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THE NATURE OF THE CHEMICAL BOND.
APPLICATION OF RESULTS OBTAINED FROM THE
QUANTUM MECHANICS AND FROM A THEORY OF
PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE
OF MOLECULES

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During the last four years the problem of the nature of the chemical bond has been attacked by theoretical physicists, especially Heitler and London, by the application of the quantum mechanics. This work has led to an approximate theoretical calculation of the energy of formation and of other properties of very simple molecules, such as H_2 , and has also provided a formal justification of the rules set up in 1916 by G. N. Lewis for his electron-pair bond. In the following paper it will be shown that many more results of chemical significance can be obtained from the quantum mechanical equations, permitting the formulation of an extensive and powerful set of rules for the electron-pair bond supplementing those of Lewis. These rules provide information regarding the relative strengths of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes, the relation between the quantum numbers of bonding electrons and the number and spatial arrangement of the bonds, etc. A complete theory of the magnetic moments of molecules and complex ions is also developed, and it is shown that for many compounds involving elements of the transition groups this theory together with the rules for electron-pair bonds leads to a unique assignment of electron structures as well as a definite determination of the type of bonds involved.¹

I. The Electron-Pair Bond

The Interaction of Simple Atoms.—The discussion of the wave equation for the hydrogen molecule by Heitler and London,² Sugiura,³ and Wang⁴ showed that two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation, the other

¹ A preliminary announcement of some of these results was made three years ago [Linus Pauling, *Proc. Nat. Acad. Sci.*, 14, 359 (1928)]. Two of the results (90° bond angles for *p* eigenfunctions, and the existence, but not the stability, of tetrahedral eigenfunctions) have been independently discovered by Professor J. C. Slater and announced at meetings of the National Academy of Sciences (Washington, April, 1930) and the American Physical Society (Cleveland, December, 1930).

² W. Heitler and F. London, *Z. Physik*, 44, 455 (1927).

³ Y. Sugiura, *ibid.*, 45, 484 (1927).

⁴ S. C. Wang, *Phys. Rev.*, 31, 579 (1928).

to attraction and the formation of a stable molecule. These two modes of interaction result from the identity of the two electrons. The characteristic resonance phenomenon of the quantum mechanics, which produces the stable bond in the hydrogen molecule, always occurs with two electrons, for even though the nuclei to which they are attached are different, the energy of the unperturbed system with one electron on one nucleus and the other on the other nucleus is the same as with the electrons interchanged. Hence we may expect to find electron-pair bonds turning up often.

But the interaction of atoms with more than one electron does not always lead to molecule formation. A normal helium atom and a normal hydrogen atom interact in only one way,⁵ giving repulsion only, and two normal helium atoms repel each other except at large distances, where there is very weak attraction.^{5,6} Two lithium atoms, on the other hand, can interact in two ways,⁷ giving a repulsive potential and an attractive potential, the latter corresponding to formation of a stable molecule. In these cases it is seen that only when each of the two atoms initially possesses an unpaired electron is a stable molecule formed. The general conclusion that an electron-pair bond is formed by the interaction of an unpaired electron on each of two atoms has been obtained formally by Heitler⁸ and London,⁹ with the use of certain assumptions regarding the signs of integrals occurring in the theory. The energy of the bond is largely the resonance or interchange energy of two electrons. This energy depends mainly on electrostatic forces between electrons and nuclei, and is not due to magnetic interactions, although the electron spins determine whether attractive or repulsive potentials, or both, will occur.

Properties of the Electron-Pair Bond.—From the foregoing discussion we infer the following properties of the electron-pair bond.

1. *The electron-pair bond is formed through the interaction of an unpaired electron on each of two atoms.*
2. *The spins of the electrons are opposed when the bond is formed, so that they cannot contribute to the paramagnetic susceptibility of the substance.*
3. *Two electrons which form a shared pair cannot take part in forming additional pairs.*

In addition we postulate the following three rules, which are justified by the qualitative consideration of the factors influencing bond energies. An outline of the derivation of the rules from the wave equation is given below.

