 (1931); H. Weyl, Nach. Ges. Wiss. Gött, N. P. Klasse 1930, 285; 1931, 33; G. Rumer, Nach. Ges. Wiss. Gött, M. P. Klasse 1932, 337. Much of the theory of invariants developed in these articles could be used in connection with the directional theory as well.

not treat all the valence electrons as alike. Instead one assumes that only certain electrons have their bonds changed during their activation process. The other electrons are regarded as so firmly paired that they need not be considered in the calculation. It is only the electrons whose pairing is being converted that are regarded as effectively in S states. Thus in the reaction $H_2+C_2H_4\rightarrow C_2H_6$ one would not regard all the C electrons as alike, but would regard the system as effectively a four electron one (the two electrons contributed by H_2 and the two C electrons which formed the second $C-C$ bond). It is clear that activation energies could never be computed with the approximation of electron pairing, because the chemical transformation is, by its very nature, a transformation from one bond type to another (e.g., in the preceding example from $H-H$, $C-C$, to $C-H$ pairing) and the activation hill is just the zone where affinities are being changed and there is no natural system of partnership. To simplify calculations, the directional properties of the orbitals whose bonds are being changed are usually ignored, but this approximation is not really necessary, and is clearly a less violent assumption now that our interest is in relative energies, than it was when our attention was focused on geometrical arrangement.

The general subject of valence is really concerned with the stability of molecules in a kinetic sense,—i.e., a molecule is stable at a given temperature if its rate of decomposition or reaction with other molecules is slow at that temperature. It follows, therefore, that there are all degrees of stability, and that stability is a function of the temperature,—all molecules becoming unstable at sufficiently high temperatures. Any review of valence, consequently, should preferably include a section devoted to the discussion of the rates of chemical reactions, or to quantities determining these rates.

The activation energy A of a chemical reaction is defined in practice by the empirical Arrhenius equation

$$d \log k/dT=A/RT^2, \qquad (63)$$

where k is the specific reaction rate constant,—i.e., the rate of the reaction when the concentration of the reacting substances is unity. It should be pointed out here that it is not a simple task to calculate A from experimental data, with Eq. (63), because most reactions studied in the laboratory do not fall into the simple scheme of first, second, or third order reactions. Hence one cannot calculate a k which is really a constant over any great variation in the concentration of the reacting substances. This is true because most reactions are not simple as carried out in the laboratory,—i.e., a chain reaction may be present, or a back reaction, or two or more reactions may be occurring simultaneously, or the reaction may be partly homogeneous and partly heterogeneous, etc.

Eq. (63) may be written in the form

$$k=Ze^{-A/RT}. \qquad (64)$$

Now Z is approximately the same order of magnitude for similar reactions, and hence the magnitude of k is determined by the value of A. In particular, a knowledge of the difference between the activation energies (A_1-A_2) of two chemical reactions whose specific reaction rate constants are k_1 and k_2 will enable one to calculate the ratio k_1/k_2 and hence one can say which reaction will, at a given temperature, proceed more rapidly.

According to simple kinetic theory, Z in (64) is the number of collisions occurring between reaction molecules. Only a fraction of these collisions, are successful in causing reaction, however, these being characterized by being "energy rich," thus possessing sufficient kinetic energy so as to bring the molecules into a proper close configuration to react. The quantity $e^{-A/RT}$ is, according to kinetic theory, the fraction of collisions occurring in a two dimensional gas in which the total kinetic energy of the colliding molecules is A or greater.

The so-called semi-empirical calculations on activation which we now discuss have been made by Eyring and his collaborators.[93] Before one

---

[93] For example, Eyring and Polyanyi, Zeits. f. physik. Chemie **B12**, 279 (1931); H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931); Rollefson and Eyring, J. Am. Chem. Soc. **54**, 170 (1932); A. Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932); Kimball and Eyring, J. Am. Chem. Soc. **54**, 3876 (1932); Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933); Sherman, Sun and Eyring, J. Chem. Phys. **3**, 49 (1935); also references 95, 98 and 99.

can compute the energy of the activated state for a reaction like $XY+WZ\rightarrow XW+YZ$ (with each atom monovalent), it is necessary to have the formula

$$W_{\text{ex}}=\{\tfrac{1}{2}[(J_{12}+J_{34}-J_{13}-J_{24})^2+(J_{12}+J_{34}-J_{14}-J_{23})^2+(J_{13}+J_{24}-J_{14}-J_{23})^2]\}^{\frac{1}{2}} \tag{65}$$

for the exchange energy for a system of four electrons in the state $S=0$, without the assumption of electron pairing. Eq. (65) is derived in the appendix by means of the vector model, although it was first obtained by London[94] by a different procedure. Eq. (66) gives the corresponding expression, also derived in the appendix, for a system of three electrons in the state $S=\frac{1}{2}$

$$W_{\text{ex}}=\{\tfrac{1}{2}[(J_{12}-J_{13})^2+(J_{12}-J_{23})^2+(J_{13}-J_{23})^2]\}^{\frac{1}{2}}. \tag{66}$$

This formula is needed in the connection with the reaction

$$W+XY\rightarrow WX+Y. \tag{67}$$

To (65) and (66) one must of course, add the ordinary Coulomb energy which does not involve the exchange degeneracy or apparent spin coupling problem. Eyring and Kimball[95] have set up the secular equation for systems containing up to eight electrons. The formulas for the exchange energy are then much more complicated (roots of a 14th degree Eq. when $n=8$, unless there is special symmetry; cf. section 17). The energy of the activated state is that of the intermediate state of highest energy through which the system must pass from the initial to the final configuration, and the activation energy is the energy of this state minus the initial energy.

Let us now consider the reaction (67). It is readily shown that W will approach XY with the least expenditure of energy on an extension of the straight line connecting the nuclei X and Y. Let the distance between atoms W and X be r_{WX}, and that between X and Y be r_{XY}. Then $r_{\text{WY}}=r_{\text{WX}}+r_{\text{XY}}$. At the beginning of the reaction r_{WX} will be very large and r_{XY} will be the normal distance between nuclei in the xy molecule. There will be some intermediate configuration,—i.e., the activated state, where r_{WX} and r_{XY} are comparable. After reaction, the final state of the system will have r_{WX} equal to the normal inter-nuclear distance in the r_{WX} molecule, and r_{XY} will be very large. If we plot r_{XY} as the ordinate and r_{WX} as the abscissa in the xy plane, and let the z coordinate specify the corresponding values of the energy, we may think of the reaction as corresponding to the motion of a ball over this potential energy surface, from an initial region of low potential energy, through an intermediate region of relatively high energy, to a final state of low energy. Of all the various paths the ball may take in going from the initial to the final state it will prefer that path which requires the least expenditure of energy. The minimum energy required in getting over the potential energy hill is the activation energy. This situation is illustrated by Fig. 13 for the reaction $H+H_2=H_2+H$ in which the energy is indicated by means of contour lines, and in which the course of the reaction is shown by broken arrows.

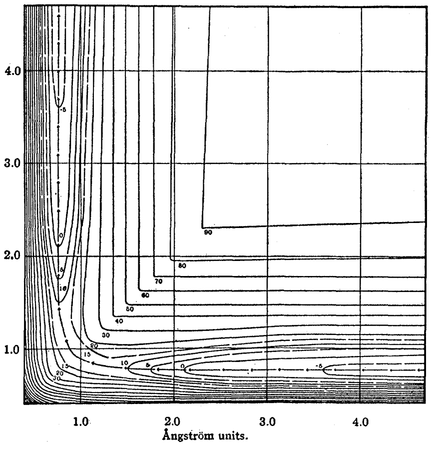


FIG. 13.

---

[94] F. London, Zeits. f. Electrochemie **35**, 552 (1929).

[95] Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933); cf. also Serber, reference 54.

If, from what has just been said, we can calculate the energy of the system for any arbitrary value of r_{WX} and r_{XY} we can calculate the activation energy of the reaction (67). Eq. (66), augmented by the Coulomb energy, enables us to do this providing we are able to evaluate the various integrals. Now it was Eyring's happy thought that this could be done empirically, if we neglect all directional valence effects, by constructing a Morse potential energy curve for each pair of atoms. This curve gives the energy of an electron-pair bond as a function of the distance between nuclei,—i.e., it gives the *sum* of the Coulomb and exchange energies. In order to evaluate each energy separately, however, it is also necessary to know their *ratio*. Eyring makes the further quite arbitrary assumption that this ratio is 14/86, since this is the value which makes his theory yield the observed activation energy, determined from para-ortho conversion, for the simplest chemical reaction $H+H_2 \rightarrow H_2+H$. (Incidentally, agreement with experiment is obtained with this ratio only if we neglect the zero point energy of the activated state.) He also supposes that the ratio is the same for all nonmetallic electron-pair bonds. The reason why the method is called "semi-empirical" is now clear. With these assumptions Eyring and his collaborators have been able to calculate activation energies for a wide variety of reactions, the agreement with experiment in all cases being surprisingly good. A few examples of its value in chemical kinetics will now be given.

As is often the case in calculating quantities approximately, we may expect that the difference in two values is more reliable than the absolute value of either one of them. Fortunately, it is a knowledge of just such differences which is necessary for deciding between various mechanisms for a chemical reaction, and hence renders the calculations quite useful to the chemical kineticist. For example, the thermal conversion of para to ortho-hydrogen may occur by one of two mechanisms:

$$\text{(a)} \qquad H_{2(p)}+H_{2(p)} \rightarrow H_{2(o)}+H_{2(o)},$$

$$\text{(b)} \qquad H_2 \rightleftarrows 2H, \quad H+H_{2(p)} \rightarrow H_{2(o)}+H.$$

Whether mechanism (a) or (b) is operative will of course depend upon which mechanism involves the lowest over-all activation energy. This energy for the first mechanism will simply be that for the reaction between two hydrogen molecules. The activation energy for the second mechanism will equal approximately the activation energy for the reaction $H+H_2 \rightarrow H_2+H$ plus one-half[96] the heat of dissociation of H_2. The calculated results are

	Reaction	A
(a)	$H_2+H_2 \rightarrow H_2+H_2$	68.7 cal.
(b)	$H+H_2 \rightarrow H_2+H_2$	7.9
	$\frac{1}{2}D_{H_2}$	=51.2
		59.1

Thus, one would predict the thermal conversion of para to ortho-hydrogen to go via the atom mechanism, in agreement with experiment.[97]

The calculations lead one to expect that the hydrogen, chlorine combination will go via an atom mechanism, whereas the hydrogen, iodine combination will be a direct bimolecular reaction,—in agreement with experiment.

For the 1,4 addition of Br_2 to butadiene one calculates[98] an activation energy of 31.3 kg. cal., whereas the 1,2 addition involves an energy of 41.7 kg. cal.,—leading to a prediction in agreement with experiment, but superior to the old organic explanation of the 1,4 addition (Thiele's theory of partial valence) because it allows some 1,2 compound to be formed. Recent experimental evidence[98a] confirms the theoretical conclusions.

One calculates a lower activation energy for the addition of hydrogen to cyclohexene than to 1,2 dihydrobenzene. The activation energy for the addition of a molecule of hydrogen to 1,2-dihydrobenzene is in turn lower than that to

---

[96] To prove this fact, we note that the speed of the second part of the reaction (b) is given by

$$-d(H_{2(p)})/dt = a(H)(H_{2(p)})e^{-A/RT},$$

where (H) denotes the concentration of monatomic H present, etc. Now from the usual equilibrium constant relation, we have $(H)^2/(H_{2(p)}) = e^{-\Delta F/RT}$. Next we notice that for our purposes it will be an adequate approximation to replace the change in free energy ΔF by the Heat ΔH of the reaction, $H_2 \rightarrow 2H$. Then $-d(H_{2(p)})/dt = a(H_{2(p)})^{3/2}e^{-(A+\Delta H/2)/RT}$ and the exponent, or effective activation energy, thus contains $\Delta H/2$ as an additive term.

[97] L. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930).

[98] Eyring, Sherman and Kimball, J. Chem. Phys. **1**, 586 (1933).

[98a] G. B. Heissig and J. L. Wilson, J. Am. Chem. Soc. **57**, 859 (1935).

benzene. Thus one calculates that in the reactions benzene $\xrightarrow{+H_2}$1,2-dihydrobenzene $\xrightarrow{+H_2}$ cyclohexene $\xrightarrow{+H_2}$ cyclohexane, the third reaction is faster than the second, and the second faster than the first. Therefore one would predict the hydrogenation of benzene would lead to cyclohexane and not 1,2-dihydrobenzene. If one is willing to admit that this same *relative* order of reaction rates will hold on a surface, one would predict the same thing for the heterogeneous reaction,—in agreement with experiment.

One might expect by chance that a reaction may proceed by two mechanisms, the activation energies of which are practically the same. In this case both mechanisms would be simultaneously operative. An example of such a reaction is the decomposition of $C_2H_4I_2$, which may proceed as a straightforward unimolecular decomposition, or as an iodine atom catalyzed reaction. The former mechanism involves an activation energy, according to Sherman and Sun,[99] of 30.0 kg cal., whereas they calculate for the latter mechanism an energy of 28.1 kg cal. Thus, they predict the two mechanisms would be concerned in the decomposition of $C_2H_4I_2$, and this is just what Arnold and Kistiakowsky[100] find experimentally.

The examples given above serve to illustrate the usefulness of the calculation of activation energies in chemistry, particularly to the chemical kineticist. They also serve to emphasize what has already been previously mentioned,—namely, the arbitrary nature of ordinary valence theory, which simply predicts whether a molecule is stable or not. Thus, $C_2H_4I_2$ is stable from almost any valence theory point of view, but is certainly unstable under the conditions of temperature and pressure which Arnold and Kistiakowsky[100] used in their experiments for measuring its rate of decomposition.

In the foregoing discussion, we have concentrated primarily on the qualitative determination of relative activation energies for different processes. The quantitative agreement which Eyring obtains with experiment is exceedingly good, but we do not lay too much stress upon it, because it seems to be destroyed when the corrections for nonorthogonality and higher order permutations are taken into account, as Coolidge and James[55] have shown. Perhaps, as Professor Slater has suggested to us, one reason why Eqs. (65) and (66) work so well in activation processes is that they may in a certain sense be regarded as convenient simple interpolation formulas between known energies for the initial and final configurations, which might conceivably be approximately correct even though the Heitler-London theory were completely wrong. Even if (65) and (66) are regarded as interpolation formulas, there is still the unsettled question why it works so well always to take the exchange and Coulomb integrals in the ratio 86 to 14 whereas direct computation seems to show that the ratio can vary considerably from atom to atom.[101, 102] It is to be stressed that in any case Eyring's method is as useful as it is non-rigorous, for it really enables one to predict processes correctly in advance of measurement.

29. Resonance energies—aliphatic and aromatic compounds

In the present section we consider a variety of molecules in which one must use the directed theory of valence, but cannot make the approximation of electron pairing. The standard example is benzene, which was first studied by Hückel.[103] For the bonds whose dumb-bell axes are in the plane of the benzene ring it is at least a first approximation to assume electron pairing. One can use for each carbon atom the three sp^2 functions described in section 25. They will give three coplanar bonds projecting from the C atom and making mutual angles of 120°. Clearly one of these bonds is to be used to attach the H atoms, and the other two to form electron pairs with the appropriate adjacent C atoms. In addition there are the three $\pi\pi$ bonds connecting

---

[99] A. Sherman and C. E. Sun, J. Am. Chem. Soc. **56**, 1096 (1934).

[100] L. B. Arnold, Jr. and G. B. Kistiakowsky, J. Chem. Phys. **1**, 166, 287 (1933).

[101] Cf. Eyring, Chem. Rev. **10**, 119 (1932); the Coulomb percentage is for instance 22 rather than 14, in Li_2,[35] and is 28 in Na_2[48]. In H_2 it is about 10.

[102] Dr. Kimball points out to the writer that the 86 percent ratio cannot possibly hold clear down to $r=0$ and so cannot really be independent of r. Actually the potential energy to curves go $+\infty$ at $r=0$ for both the singlet and triplet state. With an 86 percent ratio, however, one would go to $+\infty$, and the other to $-\infty$ or *vice versa*, an absurdity.

[103] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

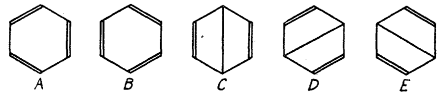


FIG. 14.

the six $2p$ dumb-bells whose axes are perpendicular to the plane of the paper. These bonds are represented by the second or inside lines in Fig. 14. It is obvious that there is no unique scheme of pairing for these $\pi\pi$ bonds, as either scheme A or B is equally good. There are also three other schemes of pairing C, D, E which are not as good, and which are hence called "excited structures" by Pauling. In addition one might seek to construct figures in which the lines crossed, but it can be shown that they are not linearly independent of the five structures shown in Fig. 14, in agreement with the deduction in section 17 that the corresponding secular problem $n=6$ is of degree five. The linearly independent electron pair structures are called by Pauling[51] a "canonical" set. The wave function for benzene is represented by a linear combination of the five canonical functions, each corresponding to a particular scheme of electron pairing: i.e.,

$$\Psi=\sum_{k=1}^{5} a_k\Psi_k.$$

If one of the five coefficients were large compared with the other, electron pairing would be a good approximation, but clearly two are equally dominant in benzene. The exchange energy which one would calculate with one of the structures A, B in Fig. 14 is $1.5J_{\pi\pi}$, where $J_{\pi\pi}$ is the $\pi\pi$ exchange integral between adjacent atoms. We have not included exchange integrals between non-adjacent atoms, nor the large amount of energy involving bonds in the plane of the benzene ring, for which the deficiencies of electron pairing do not arise acutely. This result $1.5J_{\pi\pi}$ is seen by using (40), as three of the exchange coefficients (*viz.* those pairing say 1–2, 3–4, 5–6) have the value $+1$ and the other three (those involving 2–3, 4–5, 6–1) have the value $-\frac{1}{2}$. Accurate solution of the secular problem[104] shows that the exchange energy should be $2.6055J_{\pi\pi}$. The value $2.4J_{\pi\pi}$ is obtained[105] if one includes only the two structures A, B in Fig. 14 but not C, D, E.

In sharp contrast to the situation in benzene is that in methane. Instead of using the approximate formula (41) or (59) based on a *natural* system of electron pairing discussed in section 17 one can use a more accurate expression not assuming electron pairing. However, it is found[69] that the difference is negligible, and that (59) differs by only 3 percent or so, from the correct exchange formula.

The variational theory discussed in section 12 shows that a lower energy (firmer binding) is obtained, the more complete the wave functions used in (27). Hence the energy computed with the assumption of electron pairing is always higher than that computed without the specialization to this energy. The difference between the two energies is called by Pauling the resonance energy. Thus in the benzene case mentioned above, the resonance energy was $1.1055|J_{\pi\pi}|$. The term owes its name to the fact that there is no unique scheme of electron pairing, so that the molecule may be said to spend part of its time in, or "resonate between" each of the various structures.

It would be an obvious triumph of quantum mechanics if it could account for the stability of the benzene ring, i.e., why benzene is the most stable cyclo hydrocarbon. This goal cannot be achieved simply by the consideration of resonance energies, as with the H-L-S-P approximation benzene has a resonance energy per atom inferior to that of the unknown compound cyclobutadiene (C_4H_4), which has a ring of 4 rather than 6, and which can be shown to be the best ring from the standpoint of resonance energy in the H-L-S-P method. Namely, it can be shown[103] that the C_4H_4 exchange energy is $2J_{\pi\pi}$, of which $J_{\pi\pi}$ is the value obtained with the assumption of electron pairing, and the absolute value of the remainder $J_{\pi\pi}$ is "resonance energy." Thus the $\pi\pi$ exchange energy per particle is $2J_{\pi\pi}/4$, superior in magnitude to the value $2.6J_{\pi\pi}/6$ in benzene. However, it is not surprising that a superior stability is not indicated for

---

[104] E. Hückel, Zeits. f. Physik **70**, 279 (1931); also Pauling and Wheland, reference 105; Seitz and Sherman, reference 54; Serber, reference 54 (arranged approximately in order of increasing simplicity).

[105] Pauling and Wheland, J. Chem. Phys. **1**, 362 (1932).

benzene, as the most important bonds are those in the plane of the benzene ring, and it is not to be expected that the $\pi\pi$ bonds are the determining factor in stability. A correct calculation should therefore investigate the directional valence in the plane of the benzene ring. Such an investigation has been made by W. G. Penney.[106] He finds superior stability for the group of six as compared to other rings. The nice thing is that the result is independent of the values assumed for the various exchange integrals, over a reasonably wide interval. The theoretical stability relative to $3C_2H_2$ is still uncertain. If one does not use the directional properties of the wave functions, then one finds that energy is liberated on dissociation of benzene into three acetelyene molecules. This Markov[107] showed with a calculation based on the nondirectional theory of valence wherein each C atom is given a spin of 3/2, the remaining spin being considered bound by the H atom. Since actually directional effects are important, little weight can be attached to Markov's conclusion, which is in contradiction to experiment.

Pauling, Wheland, and J. Sherman[105, 108, 109] have ingeniously calculated theoretical resonance energies for a large number of aromatic and aliphatic compounds, most of which involve benzene, or conjugated benzene rings as, for example, naphthalene, anthracene, hexaphenylethane, etc. The secular equations are usually too large to solve accurately but are tractable with certain reasonable simplifying assumptions. Their general idea of resonance energy as an important factor in hydrocarbon compounds seems to us a very fundamental and interesting one, but we believe that only an empirical significance can be given to the purported comparison of theoretical and observed resonance energies, much of the trouble being with the latter. The so-called observed values are obtained by assuming bond additivity, i.e., by taking values for the first and second C−H bonds, as deduced from C_2H_6 and C_2H_4 and multiplying them respectively by the number of first and second bonds in the compound. The excess of the observed energy over the bonding energy thus computed is termed the "observed" resonance energy. In other words, in compounds permitting resonance, Pauling and collaborators attribute all the departures from bond additivity to resonance. There are, however, many other factors which can cause deviations from additivity.

In the first place the CH bonds are themselves dependent upon the type of surroundings of the various C atoms. Thus a CH bond in C_3H_4 is not the same as one in C_2H_4 since in the former the central C atom presumably has sp instead of sp^2 hybridization. Furthermore the C−C distances are known not to be the same in all compounds compared. They are different, for instance, in C_2H_2 than in C_6H_6. Also there is the difficulty that even in nonresonating systems the $\pi\pi$ part, for instance, of the exchange energy is not equal to the number of bonds times the energy of one bond. Thus in benzene, this part was not $3J_{\pi\pi}$, i.e., three times the strength of the second C bond, but rather $3/2J_{\pi\pi}$, the difference being due to the exchange terms with coefficients $-1/2$. Similar complications arise in connection with the part of the energy involving the bonds in the plane of the benzene ring, although the difficulty may not be as acute, as here the wave functions overlap less for the terms with exchange coefficients $-1/2$ than those with exchange coefficients $+1$. Furthermore, the number n of C atoms to be promoted to the valence state is not in general the same as the number m of C−C bonds, so that the promotional energy per bond is n/m times the excitation energy for the valence state, and thus is not independent of n.

Of course it can well be argued that the observed deviations from additivity are found experimentally to be small in compounds not permitting resonance, and so one can attach qualitative significance to the so-called observed resonance energies, but they do seem of rather limited meaning from a fundamental theoretical standpoint. It appears to be a pure accident due to the cancellation of various sizable terms mentioned in the preceding paragraph that bond additivity holds as well as it does. Calculations relevant to this subject have been made by R. Serber.[110] He allows for most of the various complications mentioned in the preceding paragraph and computes the binding energies listed in Table IV. The experimental values have been taken from papers by Rossini and Pauling. The exchange integrals necessary to Serber's calculations have been deduced in a somewhat arbitrary fashion partly from empirical spectroscopic

---

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

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

[108] Pauling and J. Sherman, J. Chem. Phys. **1**, 606, 679 (1933).

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

[110] R. Serber, J. Chem. Phys. **3**, 81 (1935).