⁵ G. Gentile, *Z. Physik*, **63**, 795 (1930).

⁶ J. C. Slater, *Phys. Rev.*, **32**, 349 (1927).

⁷ M. Delbrück, *Ann. Physik*, **5**, 36 (1930).

⁸ W. Heitler, *Z. Physik*, **46**, 47 (1927); **47**, 835 (1928); *Physik. Z.*, **31**, 185 (1930), etc.

⁹ F. London, *Z. Physik*, **46**, 455 (1928); **50**, 24 (1928); "Sommerfeld Festschrift," p. 104; etc.

4. *The main resonance terms for a single electron-pair bond are those involving only one eigenfunction from each atom.*

5. *Of two eigenfunctions with the same dependence on r , the one with the larger value in the bond direction will give rise to the stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.*

6. *Of two eigenfunctions with the same dependence on θ and φ , the one with the smaller mean value of r , that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond.*

Here the eigenfunctions referred to are those for an electron in an atom, and r , θ and φ are polar coördinates of the electron, the nucleus being at the origin of the coördinate system.

It is not proposed to develop a complete proof of the above rules at this place, for even the formal justification of the electron-pair bond in the simplest cases (diatomic molecule, say) requires a formidable array of symbols and equations. The following sketch outlines the construction of an inclusive proof.

It can be shown¹⁰ that if Ψ is an arbitrary function of the independent variables in a wave equation

$$(H - W)\Psi = 0$$

then the integral

$$E = \int \Psi^* H \Psi d\tau$$

called the variation integral, is always larger than W_0 , the lowest energy level for the system. A function Ψ containing several parameters provides the best approximation to the eigenfunction ψ_0 for the normal state of the system when the variational integral is minimized with respect to these parameters. Now let us consider two atoms A and B connected by an electron-pair bond, and for simplicity let all the other electrons in the system be paired, the pairs being either lone pairs or pairs shared between A or B and other atoms. Let us assume that there are available for bond formation by atom A several single-electron eigenfunctions of approximately the same energy, and that the change in energy of penetration into the core is negligible compared with bond energy. Then we may take as single-electron eigenfunctions

$$\psi_{Ai} = \sum_k a_{ik} \psi_{Ak}^0$$

in which the a_{ik} 's are numerical coefficients and the ψ_{Ak}^0 's are an arbitrary set of single-electron eigenfunctions, such as those obtained on separating the wave equation in polar coördinates. From the ψ_{Ai} 's there is built up a group composed of atom A and the atoms to which it is bonded except atom B, such that all electrons are paired except one, corresponding to the eigenfunction ψ_{Ai} , say. From atom B a similar group with one unpaired electron is built. The interaction energy of these two groups can then be calculated with the aid of the variational equation through the substitution of an eigenfunction for the molecule built of those for the two groups in such a way that it has the correct symmetry character. The construction of this eigenfunction and evaluation of the integral would be very laborious; it will be noticed, however, that this problem is formally similar to Born's treatment¹¹ of the interaction of two atoms in S states, based on Slater's treatment of atomic eigenfunctions, and the value of E is found to be

$$E = W_A + W_B + J_{II} + J_{IX} - \Sigma_I J_{II} - 2\Sigma_{II} J_{II}$$

¹⁰ A clear discussion is given by C. Eckart, *Phys. Rev.*, **36**, 878 (1930).

¹¹ M. Born, *Z. Physik*, **64**, 729 (1930).

Here W_A and W_B are the energies of the separate groups, and J_S represents the Coulomb interaction of A and B, neglecting resonance. The resonance term J_X corresponds to a permutation of the two AB bond electrons; J_Y corresponds to a permutation of the AB bond electron on B with a paired electron with similarly directed spin on A, or *vice versa*; and J_Z corresponds to a permutation of a paired electron on A with one on B. (For explicit expressions for these see Born.¹¹) The resonance integrals J_X , J_Y and J_Z have been found to have negative signs in the case of simple molecules for which calculations have been made, and it is probable that these signs obtain in most cases. The resonance integrals depend qualitatively on what may be called the *overlapping* of the single-electron eigenfunctions involved; if ψ_A and ψ_B are two single-electron eigenfunctions, the product $\psi_A(1) \psi_B(2) \psi_A^*(2) \psi_B^*(1)$ occurs in the resonance integral corresponding to the permutation involving electrons 1 and 2, and the value of the integral increases as the magnitude of this product in the region between the two nuclei increases.