TABLE IV. *Energies of hydrocarbons.*

		Calc.	Obs.
Methane	CH_4	(16.3)v	16.3v
Ethane	C_2H_6	(27.6)	27.6
Propane	C_3H_8	38.9	38.9
Butane	C_4H_{10}	50.2	50.2
Ethylene	C_2H_4	(21.8)	21.8
Propylene	C_3H_6	33.1	33.1
1,2,3,4 tetrahydrobenzol	C_6H_{10}	61.9	61.8
Cyclohexane	C_6H_{12}	67.4	67.1
Acetylene	C_2H_2	14.9	15.2
Benzene	C_6H_6	52.2	52.2
1,2 dihydrobenzol	C_6H_8	56.3	56.7
Naphthalene	$C_{10}H_8$	81.4	82.5

data and partly from the binding energies inclosed in parenthesis in the table, which have been purposely fitted. The computed values for the other molecules in the table agree better with experiment than do the values computed on the basis of additivity. The agreement would presumably be spoiled if the nonorthogonality and higher order permutations mentioned in section 18 were included. Here again we have an illustration of the strange fact that the Heitler-London method seems to work best in its crudest form.

Chemists are coming to realize increasingly the importance of "free radicals," which have one free spin, such as e.g., the phenylmethyl radical $(C_6H_5)CH_2$. Their reality has been demonstrated most conclusively by magnetic measurements, which often reveal paramagnetic susceptibilities[20] conforming to the theoretical value for $S=\frac{1}{2}$. Saturated compounds are, of course, diamagnetic. Pauling and Hückel have indepently given a very nice interpretation of the possibility of the existence of free radicals in terms of resonance energies.[108, 111] In a free radical, there is one uncompensated spin which has various possible locations. The various possible locations in the case of phenylmethyl are shown in Fig. 15. The free spin is indicated by x. The free radical can resonate through these many different positions for the free spin, thus lowering the energy. On the other hand when two free radicals team together to form a saturated compound, the extra spin can only be located in one place (e.g., form A of Fig. 15) if it is to lose its freedom and pair with the spin of another radical, the mirror image of A. Hence resonance effects put a premium on dissociation into radicals. Against this idea it may be said that even in the saturated compound the bond between the two radicals may be broken a fraction of the time, so that here still the molecule can resonate through the extra phases. However, the breaking of this bond is a large sacrifice, and these other phases are less important than in the free radical. Hence Pauling and Wheland's calculation of the heat of dissociation into free radicals can be regarded as probably qualitatively sound even though it considers resonance possible only after dissociation.

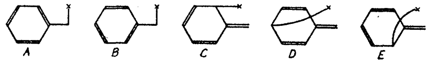


FIG. 15. The five unexcited canonical structures contributing to the normal state of the phenylmethyl radical.

CHAPTER IV. POLYATOMIC MOLECULES BY THE METHOD OF MOLECULAR ORBITALS

30. The electron pair bond

We now turn to the method of molecular orbitals. In this procedure, the concept of the electron pair bond finds expression in the fact that a given molecular orbital can, by the Pauli principle, house two electrons, whose spins are then necessarily anti-parallel. Consequently most molecules are diamagnetic. One can immediately understand, at least in a vague qualitative way, the valence rules derived in section 21 by the Heitler-London method. An important feature of these rules was the occurrence of higher valences for periods beyond the second in the Mendeléef table (e.g., valence of 1 for fluorine, up to 7 for chlorine). This behavior is now interpreted as follows. The molecular orbital can, to a first approximation, be regarded as a linear combination of atomic orbitals of the various constituent atoms. In a fluorine compound there are four different molecular orbitals whose fluorine constituents are, respectively, $2s$, $2p\sigma$, $2p\pi_+$, $2p\pi_-$ or, better, four linear orthogonal combinations thereof. These four molecular orbitals can house eight electrons, so

---

[111] E. Hückel, Zeits. f. Physik **76**, 628 (1933); Trans. Faraday Soc. **30**, 40 (1934).

that one extra electron besides fluorine's contribution $2s^2 2p^5$ is desired. A valence of 1 is thus implied. Of course one could have molecular orbitals involving d orbitals of F in fluorine compounds, but they would be excited states not useful for valence purposes, as the increase in the principal quantum number for $3d$ as compared with $2s$, $2p$ raises the energy so much that such molecular orbitals could not be classed as ground states normally occupied. On the other hand, in chlorine, there are nine different molecular orbitals whose chlorine ingredients are $3s$, $3p^3$, $3d^5$, all of the same principal quantum number. There are extra housing accommodations thus available for up to $18-7=11$ electrons. One would thus expect valences of 1, 3, 5, 7, 9, 11. That the number of valences is odd is in agreement with experiment, and is a consequence of the ability of each molecular orbital to house two electrons. Namely, the molecular orbitals do not in general all have the same energy, so that only a certain number of them will be populated, but then accommodations are available for an even number of electrons in all. Since chlorine has seven valence electrons, an odd number of electrons can be accommodated from neighboring atoms. It is not immediately clear why there could not be valences of 9 or 11, but they are probably to be excluded on energetic grounds.

The nice feature of the method of molecular orbitals is that it is noncommittal on the amount of polarity for the compound and so has general applicability. As in section 2, consider, as a simple illustration, a diatomic compound involving two atoms A, B and assume that a molecular orbital can be regarded as a linear combination

$$\psi = a\psi_{\mathrm{A}} + (1-a^2)^{\frac{1}{2}}\psi_{\mathrm{B}} \tag{68}$$

of the appropriate atomic orbitals of A and B. We shall neglect the nonorthogonality, or "overlap" integral (4), and with this approximation (68) is normalized to unity if ψ_{A} and ψ_{B} are. By varying a from 0 to 1 we have all grades of polarity from $\mathrm{A^+B^-}$ to $\mathrm{A^-B^+}$ (cf. section 3). The ideally covalent case is given by $a=\sqrt{\frac{1}{2}}$. Whether ψ_{A} or ψ_{B} is preponderant in (68) depends on whether atomic orbital A or atomic orbital B has the deepest energy. The covalent case arises when the energy separation of A and B is small compared to the "resonance integral" defined below which is the dominant factor in binding. Thus the ionization potentials of two atoms united by a covalent bond must not differ too widely.

To give these ideas mathematical shape and basis, one sets up the secular problem connected with the determination of the coefficients in (68). This can be easily formulated by means of the variational method, although other procedures could be used, leading to the same result. If we substitute (68), the energy integral (27) becomes

$$a^2 W_{\mathrm{A}} + 2a(1-a^2)^{\frac{1}{2}}R + (1-a^2)W_{\mathrm{B}}. \tag{69}$$

Here R denotes the so-called resonance integral[112]

$$R = \int\int\int \psi_{\mathrm{A}} \mathbf{H} \psi_{\mathrm{B}} dv = \int\int\int \psi_{\mathrm{B}} \mathbf{H} \psi_{\mathrm{A}} dv, \tag{70}$$

while

$$W_{\mathrm{A}} = \int\int\int \psi_{\mathrm{A}} \mathbf{H} \psi_{\mathrm{A}} dv, \quad W_{\mathrm{B}} = \int\int\int \psi_{\mathrm{B}} \mathbf{H} \psi_{\mathrm{B}} dv$$

are, respectively, the internal energies of the two atoms augmented by the Coulomb energy due to the other atom. The Coulomb energies are presumably small, so that W_{A}, W_{B} are approximately the energies of free A and B atoms. Do not confuse the resonance integral (70), which is a one-electron affair, and the exchange integral (19) which involves a six-dimensional integration over the coordinates of two electrons. The resonance integral is characteristic of the method of molecular orbitals while the exchange intergal is the major source of binding in the Heitler-London theory.[113] The expression (70) ought really to have a denominator $1+2Ta(1-a^2)^{\frac{1}{2}}$ where T is the over-lap integral (4), but we have agreed to neglect T in comparison with unity. This approximation is allowable for the present qualitative study. In accordance with the variational method, we now minimize (70) with respect to a, thus obtaining the following values of a

$$a^2 = \tfrac{1}{2} \pm [(W_{\mathrm{A}} - W_{\mathrm{B}})/2X], \text{ with } X^2 = 4R^2 + (W_{\mathrm{A}} - W_{\mathrm{B}})^2. \tag{71}$$

The corresponding minima of (69) are

$$W = \tfrac{1}{2}(W_{\mathrm{A}} + W_{\mathrm{B}}) \pm \tfrac{1}{2}X, \tag{72}$$

and are the energy levels corresponding to (71). Clearly if $(W_{\mathrm{A}} - W_{\mathrm{B}})^2 \gg R^2$ then a^2 will be nearly 0 or 1 (polar behavior), while $a^2 = \frac{1}{2}$ (covalence) if the inequality is reversed.

When we have a compound involving more than two atoms, the atomic orbital of the central atom will be mingled with the atomic orbitals of all the attached atoms, as we shall see in section 33 that we cannot apportion different molecular orbitals to different attached atoms. Instead in general the various attached atoms all participate

---

[112] The two integrals in (70) are equal because **H** is a self-adjoint operator.

[113] It may be noted that the Heitler-London theory indirectly involves the resonance integral, as the second term in the exchange integral (19) is the Hund resonance integral for $\mathrm{H_2^+}$ multiplied by twice the overlap-integral (13).

together in the construction of a given molecular orbital. Hence with more than two atoms, we must replace the second term of (68) by a sum

$$(1-a^2)\Sigma_k c_k \psi_k, \quad (\Sigma_k c_k{}^2 = 1)$$

over all the attached atoms k. The covalent case is still $a=\surd\frac{1}{2}$, as then the bonding electrons spend as much time on the totality of attached atoms as on the central atom.

31. Difficulty with affinity for extra atoms[114]

There is one weakness in all the above argument. Namely, it has been assumed that the number of attached atoms equals the number of bonds, or deep molecular orbitals. However, according to crude calculations by the method by molecular orbitals, it is usually desirable to have extra atoms even though they cannot contribute any bonding electrons. The reason is that even though the number of bonding electrons stays the same, these electrons have increased freedom because there are more atoms that they can migrate between, and hence greater play is given to the resonance integrals. Thus H_3 is found to have less energy than H_2, an absurd result. We shall show near the end of the appendix that a similar difficulty does not arise in the Heitler-London method.

This statement regarding the molecular orbitals of H_3 is established by a simple calculation. If there are three equally spaced attracting centers forming a linear configuration, one finds that the secular equation analogous to (72) is

$$\begin{vmatrix} W_{\mathrm{H}}-W & R & 0 \\ R & W_{\mathrm{H}}-W & R \\ 0 & R & W_{\mathrm{H}}-W \end{vmatrix} = 0. \qquad (73)$$

Here we have neglected, besides the nonorthogonality, the resonance integrals not connecting adjacent atoms, and also the inter-atomic Coulomb energy. Without disregard of the latter the entries along the principal diagonal would not all be the same.

The simplest way of establishing (73) is to substitute an assumed solution

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3$$

in the wave equation $(\mathbf{H}-W)\psi=0$. On integrating the resulting expression over ψ_1, ψ_2, or ψ_3, we obtain three linear expressions in c_1, c_2, c_3 which must vanish if the wave equation is satisfied. For a non-trivial solution to exist for c_1, c_2, c_3 the determinant of the coefficients must vanish, yielding (73). The same result is obtained by the variational method by a little more labor, but more rigorously, as one then sees that (73) represents the deepest possible energy levels which it is possible to obtain by the assumed construction of molecular orbitals out of atomic ones.

The roots of (73) are

$$W = W_{\mathrm{H}} - \sqrt{2}R, \quad W_{\mathrm{H}}, \quad W_{\mathrm{H}} + \sqrt{2}R, \qquad (74)$$

whereas (72), specialized to the case A = B gives

$$W = W_{\mathrm{H}} \pm R. \qquad (75)$$

Comparison of (74) and (75) shows that the addition of the third attracting center has considerably lowered the energy of the deepest molecular orbital $W-\sqrt{2}R$. Here and elsewhere we assume that the resonance integral R is positive; this supposition involves no loss of generality since the sign of R is really arbitrary on account of ambiguous phase factors in the wave function. Of course this deep orbital can house only two electrons, and the third must be placed in the nonbonding orbital $W=W_{\mathrm{H}}$, but even so the energy of H_3 is

$$W = 2(W_{\mathrm{H}} - \sqrt{2}R) + W_{\mathrm{H}} \qquad (76)$$

and thus is lower than that $2(W_{\mathrm{H}}-R)+W_{\mathrm{H}}$ of H_2+H.

One can show that with similar approximations the energy of CH_6 is lower than that of CH_4+2H, and that of HClH lower than that of HCl. In fact one can find any number of cases where increased stability is obtained by adding atoms to form compounds which are a barbarism from a chemical standpoint.

A partial answer to the difficulty is that though the total energy is usually increased by the addition of extra atoms not allowed by the usual valence rules, the energy per atom is diminished. Thus in H_3, the bonding energy per atom is $2\sqrt{2}R/3 = 0.94R$, against R in H_2. However, examples can be found where even the

---

[114] The difficulty stressed in this section was first called to the writer's attention in a conversation with Dr. London. Another discussion of H_3 (and $H_3{}^+$) has recently been published by C. A. Coulsen, Proc. Camb. Phil. Soc. **31**, 244 (1935).

energy per atom is increased. Thus in section 35 we shall see that with the same type of calculation as in (73), the energy per atom would be lower in H_6 than in H_2. Of course the real answer is that the method of calculation used in Eqs. (73), (74), (75) is too naïve. The insertion of the resonance integrals between non-adjacent atoms might improve matters somewhat. Also it would be much better if we did not seek to approximate the molecular orbitals as linear combinations of atomic orbitals. This approximation is not an inherent feature of molecular orbitals, and improved wave functions obtained by a variational procedure or otherwise would doubtless yield less shocking conclusions. Perhaps the improvement needed most of all is the inclusion of r_{12} repulsions. With these repulsions the nonbonding orbital would presumably become anti-bonding. After such refinements the difficulties would ultimately disappear, but it is probably fair to say that the crudest forms of the method of molecular orbitals do not give the elementary valence rules as sharply and succintly as the Heitler-London method.

It is clear that simple calculations such as (73) by means of the method of molecular orbitals expressed as linear combinations of atomic orbitals, are grossly inadequate for determining energies of activation, since the approach of another atom will lower the energy rather than introduce a potential hill. The critical intermediate, or activation stage, for instance, through which the system must pass in the reaction $H+H_2 \rightarrow H_2+H$ is a temporarily symmetrical H_3 form. A method of calculation which makes H_3 below H_2+H manifestly cannot yield reasonable results on activation without a great deal of refinement. Hence the reader will find no section on activation energies in the present chapter.

32. Geometrical arrangement—the H_2O molecule

The method of molecular orbitals leads to the same conclusions on the spatial arrangement of the atoms in simple compounds like methane, water, etc., as does the H-L-S-P method, and if, anything, still more simply. Thus the molecular orbital procedure embodies properly the essential ideas of directed valence. We shall prove in the next paragraph, for instance, that it leads to a right-angled model of H_2O if we neglect $H-H$ repulsions. One of us has made calculations on methane and related molecules by the method of molecular orbitals. The secular equation proves to be of the eighth degree, and too complicated to solve in general. However, various different simplifying approximations can be made, each of which enables the secular equation to be solved and it is shown that in every case the tetrahedral model is the one of lowest energy.[115] It is particularly satisfactory that this result is obtained without the rather artificial assumption of hybridization, especially as the sp separation is really not small.[75] Instead the s state can be much more deeply bound than the p, so that the major valence effects are from the p orbits, and still the tetrahedral model is best. Furthermore one predicts[115] in $CHCl_3$ and CH_2Cl_2 deviations from tetrahedral symmetry of the same sign as in the H-L-S-P procedure. Penney[84] has considered C_2H_4 on the Hund-Mulliken scheme, and the problem, where tractable leads to the same conclusions as in the H-L-S-P method of electron pairs.

In section 23, H_2O was treated by the H-L-S-P theory. It is therefore of some interest to examine this same molecule here in a little detail. The present method of calculation[116] not only forms an interesting contrast to the H-L-S-P but also throws instructive light on the molecular orbital procedure. The problem is considered to involve four electrons, namely one from each hydrogen atom, and two $2p$ electrons from the oxygen atom as shown in Fig. 7, section 23. Of course there are four other two quantum orbits in oxygen, two $2s$ and two $2p$ functions, but the $2s$ give no directional effects on account of their centro-symmetric charge clouds, while the other $2p$ functions can be taken to have their dumb-bell axes perpendicular to the plane of the paper in Fig. 7. They then have nodal surfaces in the plane of the paper, and so exert no bonding effect. For the four important electrons, the molecular orbitals can be taken to be a linear combination of the following four atomic orbitals:

---

[115] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933).

[116] Calculations of the present general sort on H_2O were first made by Hund, Zeits. f. Physik **73**, 24; **74**, 429 (1931–2).

$$\psi_{2p\sigma x},\ \psi_{2p\sigma y},\ \psi_{\mathrm{H}_a},\ \psi_{\mathrm{H}_b}. \tag{77}$$

The first two functions of (77) belong to the oxygen atom, and are of the type explained in section 22. We can immediately write down the proper secular equation, which will be of degree 4. It is, however, convenient to introduce in place of (77) new wave functions

$$\begin{aligned}\psi_{\mathrm{O}}' &= (1/\sqrt{2})(\psi_{2p\sigma x}+\psi_{2p\sigma y}),\\ \psi_{\mathrm{H}}' &= (1/\sqrt{2})(\psi_{\mathrm{H}_a}+\psi_{\mathrm{H}_b}),\end{aligned} \tag{78}$$

$$\begin{aligned}\psi_{\mathrm{O}}'' &= (1/\sqrt{2})(\psi_{2p\sigma x}-\psi_{2p\sigma y}),\\ \psi_{\mathrm{H}}'' &= (1/\sqrt{2})(\psi_{\mathrm{H}_a}-\psi_{\mathrm{H}_b}),\end{aligned} \tag{79}$$

as then the secular equation factors into two quadratics in the symmetrical case $\alpha=\alpha'$ shown in Fig. 7. Assumption of this symmetry involves no loss of generality, as the x and y axes can always be oriented so that it is achieved. The factorization is a consequence of the fact that ψ_{O}', ψ_{H}' and the Hamiltonian operator $\mathbf{H}$ are all even, while ψ_{O}'', ψ_{H}'' are odd with respect to reflection in a line inclined at 45° to the x axis in Fig. 7. Hence $\mathbf{H}$ can yield no matrix elements connecting ψ_{O}', ψ_{H}' to ψ_{O}'', ψ_{H}''. (The vanishing of the matrix element is equivalent to saying that the resonance integral $\int\int\int\psi''\mathbf{H}\psi' dv$ equals zero, and this will be the case if the integrand is odd, i.e., contains one or three odd factors.) The secular equations are thus

$$\begin{vmatrix} W_{\mathrm{H}}-W & R(\mathrm{O}';\mathrm{H}') \\ R(\mathrm{O}';\mathrm{H}') & W_{\mathrm{O}}-W \end{vmatrix}=0, \tag{80}$$

and a similar equation involving O″, H″. For simplicity, we have, as in (73), disregarded nonorthogonality, and the Coulomb terms, so that W_{O}, W_{H} can be identified with the energies of the free O, H atoms. Also we have not included resonance integrals connecting two H atoms, as we are focusing attention on the directional effects emanating from the central atom. In virtue of the transformation properties expressed in (48), the resonance integrals are

$$\begin{aligned} R(\mathrm{O}';\mathrm{H}') &= Q_\sigma\cos\alpha+Q_\sigma\sin\alpha,\\ R(\mathrm{O}'';\mathrm{H}'') &= Q_\sigma\cos\alpha-Q_\sigma\sin\alpha,\end{aligned} \tag{81}$$

with $\alpha=\alpha'$ as in Fig. 7. Here we have introduced the notation

$$Q_\sigma=\int\int\int\psi_{2p\sigma i}\mathbf{H}\psi_{\mathrm{H}_i}dv,$$

where $\psi_{2p\sigma i}$ means a $2p\sigma$ wave function of O when the quantization is relative to the axis $\mathrm{O}-\mathrm{H}_i$. The value of Q_π is zero.

We are interested in twice the sum Σ of the lower root of (80) and the lower root of the corresponding equation with double primes, as these two roots together can house four electrons in all.[117] The formula for 2Σ is, by (80–81)

$$\begin{aligned}2\Sigma = 2W_{\mathrm{H}}+2W_{\mathrm{O}} &-[(W_{\mathrm{H}}-W_{\mathrm{O}})^2+4R(\mathrm{O}';\mathrm{H}')^2]^{\frac{1}{2}}\\ &-[(W_{\mathrm{H}}-W_{\mathrm{O}})^2+4R(\mathrm{O}'';\mathrm{H}'')^2]^{\frac{1}{2}}.\end{aligned} \tag{82}$$

Since (81) shows that (82) is unaltered when α is replaced by $\frac{1}{2}\pi-\alpha$, it follows that (82) has extrema at $\alpha=0$, $\pi/4$ (mod. $\pi/2$). Also one finds, by second differentiation, or otherwise, that $\alpha=\pi/4$ yields a maximum and $\alpha=0$ a minimum. Hence the right-angled model is the most stable.

33. Absence of localized bonds—tetrahedral and octahedral compounds

The Slater-Pauling theory of directed valence is characterized by wave functions of the central atom which project out in one particular direction, and so are particularly fit to attach one particular atom. The situation is quite different in the method of molecular orbitals, as here a given molecular orbital or bonding wave function will in general involve the atomic orbitals of several attached atoms. For instance in (78–79) ψ_{H}' (also ψ_{H}'') contains both ψ_{H_a} and ψ_{H_b}. This means that one cannot assign "localized bonds" each of which embrace one particular attached atom. The physical picture is that in the method of molecular orbitals one has itinerant electrons which vagabond from one attached atom to another. Of course, more than one itinerant electron may happen to visit the same attached atom at the same time. As we saw in section 3, a weakness of the method of molecular orbitals is that there is an excessive number of such coincidences.

---

[117] As Dr. Coolidge points out to the writer, the expression (82) is not really the binding energy, as it counts the mutual potential energy of the electrons twice rather than once. (Such a difficulty is inherent in any Hartree procedure when one adds up energies of individual electrons.) The resulting error is, however, probably not serious as long as we are interested in qualitative directional behavior rather than quantitative binding energies.

TABLE V. *Molecular orbitals of various symmetry types.*

Irreducible representation			
Mulliken	(Bethe)	Central portion	Attached portion
		Tetrahedral configurations (CH_4, etc.; group T_d)	
A_1	(Γ_1)	$\psi(s)$	$\frac{1}{2}(\psi_1+\psi_2+\psi_3+\psi_4)$
T_2	(Γ_5)	$\psi(p\sigma_x)$, $\psi(d\epsilon_3)$	$\frac{1}{2}(\psi_1+\psi_2-\psi_3-\psi_4)$
		$\psi(p\sigma_y)$, $\psi(d\epsilon_2)$	$\frac{1}{2}(\psi_1+\psi_3-\psi_2-\psi_4)$
		$\psi(p\sigma_z)$, $\psi(d\epsilon_1)$	$\frac{1}{2}(\psi_1+\psi_4-\psi_2-\psi_3)$
E	(Γ_3)	$\psi(d\gamma_1)$	None
		$\psi(d\gamma_2)$	None
		Pyramidal Configurations (NH_3 etc.; group C_{3v})	
A_1	(Γ_1)	$\psi(s)$, $\psi(p\sigma_z)$, $\psi(d\gamma_1)$	$\sqrt{\frac{1}{3}}(\psi_1+\psi_2+\psi_3)$
E	(Γ_3)	$\psi(p\sigma_x)$, $\psi(d\epsilon_2)$, $\psi(d\gamma_2)$	$\sqrt{\frac{2}{3}}(\psi_1-\frac{1}{2}\psi_2-\frac{1}{2}\psi_3)$
		$\psi(p\sigma_y)$, $\psi(d\epsilon_1)$, $\psi(d\epsilon_3)$	$\sqrt{\frac{1}{2}}(\psi_2-\psi_3)$
		Octahedral Configurations (FeF_6^{---} etc.; group O_h)	
A_{1g}	(Γ_1)	$\psi(s)$	$\sqrt{\frac{1}{6}}(\psi_1+\psi_2+\psi_3+\psi_4+\psi_5+\psi_6)$
T_{1u}	(Γ_4)	$\psi(p\sigma_x)$	$\sqrt{\frac{1}{2}}(\psi_1-\psi_4)$
		$\psi(p\sigma_y)$	$\sqrt{\frac{1}{2}}(\psi_2-\psi_5)$
		$\psi(p\sigma_z)$	$\sqrt{\frac{1}{2}}(\psi_3-\psi_6)$
E_g	(Γ_3)	$\psi(d\gamma_1)$	$\sqrt{\frac{1}{12}}(2\psi_3+2\psi_6-\psi_1-\psi_4-\psi_2-\psi_5)$
		$\psi(d\gamma_2)$	$\frac{1}{2}(\psi_1+\psi_4-\psi_2-\psi_5)$
T_{2g}	(Γ_5)	$\psi(d\epsilon_1)$	None
		$\psi(d\epsilon_2)$	None
		$\psi(d\epsilon_3)$	None
		Tetragonal or Square Configurations; $Ni(CN)_4^{--}$ etc.; group D_{4h}	
A_{1g}	(Γ_{1g})	$\psi(s)$, $\psi(d\gamma_1)$	$\frac{1}{2}(\psi_1+\psi_2+\psi_3+\psi_4)$
E_u	(Γ_{5u})	$\psi(p\sigma_x)$	$\sqrt{\frac{1}{2}}(\psi_1-\psi_3)$
		$\psi(p\sigma_y)$	$\sqrt{\frac{1}{2}}(\psi_2-\psi_4)$
B_{1g}	(Γ_{3g})	$\psi(d\gamma_2)$	$\frac{1}{2}(\psi_1+\psi_3-\psi_2-\psi_4)$
A_{2u}	(Γ_{2u})	$\psi(p\sigma_z)$	None
B_{2g}	(Γ_{4g})	$\psi(d\epsilon_1)$	None
E_g	(Γ_{5g})	$\psi(d\epsilon_2)$	None
		$\psi(d\epsilon_3)$	None

If the molecule possesses elements of symmetry, the molecular orbitals will have symmetry properties, associated usually with whether or not the wave function changes sign under certain reflections or inversions. If one is fortunate enough to recognize these symmetry properties at the outset, there is resulting simplification because the secular determinant will factor owing to the absence of matrix components between states of different symmetry. For instance, in the case of the H_2O molecule, the functions ψ_O' and ψ_H' were even, while ψ_O'' and ψ_H'' were odd as regards a plane orthogonal to the plane of the paper and intersecting Fig. 7 in a line inclined at 45° to the x axis. In consequence ψ_O', ψ_H' did not combine with ψ_O'', ψ_H''. In molecules where the bonds all emanate from a central atom, one may distinguish between what we call the central and attached orbitals, which correspond respectively to the portions of the complete molecular orbital contributed by the central and attached atoms. The central orbital is thus simply an atomic orbital of the central atom, or where there is hybridization, linear combinations of such orbitals. The attached orbital is a combination of the atomic orbitals of the several attached atoms. Thus in our H_2O molecule, ψ_H', ψ_H'' are attached orbitals, while ψ_O', ψ_O'' are central ones. Incidentally, ψ_O' and ψ_O'' are, by (48), the same as pure $2p\sigma_x'$, $2p\sigma_y'$ orbitals when referred to axes inclined at 45° to the xy axes in Fig. 7, so that really no hybridization is involved in ψ_O' or ψ_O''. In the construction of molecular orbitals, only attached and central atoms of the same symmetry can combine. The resulting restrictions are summarized in Table V for the cases of tetrahedral, pyramidal, octahedral and tetragonal symmetry, which correspond respectively to the crystallographic symmetry groups T_d, C_{3v}, O_h and D_{4h}. A molecular orbital is a linear combination of the central and attached orbitals listed on the same line. The percentages of attached and central portions determine the degree of polarity of the compound. All the different molecular orbitals corresponding to different lines included in the same parenthesis will involve the same percentages and yield the same energy.[118]

The various d functions occurring in the table have been defined in (61–62). The wave functions of attached atoms, 1, 2, $\cdots$ are denoted by ψ_1, ψ_2, $\cdots$, respectively. In the tetrahedral case the x, y, z axes are chosen perpendicular to the faces of a cube whose alternate corners are the vertices of the tetrahedron. In the pyramidal structure, the z axis has been taken as that of symmetry. By a tetragonal compound we mean one such as $\mathrm{Ni(CN)_4^{--}}$ in which the attached atoms are at the corners of a square, which we consider to be located in the x, y plane.

The information documented in Table V is obtained and codified most completely by means of group theory, into which we shall not enter. The orbitals inside the same parenthesis all belong to the same "irreducible representation," in the language of group theory, and possess the property that they transform only among themselves under the covering operations of the symmetry group. We give in each case Mulliken's[118] notation for the irreducible representation, and also, in parenthesis, that of Bethe.[87] There are other irreducible representations of the various groups besides those given in the table, but these are not listed since they do not enter into the construction of either "attached" or "central" orbitals. (They would enter in central orbitals built out of f, g, h, $\cdots$ wave functions, but never in the attached orbitals, and so are clearly of no use for bonding purposes.) A characteristic property of many irreducible representations is a degeneracy in virtue of which two or more levels coincide in energy. The degree of degeneracy is called the "number of dimensions" or "degree" of the representation and is equal to the number of lines occupied by the irreducible representation in the table. Thus in the octahedral case, there is a threefold degeneracy for T_{1u}, so that T_{1u} can house six electrons in its deepest state. From a given line of the table one can form as many linearly independent molecular orbitals as the total number of central and attached orbitals contained therein. The number of such linear combinations is equal to the degree of the secular equation. Thus from the first line of E in the pyramidal case one can form four molecular orbitals, found by solving a biquadratic secular equation. Only the lowest root will ordinarily be of interest, and this will be the same as the lowest root for the second line of E.

Instead of using group theory one may deduce, or at least make plausible many of the results in the table by examination of the nodal planes of the wave functions.[119] Let us consider, for example, the octahedral group. Here the $\psi(s)$ wave function has no nodal plane coincident with one of the three coordinate planes. The $\psi(d\epsilon)$ functions have two nodal planes, coincident with two of these coordinate planes, as we see from (62). The nodal planes of the functions $\psi(d\gamma_2)$ and $[(\frac{3}{4})^{\frac{1}{2}}\psi(d\gamma_1)-\frac{1}{2}\psi(d\gamma_2)]$ are[120] of a different type, inclined at 45° to the coordinate planes. One can verify that the nodal behavior of the corresponding attached functions is similar. Functions whose nodal planes are equal in number and equivalent in virtue of the assumed symmetry clearly should have the same energy. One can deduce much information concerning the "noncombining" properties from the fact that the matrix element of the Hamiltonian function connecting two states vanishes if their wave functions are respectively even and odd with respect to reflection in a symmetry center or in some plane, which is clearly then a nodal plane for the odd function. For this argument to apply it is necessary that the Hamiltonian function have the assumed symmetry, so that it is itself even with respect to this reflection. Thus T_{1u} and T_{2g} states, respectively odd and even for inversion in the center, cannot combine. Also a wave function of A_{1g} does not combine with one of T_{2g} as any nodal plane for T_{2g} is a symmetry plane for A_{1g}. By examining the nodal and symmetry planes of $\psi(d\gamma_2)$ or $[(\frac{3}{4})^{\frac{1}{2}}\psi(d\gamma_1)-\frac{1}{2}\psi(d\gamma_2)]$ one sees that E_g cannot combine with A_{1g} or T_{2g}, provided, of course that $\mathbf{H}$ has octahedral symmetry.

In the case of the tetrahedral group some of the symmetry elements are rotation-reflections (i.e., reflections in a plane followed by rotation by 90° about an axis perpendicular to this plane) rather than simple reflections and so only a limited amount of information can be gathered by the examination of nodal planes. Instead the covering operations of the tetrahedron are most easily visualized as permutations of its vertices. For instance, regardless of how we permute the

---

[118] Much, but not all, of the information in Table V was contained in Mulliken, Phys. Rev. **43**, 279 (1933); J. Chem. Phys. **1**, 492 (1933) and Van Vleck, references 7, 115.

[119] For derivation of symmetry properties without the use of group theory see especially Placek's article on the Raman effect in Vol. VI of the Handbuch der Radiologie, 2nd Ed.

[120] The difference $(\frac{3}{4})^{\frac{1}{2}}\psi(d\gamma_1)-\frac{1}{2}\psi(d\gamma_2)$ is here used rather than $\psi(d\gamma_1)$ in order to have a wave function whose nodal surface is a plane rather than surface of revolution (cf. Eq. (61)).

subscripts 1, 2, 3, 4, an attached orbital listed under T_2 still remains a linear combination of the attached orbitals comprised in T_2. To illustrate, the permutation (1234) applied to $\psi_1+\psi_2-\psi_3-\psi_4$ yields $+(\psi_2+\psi_3-\psi_1-\psi_4)$, included in the third line of T_2, in agreement with our assertion that the covering operations interrelate only functions of the same irreducible representation. The transformation scheme for the corresponding central orbitals can be shown to be precisely the same. We have not labelled where the attached atoms corresponding to the various subscripts are located, but this information can be determined by comparison with the symmetry of the central wave function. Thus in the group O_h, atoms 1, 4 must be located on the x axis since $\psi(p\sigma_x)$ is odd with respect to reflection in the yz plane. In the pyramidal case, atom 1 has been chosen to be on the x axis.

Central orbitals which can be mated to attached orbitals of similar symmetry may be termed "bonding," while those without mates are non-bonding. It will be noted that for a given symmetry, precisely the same central orbitals are bonding as were involved in Pauling's linear combinations discussed in section 26. Thus Pauling utilized $sp^3d_\gamma^2$ hybridization for octahedral bonds, and did not employ d_ϵ. Reference to Table V shows that the s, p and d_γ functions form representations of the octahedral group to which attached orbitals also belong, whereas d_ϵ is isolated. The underlying reason for this coincidence is supplied by group theory and will be given elsewhere by one of us. There is thus agreement between the method of molecular orbitals and H-L-S-P on the types of central functions which can bond. So one can say that, qualitatively at least, either method is able to explain the stereochemistry of transition elements. Regarding the latter, the strength of the method of molecular orbitals is that it does not require structures such as $Ni^{--}(CN)_4$ involving excessive negative charge on the central atom. Its weakness is that it does not make it so clear why C does not attach six atoms, since in CH_6 the H atoms could be held by the s and p functions by means of the A_{1g}, T_{1u} bonds. The d states are too high to be inhabited in carbon compounds and so the E_g bonds are not operative there. Apparently it is the existence of these extra E_g bonds which stabilizes a coordination number of six in the transition elements, but it is not clear from the present standpoint why A_{1g} and T_{1u} alone are not enough. Perhaps SF_6 is an example of a compound held together largely by A_{1g} and T_{1u} bonds, but it is also possible that the old fashioned polar forces involved in the structure $S^{6+}(F^{-6})$ are the major factor. This structure can, however, be regarded as a limiting case of molecular orbitals.

Some specific remarks on particular spatial arrangements are the following:

Tetrahedral Compounds. Here the interesting point is that the s and p functions belong to different irreducible representations and do not hybridize. On the other hand one can show that with unsymmetrical arrangements there is hybridization. Table V shows that even in the pyramidal structure the s and one of the p functions belong to the same irreducible representation. There is thus an interesting contrast to the H-L-S-P method. In the latter it was the hybridization ($N_{\sigma s}$ term in Eq. (59)) which made the tetrahedron more stable than other arrangements in CH_4. On the other hand, in the method of molecular orbitals, the distinguishing feature of the tetrahedral arrangement is its absence of hybridization in the central portion. Instead the hybridization is in the attached orbitals.

Square Compounds. In $Ni(CN)_4^{--}$ we have 16 electrons in all to house, regarding each CN group as contributing one electron. With a tetrahedral arrangement it would not be enough to utilize only E, the deepest state of A_1, and the three deep levels of type T_2, obtained as roots of three identical cubics corresponding to the three lines of T_2. Only twelve electrons are thus accommodated. Consequently one would have to employ two of the higher roots of the cubics or of A_1. If they are antibonding, it is thus better to have the square configuration, since one then fills twice each of the lowest roots of each representation, and it is not necessary to resort to any of the higher roots since there are eight lines in the tetragonal part of Table V.[121] As with the H-L-S-P theory (section 26), mag-

---

[121] It is, however, possible that the second lowest root of A_{1g} is deeper than the lone root of A_{2u}. The ion will nevertheless still be diamagnetic even if this intermediate root of A_{1g} is inhabited in preference to A_{2u}.

netic data show unambiguously which of the alternatives is correct. With the tetrahedral structure the last four electrons have at their disposal three equally good (or bad) orbitals furnished by the intermediate roots of T_2, besides the single intermediate root of A_1. Since all three corresponding roots of T_2 all have the same energy, there is no incentive for the electrons to all "double up." Instead two of them can have private orbitals, and parallel spins. The parallel arrangement is preferable to anti-parallel for energetic reasons (cf. discussion of O_2 in sections 8 and 10). Paramagnetism then ensues, contrary to experiment. On the other hand, with the square or tetrahedral structure, sixteen electrons are snugly accommodated in the eight lowest states[121] and so there is diamagnetism, as is observed.

Pyramidal Structures. In NH_3, one has eight electrons to accommodate. One therefore must fill twice each deep level of A_1, E and also the second deepest level of A_1. (One prefers A_1 to E because A_1 contains both s and p portions.) The higher root will evidently correspond to electrons more easily ionized than the others, and it is indeed found experimentally that the ionization potential of NH_3 is 11.1 volts, smaller than that 14.5 volts of CH_4.

34. $\pi\pi$ bonds

In section 33 we tacitly assumed that the attached atom was either in an s state, or else was in a $p\sigma$ state with its dumb-bell axis directed towards the central atom, as in Fig. 8. An orbital which was a linear combination of the two horizontal orbitals in Fig. 8 we call, as before, a $\sigma\sigma$ bond. In addition there can be formed $\pi\pi$ orbitals, obtained by combining the two atomic orbitals shown in Fig. 10, or two other atomic orbitals which are similar except that their axes are perpendicular to the plane of the paper. As first noted by Hückel,[122] these $\pi\pi$ orbitals are the source of the second and third carbon bonds, the situation being quite similar to that in the H-L-S-P method (section 25). The first type of $\pi\pi$ orbital has a horizontal nodal plane; the second type one in the plane of the paper. Hence they do not combine with each other or with the $p\sigma$ and s orbitals if the molecular structure is invariant under reflection in these planes.

The molecular orbital structure of CO_2 is as follows. Let the x axis be the molecular axis. There are eight molecular orbitals, each occupied twice, and built up from two quantum atomic orbitals as follows:

$$\begin{aligned}
\psi_{\mathrm{I,\,II}}&=a_i[\psi(2s;O_a)+\psi(2s;O_b)]+b_i[\psi(2p\sigma_x;O_a)+\psi(2p\sigma_x;O_b)]+c_i\psi(2s;C), && (i=\mathrm{I,\,II})\\
\psi_{\mathrm{III,\,IV}}&=d_i[\psi(2s;O_a)-\psi(2s;O_b)]+e_i[\psi(2p\sigma_x;O_a)-\psi(2p\sigma_x;O_b)]+f_i\psi(2p\sigma_x;C), && (i=\mathrm{III,\,IV})\\
\psi_{\mathrm{V,\,VI}}&=g[\psi(2p\sigma_{y,\,z};O_a)+\psi(2p\sigma_{y,\,z};O_b)]+h\psi(2p\sigma_{y,\,z};C),\\
&\qquad\psi_{\mathrm{VII,\,VIII}}=k[\psi(2p\sigma_{y,\,z};O_a)-\psi(2p\sigma_{y,\,z};O_b].
\end{aligned}\tag{83}$$

Here the subscript y applies to V, VII and z to VI, VIII. That there are two completely filled (i.e., two twice-occupied) molecular orbitals of each of the first two structures, involving different coefficients, evidently originates in the fact that they contain both the $2s$ and $2p\sigma_x$ states of oxygen. The orbitals $\psi_{\mathrm{V}}\cdots\psi_{\mathrm{VIII}}$ are $\pi\pi$ ones, with V, VI involving 3 rather than 2 parallel dumb-bells as in Fig. 12. The result (83) has been obtained by combining only those functions which possess the same symmetries as regards reflection in each of the three coordinate planes which intersect at the C atom. It is illuminating to compare this model with the treatment by the H-L-S-P method given in section 25. There is the difference that now the bonds involve both oxygen atoms at once, instead of certain bonds being directed towards O_a and the others towards O_b. This is evidently in accord with our statements regarding the inability to localize bonds in the method of molecular orbitals.

35. Resonance energies

The method of molecular orbitals is about as successful as the H-L-S-P procedure when it comes to the subject of resonance energies.

---

[122] E. Hückel, Zeits. f. Physik **60**, 423 (1930). This was the first quantum-mechanical treatment of the double bond.

The former was first applied to resonance by Hückel,[123] and it is indeed remarkable that such a simple procedure should make as much headway as it does with such a complex phenomenon. A rather interesting and amusing example of probably fortuitous agreement between the m.o. and H-L-S-P methods is provided by the ratio r of the resonance energy of naphthalene ($C_{10}H_8$) to benzene. Both[123, 109] give $r=1.84$. The so-called observed value (see section 29) is $r=1.90$. Almost as close agreement between the two methods is also found for a variety of other organic compounds. For a detailed comparison of the calculation of resonance energies by the two methods, the reader is referred to a valuable article by Wheland.[124]

The calculation of resonance energies by means of molecular orbitals is particularly simple in the case of ring compounds. For benzene, for instance, the secular determinant for the $\pi\pi$ bonds is

$$\begin{vmatrix} -W & R & 0 & 0 & 0 & R \\ R & -W & R & 0 & 0 & 0 \\ 0 & R & -W & R & 0 & 0 \\ 0 & 0 & R & -W & R & 0 \\ 0 & 0 & 0 & R & -W & R \\ R & 0 & 0 & 0 & R & -W \end{vmatrix} = 0, \quad (84)$$

where R is the $\pi\pi$ resonance integral, and the origin of energy has been shifted so that the diagonal term of $\mathbf{H}$ is zero. Eq. (84) should be reasonably apparent by comparison with (73). There would, of course, be n rows and columns were there n rather than 6 atoms in the ring, and the element in the extreme upper right and lower left corners would be wanting were the compound a chain rather than ring. The roots of (84), generalized to arbitrary n but still with the ring arrangement can be shown[123] to be

$$W=-2R\cos(2\pi k/n), \quad k=0,\cdots,n-1 \quad (85)$$

provided $n>2$. When $n=2$, the roots are $\pm R$. If n is even, the total energy is twice the sum of the $n/2$ lowest roots of (88). If n is odd, one fills $\frac{1}{2}(n-1)$ roots twice, and one root once. The energy W_{AT} per atom is, of course, the total energy divided by n. By means of (85), the following values are found

n	3	4	5	6	7	8	9	10
$-W_{AT}/R$	1	1	1.17	1.33	1.22	1.21	1.13	1.29

The resonance energy per atom is $|W_{AT}|-R$. It is seen that benzene has the greatest resonance energy of any of the ring compounds. At first thought, this fact might be heralded as a triumph of the theory. It would be simple indeed if the stability of the benzene ring could be attributed to $\pi\pi$ resonance effects. The flaw in the argument is that exactly the same calculation would predict that H_6 is more stable than $3H_2$, and so the approximations are questionable, to say the least, although they are perhaps better in benzene than in H_2, since the $p\pi$ orbitals no doubt overlap less than the s ones do. As we have already emphasized in section 29, the cause for the stability of the benzene ring is no doubt to be found in the directional valence in the plane of the ring rather than in the $\pi\pi$ effects. However, calculations on the former by the method of molecular orbitals are wanting.

It will be noted that according to (85) there is no resonance in a ring of 4. This result is in sharp contrast with the H-L-S-P procedure, which as we saw in section 29, gave maximum resonance for this value of n. On the other hand, the situation is different for a chain of 4. Here it can be shown that molecular orbitals give an energy per atom of $1.12R$, i.e., a resonance energy of $0.12R$,[123] whereas without excited structures there can be no resonance according to H-L-S-P, as the only possibility is two pairs, (1,2) (3,4), end to end. A slight resonance energy $0.23J_{\pi\pi}/4$ is obtained[125] when one includes the excited structure (2,3) (1,4). These results on a chain of four are of interest in connection with dihydrobenzene (C_6H_8). According to molecular orbitals the deepest energy is obtained by substitution of the H atoms in the 1,2 positions, as then one has a chain of four associated with the four $\pi\pi$ bonds connecting 3, 4, 5, 6.

---

[123] E. Hückel, Zeits. f. Physik 70, 240 (1931).

[124] G. W. Wheland, J. Chem. Phys. 2, 474 (1934).

[125] L. Pauling and J. Sherman, J. Chem. Phys. 1, 682 (1933).

Substitution in the 1,4 positions is regarded as leaving two isolated $\pi\pi$ bonds (2,3) (5,6) making the energy $4R$ rather than $4\times 1.12R$. Substitution in the 1,3 positions would give a chain of 3, and hence an energy $2.84R$ by (74). The H-L-S-P method is indifferent to whether one has the 1, 2 or 1,4 substitution, except when one considers the effect of excited structures, which give a resonance energy $0.23J_{\pi\pi}$ favoring 1, 2. Either is much better than the 1, 3 form which allows only one electron pair bond. Actually the 1,3 form is unknown. The 1,2 variety is somewhat more stable than the 1,4, but not enough so to be capable of isolation from the latter. The experimental results thus are about what one would expect with either of the two theories.

Hückel[111] has shown that with molecular orbitals also, the existence of free radicals is understandable on the ground of increased resonance. As in the H-L-S-P case, it seems to us that from a quantitative standpoint the calculations are not beyond question since they again allow for resonance only after dissociation.

36. Conclusion

Since molecular orbitals and the H-L-S-P procedures represent two different types of approximation, neither any too good, it is clear that much more confidence can be placed in the results of the two methods when they agree than can otherwise. If certain properties are found to be true under these two different kinds of approximation, warranted under different idealized limiting conditions, it is natural to suppose that the same properties are also valid in the actual, more complicated intermediate case. It is therefore a comfort that both theories predict a nearly right-angled model for water, a tetrahedron for methane, and other geometrical configurations for carbon and nitrogen compounds which we have described earlier in the paper. Also both schemes furnish an understanding of the stereochemistry and magnetic behavior of the transition groups, and of the resonance energies in aliphatic and aromatic compounds. The molecular orbitals are the simpler conceptually, and enable one to visualize various gradations of polarity more easily, but at the expense of excessive ionic terms, i.e., excessive instantaneous though not average polarity. They have the great merit that their one-electron functions have the symmetry appropriate to the entire molecule rather than just one atom. To date the H-L-S-P method has been more fruitful and has yielded more numerical results on binding energies, but many of the computations are open to question because of the neglect of higher order permutations, nonorthogonality, or inner shells.

The H-L-S-P procedure is more succinct on the subject of the electron pair bond and the valence rules appropriate to light atoms. Also it furnishes a simple and empirically quite successful model for activation processes. On the other hand, molecular orbitals, at least when limited to linear combinations of atomic orbitals, yield too much affinity for extra atoms, and furnish potential depressions where potential hills are needed to understand activation. The idea of constructing molecular orbitals out of atomic orbitals is often convenient for qualitative or conceptual purposes, but quantitatively it is bad. The calculations of Hylleraas and of James indicate that when this idea is abandoned, the method of molecular orbitals has great computational possibilities. A similar indication is given by the recent work of Wigner, Seitz and Slater[126] on crystals, which closely resembles the method of molecular orbitals except that the structural unit is the entire crystal rather than molecule.

The writers wish to express their gratitude to Professors Kemble, Pauling and Slater, and Dr. E. B. Wilson, Jr. for the critical reading of early drafts of the manuscript. Also we are particularly indebted to Dr. Hubert James, who wrote sections 15 and 16. One of us (A.S.) wishes to thank the Wisconsin Alumni Research Foundation for a Research Assistantship, under which part of this paper was written.

---

[126] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); Slater, Phys. Rev. **45**, 794 (1934); Rev. Mod. Phys. **6**, 209 (1934); E. Wigner, Phys. Rev. **46**, 1002 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935).

APPENDIX. THE DIRAC VECTOR MODEL

The two vector problem. Before we discuss the applications of the vector model to valence problems, it is perhaps well to say something regarding angular momentum vectors. The square of the magnitude of an angular momentum vector $\mathbf{S}_1$ is in quantum mechanics a matrix whose characteristic values (i.e., diagonal elements after the matrix has been transformed to diagonal form) are[127]

$$\mathbf{S}_1^2 \doteq S_1(S_1+1), \tag{86}$$

where S_1 is an integer or half-integer. We throughout suppose angular momentum measured in multiples of $h/2\pi$. The dot over the equality sign means that the right hand side gives the characteristic values of the matrix on the left. It is included to show that we do not have a true equality, as a whole matrix cannot be equated to one of its characteristic values. Expressions printed in bold-face type are vector matrices, except for the energy matrix $\mathbf{H}_{ij}$, which is a scalar.

Let us now consider the square of a vector which is the sum $\mathbf{S}_1+\mathbf{S}_2$ of two other vectors. Then

$$(\mathbf{S}_1+\mathbf{S}_2)^2 \doteq S_{1+2}(S_{1+2}+1), \tag{87}$$

with $S_{1+2}=|S_2-S_1|,\ |S_2-S_1+1|,\ \cdots,\ S_1+S_2$. But $(\mathbf{S}_1+\mathbf{S}_2)^2=\mathbf{S}_1^2+\mathbf{S}_2^2+2\mathbf{S}_1\cdot\mathbf{S}_2$ so that, using (86, 87), we have

$$2\mathbf{S}_1\cdot\mathbf{S}_2 \doteq S_{1+2}(S_{1+2}+1)-S_1(S_1+1)-S_2(S_2+1). \tag{88}$$

This is the fundamental formula for the quantization of the scalar product of two vectors. In other words, we may say that (88) describes the coupling in the two vector problem.

The four vector problem. The problem of the coupling of more than two vectors is more complicated. Here not all the angles or scalar products can be diagonalized simultaneously—only those which involve different vectors. Thus in the four vector problem one can quantize simultaneously $(\mathbf{S}_1+\mathbf{S}_2)^2$, $(\mathbf{S}_3+\mathbf{S}_4)^2$ and the complete resultant $(\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4)^2$, or what is the same, one can diagonalize simultaneously $(\mathbf{S}_1\cdot\mathbf{S}_2)$, $(\mathbf{S}_3\cdot\mathbf{S}_4)$ and $(\mathbf{S}_1+\mathbf{S}_2)\cdot(\mathbf{S}_3+\mathbf{S}_4)$, but then we preclude the ability to diagonalize $(\mathbf{S}_1+\mathbf{S}_3)^2$, $\mathbf{S}_1\cdot\mathbf{S}_3$, etc. The algebraic basis is that $\mathbf{S}_i\cdot\mathbf{S}_j$ commutes in multiplication with $\mathbf{S}_k\cdot\mathbf{S}_l$ ($k, l\neq i, j$) but not with $\mathbf{S}_i\cdot\mathbf{S}_k$.[127] The kinematical interpretation is that when the "joint angles" ($\mathbf{S}_1$, $\mathbf{S}_2$) and ($\mathbf{S}_3$, $\mathbf{S}_4$) are constant in Fig. 16, the angles between $\mathbf{S}_1$ and $\mathbf{S}_3$ (or $\mathbf{S}_4$) or between $\mathbf{S}_2$ and $\mathbf{S}_3$ (or $\mathbf{S}_4$) are not constant as $\mathbf{S}_1$ and $\mathbf{S}_2$ precess around $\mathbf{S}_1+\mathbf{S}_2$, and $\mathbf{S}_3$ and $\mathbf{S}_4$ precess around $\mathbf{S}_3+\mathbf{S}_4$. Periodic terms in classical mechanics correspond to non-diagonal matrix elements in quantum mechanics, and indeed in a system of representation which diagonalizes $\mathbf{S}_1\cdot\mathbf{S}_2$, $\mathbf{S}_3\cdot\mathbf{S}_4$ the matrices for $\mathbf{S}_1\cdot\mathbf{S}_3$, etc. are rather complicated in structure, comprising both diagonal and non-diagonal elements. For these the reader is referred to a paper by Johnson.[128] Fortunately we shall not need them. Instead of diagonalizing $\mathbf{S}_1\cdot\mathbf{S}_2$, $\mathbf{S}_3\cdot\mathbf{S}_4$ one could, of course, equally well diagonalize, for example, $\mathbf{S}_1\cdot\mathbf{S}_3$, $\mathbf{S}_2\cdot\mathbf{S}_4$ but at the expense of $\mathbf{S}_1\cdot\mathbf{S}_2$ and the other scalar products. In the six vector problem, one could diagonalize, as a typical choice $\mathbf{S}_1\cdot\mathbf{S}_2$, $\mathbf{S}_3\cdot\mathbf{S}_4$, $\mathbf{S}_5\cdot\mathbf{S}_6$, $\mathbf{S}_{1+2}\cdot\mathbf{S}_{3+4}$, $\mathbf{S}_{1+2+3+4}\cdot\mathbf{S}_{5+6}$.

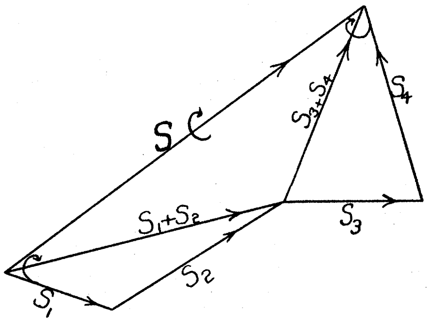


FIG. 16.

Formal equivalence of exchange interaction to spin-spin coupling. Let us now consider the particular case that the two angular momentum vectors which are being coupled in the two vector problem are the spin vectors of single electrons, indicated by small letters. Then s_1 and s_2 can only have the value $\frac{1}{2}$, while S_{1+2} can be 0, or 1. Thus by (88)

$$\begin{aligned} -\tfrac{1}{2}(1+4\mathbf{s}_1\cdot\mathbf{s}_2) &\doteq 1 \quad \text{when} \quad S_{1+2}=0; \\ -\tfrac{1}{2}(1+4\mathbf{s}_1\cdot\mathbf{s}_2) &\doteq -1 \quad \text{when} \quad S_{1+2}=1. \end{aligned} \tag{89}$$

Now we saw in section 9 that when we disregard non-orthogonality the characteristic values of the exchange energy $\mathbf{H}_{12}$ in a two electron system are $\mathbf{H}_{12}\doteq +J_{12}$, $-J_{12}$ where J_{12} is the exchange integral and the plus and minus signs go respectively with $S_{1+2}=0$ and $S_{1+2}=1$. Hence we see by (89) that the characteristic values of

$$\mathbf{H}_{12}+\tfrac{1}{2}(1+4\mathbf{s}\cdot\mathbf{s}_{12})J_{12}$$

are zero. The crux of the whole matter has been that because of the constraints imposed by the Pauli principle, the exchange energy and the resultant spin are diagonal at the same time. Now if a matrix has only zero characteristic values, it is zero in any system of representation, i.e., after any transformation. Hence we can conclude that in a system with any number of electrons, the total exchange energy $\Sigma_{j>i}\mathbf{H}_{ij}$ associated with simple permutations obeys the identity

$$\Sigma_{j>i}\mathbf{H}_{ij}+\Sigma_{j>i}\tfrac{1}{2}J_{ij}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)=0, \tag{90}$$

---

[127] For an account of the behavior of angular momentum vectors in quantum mechanics, and the related non-commutative algebra, see Dirac, *The Principles of Quantum Mechanics*, sections 43, 44, 49, or Condon and Shortley's new book.

[128] M. H. Johnson, Phys. Rev. **38**, 1628 (1931).

and the fundamental Eq. (34) of section 17 is thus established.[129]

Derivation of formula for exchange energy in the four electron problem. As an illustration of the vector model we shall now derive the expression so frequently used by Eyring and collaborators[93] for the exchange energy of a system of four electrons in a state of zero resultant spin. By Fig. 5 of section 17 there are two states of zero spin and so the secular equation will be a quadratic. Let us choose a system of representation in which $\mathbf{s}_1\cdot\mathbf{s}_2$ and $\mathbf{s}_3\cdot\mathbf{s}_4$ are diagonal. Then there are two possibilities (a) $S_{1+2}=S_{3+4}=0$ or (b) $S_{1+2}=S_{3+4}=1$. (Since the resultant spin is zero, it is impossible to have simultaneously $S_{1+2}=0$ and $S_{3+4}=1$ or *vice versa*, inasmuch as the resultant of a vanishing and a non-vanishing spin cannot possibly be zero.) In case (a) spins 1 and 2 are anti-parallel, also spins 3 and 4, and so the exchange energies $\mathbf{H}_{12}$ and $\mathbf{H}_{34}$ have respectively the characteristic values J_{12} and J_{34}. In case (b) the alignment is parallel instead of anti-parallel, and so then the corresponding characteristic values are $-J_{12}$, J_{-34}. The secular determinant for finding the total exchange energy is thus

$$\begin{vmatrix} J_{12}+J_{34}+a-W & c \\ c & -J_{12}-J_{34}+b-W \end{vmatrix}=0, \qquad (91)$$

where a, b, c are independent of J_{12}, J_{34} and are as yet undetermined linear functions of J_{13}, J_{14}, J_{23}, J_{24}, since (34) or (90) is linear in the exchange integrals. The c term is necessitated by our statement that $\mathbf{s}_1\cdot\mathbf{s}_3$, etc. are not diagonal when $\mathbf{s}_1\cdot\mathbf{s}_2$, $\mathbf{s}_3\cdot\mathbf{s}_4$ are. The term a must have the value $-\frac{1}{2}(J_{13}+J_{14}+J_{23}+J_{24})$ in virtue of the theorem given in section 19 that the exchange coefficient connecting a paired electron and any electron not in the pair is $-\frac{1}{2}$. Namely, in the state represented by the upper left corner of the determinant, the spins 1,2 are anti-parallel, corresponding to an electron pair, and similarly for spins 3,4. To evaluate the remaining elements, one could use Johnson's formulas, but we shall show that instead they can immediately be determined by considerations of symmetry. It is well known that the diagonal sum of a matrix is invariant of the system of representation. Furthermore, it is clear that this sum must be symmetrical in all the exchange integrals, since the coupling problem which we are studying is a perfectly general one. This sum is obviously zero as far as its J_{12}, or J_{34} parts are concerned, and by symmetry, similar remarks must apply to its other parts. (We could, for instance, use a system of representation which diagonalized $\mathbf{H}_{13}$, $\mathbf{H}_{24}$ instead of $\mathbf{H}_{12}$, $\mathbf{H}_{34}$. The part of the diagonal sum proportional to J_{13} or J_{24} would then be zero and this value must be conserved because of the invariance of the diagonal sum.) Hence in (91) we must have $a=-b$ and so in virtue of the value previously derived for a the roots of (91) are

$$W=[(J_{12}+J_{34}-\tfrac{1}{2}J_{13}-\tfrac{1}{2}J_{23}-\tfrac{1}{2}J_{14}-\tfrac{1}{2}J_{24})^2+c^2]^{\frac{1}{2}}. \qquad (92)$$

Now the radicand must be symmetric in all the J's. It is a homogeneous quadratic function of the J's, and will involve three types of terms respectively of the form $J_{ij}J_{kl}$, $J_{ij}J_{ik}$, J_{ij}^2 except for a multiplicative coefficient. The coefficients must be the same for any given type, and are seen from the first part of (92) to be respectively 2, -1, $+1$ inasmuch as knowledge of c is not necessary to determine a typical coefficient of each class since c does not involve J_{12}, J_{34}. Hence (92) becomes

$$W=[\Sigma(J_{ij}^2-J_{ij}J_{jl}+2J_{ij}J_{kl})]^{\frac{1}{2}}, \qquad (93)$$

which is the desired result, in agreement with (65) of section 28 when written out explicitly. (In Eq. (93), mere permutations of indices are not to be considered as giving rise to new terms.) Another substantially equivalent way of obtaining (93) from (92) is to note that the right side of (92) must always reduce to

$$\pm[J_{ij}+J_{kl}-\tfrac{1}{2}(J_{il}+J_{ik}+J_{jk}+J_{jl})]$$

if *any* two J_{ij}, J_{kl} are large compared with the other J's.

Eq. (65) or (93) may be regarded as expressing a sort of compromise between diagonalizing the various possible scalar products, none of which are in general diagonal when we diagonalize the complete exchange energy. Those products are nearest to diagonalization for which the exchange integrals are largest in absolute magnitude. If the pairs selected are 1–2, 3–4 the assumption of electron pairing is equivalent to neglecting c in (91) and then taking the upper left root.

The expression for the exchange energy of three electrons in a state of resultant spin $\frac{1}{2}$ can immediately be deduced from (65) or (93). If the resultant spin of four electrons is zero, then the resultant of any three spins is quantized to $\frac{1}{2}$ (i.e., $S_{1+2+3}=\frac{1}{2}$) since the fourth spin, being an individual spin, has a quantum number of $\frac{1}{2}$, and the resultant of two vectors (here $\mathbf{S}_{1+2+3}$ and $\mathbf{s}_4$) can vanish only if the two vectors are equal. Therefore the formula (66) given in section 28 for the three-electron case is derived simply by striking out J_{14}, J_{24}, J_{34} in (65) or (93).

Derivation of (66) *by the method of bond eigenfunctions.* By way of contrast and variety, we also include herewith a derivation of (66) by the Slater method instead of the vector model. Let f_1, f_2, f_3 be the orbital wave functions for the three electron states, and let α, β denote the spin wave functions $\delta(\frac{1}{2};\ m_s)$ and $\delta(-\frac{1}{2};\ m_s)$. The complete wave function must be antisymmetric when spin and orbit are both permuted, and so can be written as a determinant. For a given value $\frac{1}{2}$ of Σm_s there are three possible Slater determinants, as follows, corresponding to different correlations of α, β with f_1, f_2, f_3. One of these is

---

[129] For a more detailed derivation of (90), see Dirac, reference 52. It is to be emphasized that there is no question of the permutation of electrons between states in (90), as (90) has already included the effect of electron permutation. It is to be stressed that (90) is an identity valid only as long as we artificially exclude higher order permutations and related troubles connected with non-orthogonality, and as long as we neglect perturbations by other configurations. (The latter give polarization corrections expressing the fact that the wave function is not rigorously a linear combination of permutations of (33)—i.e., the "product" assumption is inadequate). For extension of the Dirac vector model to include these complications, see two papers by Serber, references 52, 54.

$$I=(\tfrac{1}{6})^{\frac{1}{2}}\begin{vmatrix}(f_1\beta)_1(f_2\alpha)_1(f_3\alpha)_1\\(f_1\beta)_2(f_2\alpha)_2(f_3\alpha)_2\\(f_1\beta)_3(f_2\alpha)_3(f_3\alpha)_3\end{vmatrix}. \tag{94}$$

The other two, II and III, are similar to I except that β occurs, respectively, in the second and third rather than first column. Here $(f\alpha)_i$ means that the state $f\alpha$ is occupied by electron i. It is convenient to define three new functions

$$\psi_1=(\mathrm{II}-\mathrm{I})/\sqrt{2},\quad \psi_2=(\mathrm{III}-\mathrm{I})/\sqrt{2},$$
$$\psi_3=(\mathrm{I}+\mathrm{II}+\mathrm{III})/\sqrt{3}. \tag{95}$$

The function ψ_3 is symmetric when any two spins are interchanged, and therefore corresponds to a spin 3/2. Consequently only ψ_1, ψ_2 are of interest for our problem and are commonly known as bond eigenfunctions. ψ_1 corresponds to a bond between f_1, f_2 and ψ_2 to one between f_1, f_3.

We now assume that the actual wave function that lifts the degeneracy is a linear combination $a_1\psi_1+a_2\psi_2$. A ψ_3 portion need not be included since states of different total spin do not combine. In this way we are led to the secular equation

$$\begin{vmatrix}H_{11}-W & H_{12}-T_{12}W\\ H_{12}-T_{12}W & H_{22}-W\end{vmatrix}=0, \tag{96}$$

where $H_{ij}=\int\psi_i\mathbf{H}\psi_j dv_1dv_2dv_3$ and $T_{ij}=\int\psi_i\psi_j dv_1dv_2dv_3$.

If one neglects higher order permutations and assumes that f_1, f_2, f_3 are mutually orthogonal (except as non-orthogonality is implicitly involved in J_{ij}; cf. section 10), one finds

$$H_{11}=J_{12}-\tfrac{1}{2}J_{23}-\tfrac{1}{2}J_{13},\quad H_{12}=\tfrac{1}{2}J_{12}+\tfrac{1}{2}J_{13}-J_{23},$$
$$H_{22}=J_{13}-\tfrac{1}{2}J_{12}-\tfrac{1}{2}J_{23},\quad T_{12}=\tfrac{1}{2}. \tag{97}$$

On substitution of the values (97), one finds that (96) agrees with (66).

Case of certain exchange integrals equal. An important special case of the vector coupling problem is that of a system of n electrons in which many of the exchange integrals coincide as follows:

$$J_{ij}=A \text{ for } i,j\leqq k;\quad J_{ij}=B \text{ for } i\leqq k, j>k;\quad J_{ij}=C \text{ for } i,j>k.$$

Then the exchange energy (34) reduces to

$$-\tfrac{1}{2}A\Sigma_{i,\,j(i<j\leqq k)}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)-\tfrac{1}{2}B\Sigma_{i,\,j(i\leqq k<j)}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)-\tfrac{1}{2}C\Sigma_{i,\,j(k<i<j)}(1+4\mathbf{s}_i\cdot\mathbf{s}_j). \tag{98}$$

Let $\mathbf{S}_k$ denote the resultant of the first k spins, and $\mathbf{S}_{>k}$ that of the remaining spins. Then

$$\mathbf{S}_k^2=(\mathbf{s}_1+\cdots+\mathbf{s}_k)^2=\tfrac{3}{4}k+2\Sigma_{i,\,j(i<j\leqq k)}\mathbf{s}_i\cdot\mathbf{s}_j,\quad \mathbf{S}_k\cdot\mathbf{S}_{>k}=\Sigma_{i,\,j(i\leqq k<j)}\mathbf{s}_i\cdot\mathbf{s}_j,\quad \mathbf{S}_{>k}^2=\tfrac{3}{4}(n-k)+2\Sigma_{i,\,j(k<i<j)}\mathbf{s}_i\cdot\mathbf{s}_j, \tag{99}$$

since the square $\mathbf{s}_i^2$ of the spin angular momentum of a single electron can only have the value $\frac{3}{4}$ (by Eq. (86) with $S_i=\frac{1}{2}$). The important thing is that when we use the relations (99) the individual spins drop out from (98), so that we really have only a coupling problem in two rather than n vectors. The two components are the collective angular momentum of the first k electrons, and that of the remaining electrons, which can be quantized in accordance with the relations

$$\mathbf{S}_k^2=S_k(S_k+1),\quad \mathbf{S}_{>k}^2=S_{>k}(S_{>k}+1),\quad (\mathbf{S}_k+\mathbf{S}_{>k})^2=S(S+1).$$

The permissible values of S_k, $S_{>k}$ are obtained by constructing "branching diagrams" such as those of Fig. 5, for system of k and $n-k$ electrons respectively. Do not confuse this two vector problem, where the quantum numbers S_k, $S_{>k}$ may be large, with the much simpler two vector problem in (89) where the two units were spins of single electrons.

The characteristic values of (89) are thus

$$-\tfrac{1}{2}A[\tfrac{1}{2}k(k-1)+2(S_k^2+S_k-\tfrac{3}{4}k)]-\tfrac{1}{2}B[k(n-k)+2(S^2+S-S_k^2-S_k-S_{>k}^2-S_{>k})]$$
$$-\tfrac{1}{2}C[\tfrac{1}{2}(n-k)(n-k-1)+2(S_{>k}^2+S_{>k}-\tfrac{3}{4}n+\tfrac{3}{4}k)]. \tag{100}$$

Eq. (100) has extensive applications to the non-directional theory of valence. For instance, it can be applied to CH_4 if all the electrons of the C atom are treated as alike. Then $n-k=k=4$ and it is convenient to use notation J_{CC}, J_{CH}, J_{HH}, S_{C}, $S_{4\mathrm{H}}$ in place of A, B, C, S_k, $S_{>k}$ respectively in order to emphasize the physical significance of the various exchange integrals and spins. Eq. (100) shows that if $J_{\mathrm{CH}}<0$, the CH part of the energy is made a minimum by making S_{C} and $S_{4\mathrm{H}}$ as large, and S as small as possible, i.e., $S_{\mathrm{C}}=S_{4\mathrm{H}}=2$, $S=0$. Then (100) becomes $-6J_{\mathrm{HH}}-6J_{\mathrm{CC}}+4J_{\mathrm{CH}}$, to be contrasted with the expression (41) or (59) based on directional valence and electron pairing. The fact that $S_{\mathrm{C}}=2$ is the ground for our statement that in the non-directional theory of valence, the C atom is in the ^5S state. Since $J_{\mathrm{HH}}<0$ and since J_{HH} has a negative coefficient -6, the H$-$H effects are repulsive.

Absence of affinity for extra atoms. Note particularly that, in general, if $B<0$, $n-k\geqq k$ the lowest value of the B part of the energy (100) is obtained by taking $S_k=\frac{1}{2}k$, $S_{>k}=\frac{1}{2}(n-k)$, $S=\frac{1}{2}n-k$ and is kB. The important thing is that this value is independent of n, as long as the premise $n-k\geqq k$ is satisfied. By identifying k and $n-k$ with the number of valence electrons on the central and equivalent attached atoms, respectively, we see that from the standpoint of the nondirectional theory, there is no advantage to be gained if a central atom annexes more attached atoms (for simplicity supposed similar and monovalent) than the central atom has valence electrons. For the particular case of molecules built exclusively of hydrogen, there is no question of directional effects, and so if we neglect the exchange forces between distant atoms, and of course nonorthogonality, the exchange energy of H_3 is exactly the same as that of H_2, for given H–H distance of separation. When the forces between the distant atoms are included, H_3 actually has more energy than H_2, in agreement with the existence of an activation energy for $H+H_2 \rightarrow H_2+H$.

The preceding paragraph supplies the basis for our statement in section 31 that the difficulty of affinity for extra atoms, found in crude forms of the method of molecular orbitals, does not appear in the Heitler-London theory.

General Remarks. For other examples of the vector model than those given in this appendix, the reader is referred to a paper by one of the authors.[52] We have tried particularly to use different examples in the two places.

The vector model is not that used in most of the chemical literature to solve the problem of the exchange degeneracy. Instead the commonest procedure is to use "bond eigenfunctions" constructed by Slater's method.[51]

Each bond eigenfunction corresponds to a definite scheme of electron pairing. There are as many different bond eigenfunctions as there are ways of pairing, but there are usually far fewer states than there are possible ways of drawing the bonds. For instance, there are 3 ways of pairing, but only two different states for the four electron problem with $S=0$. Only as many of the bond eigenfunctions are needed, i.e. are linearly independent, as there are such states. A conveniently chosen linearly independent set of bond eigenfunctions is termed a canonical set by Pauling and collaborators. The other linearly dependent bond eigenfunctions are expressed in terms of a canonical set by the so-called process of "bond uncrossing." The reason for the name is that if the various states are arranged in a ring, as in Fig. 14 for a system of six states, the canonical structures usually selected[130] correspond to bonds which do not cross (cf. Fig. 14). In general the ring arrangement will be a fictitious one, used for formal purposes, rather than of literal physical significance as in the benzene problem.

With the method of bond eigenfunctions, the first wave function for the 4 electron problem can be chosen as that in which spins 1,2 are anti-parallel to 3,4, respectively, but then the second wave function is not as in the vector model that in which spins 1 and 2 are, respectively, parallel to 3,4 but rather one in which spins 1,4 are, respectively, anti-parallel to 2,3.

As compared with the vector model, the bond eigenfunction procedure has the drawback that the wave functions are not mutually orthogonal, so that one obtains secular determinants such as (96) with the energy constant appearing off the principal diagonal. Also the introduction of wave functions probably makes the calculation rather more explicit but without quite the elegance of the more algebraic matrix method. The method of bond eigenfunctions is probably more convenient in the calculation of resonance energies, where two or more configurations are on a par with each other. In Fig. 14, configurations A and B can both be taken as canonical eigenfunctions, but in the vector method only one of the structures A or B can be taken as one of the original states of reference. Then B or A is expressible only as a linear combination of other states involving spins sometimes paired to unity rather than to zero. Even so, the calculation by the vector method[131] is no more complicated than the other procedures if we wish to include all five configurations in Fig. 14, but for the reasons just given it is not readily adapted to the simplified problem of considering only structures A, B in Fig. 14. On the other hand, the vector model seems better than the bond eigenfunction method for molecular states not of minimum spin, as such states are treated in the latter only by rather clumsy artifice of phantom orbits, i.e., nonexistent partners used to complete the pairing. A variant of the bond eigenfunction procedure has been given by Wheland[132] which seems to simplify the calculations and yields an orthogonal system, though not a Hermitian secular determinant.

---

[130] The proof that this non-crossing arrangement furnishes a canonical set is due to Rumer, reference 92.

[131] R. Serber, J. Chem. Phys. **2**, 697 (1934).

[132] G. W. Wheland, J. Chem. Phys. **3**, 230 (1935).