Now we vary the coefficients a_{ik} in such a way as to minimize E . W_A and W_B are not affected by this variation, and J_S is not changed in case that there is one electron for every eigenfunction in a subgroup on A, and is changed relatively slightly otherwise. The resonance integrals are, however, strongly affected by changing the coefficients. The positive sign preceding J_X requires that the two bond eigenfunctions ψ_A and ψ_B show the maximum overlapping in the region between the two nuclei, while the negative sign preceding J_Y requires the minimum overlapping between ψ_A and the eigenfunctions of B other than ψ_B , and between ψ_B and the eigenfunctions of A other than ψ_A . Hence the correct zeroth-order eigenfunctions for the atom A are such that one, the AB bond eigenfunction ψ_A , extends largely in the direction of atom B, while the other A eigenfunctions avoid overlapping with ψ_B . As a consequence the integral J_X is of large magnitude, while the integrals J_Y , because of the small overlapping of the eigenfunctions involved, are small.

An extension of this argument shows that the phenomenon of *concentration of the bond eigenfunctions* further increases the magnitude of J_X and decreases J_Y . The non-orthogonality of the bond eigenfunctions as well as certain second-order perturbations leads to a shrinkage of the region in which the bond eigenfunctions have appreciable values. This is strikingly shown by a comparison of H_2^+ and H; the volume within which the electron probability function $\psi\psi^*$ for H_2^+ is greater than one-tenth of its maximum value is found from Burrau's calculations to be $0.67 \text{ \AA.}^3$, less than 10% of its value $8.6 \text{ \AA.}^3$ for a hydrogen atom.¹² This concentration of the bond eigenfunctions greatly increases their interaction with one another, and decreases their interaction with other eigenfunctions, a fact expressed in Rule 4. For double or triple bonds interactions among all four or six eigenfunctions must be considered.

s and p Eigenfunctions. Compounds of Normal Atoms.—As a rule s and p eigenfunctions with the same total quantum number in an atom do not differ very much in their mean values of r (the s levels lie lower because of greater penetration of inner shells), so that Rule 6 would not lead us to expect them to differ in bond-forming power. But their dependence on θ and φ is widely different. Putting

$$\left. \begin{aligned} \Psi_{ns}(r, \theta, \varphi) &= R_{ns}(r) \cdot s(\theta, \varphi) && \text{for } s \text{ eigenfunctions} \\ \Psi_{nl}(r, \theta, \varphi) &= R_{nl}(r) \cdot \left. \begin{aligned} p_x(\theta, \varphi) \\ p_y(\theta, \varphi) \\ p_z(\theta, \varphi) \end{aligned} \right\} && \text{for } p \text{ eigenfunctions} \end{aligned} \right\} \quad (1)$$

¹² Compare Fig. 8 with Fig. 7, which is drawn to half the scale of Fig. 6, of Linus Pauling, *Chem. Rev.*, 5, 173 (1928).

the parts s , p_x , p_y , p_z of the eigenfunctions depending on θ and φ , normalized to 4π , are

$$\left. \begin{aligned} s &= 1 \\ p_x &= \sqrt{3} \sin \theta \cos \varphi \\ p_y &= \sqrt{3} \sin \theta \sin \varphi \\ p_z &= \sqrt{3} \cos \theta \end{aligned} \right\} \quad (2)$$

Absolute values of s and p_x are represented in the xz plane in Figs. 1 and 2. s is spherically symmetrical, with the value 1 in all directions. $|p_x|$ consists of two spheres as shown (the x axis is an infinite symmetry axis), with the maximum value $\sqrt{3}$ along the x axis. $|p_y|$ and $|p_z|$ are similar, with maximum values of $\sqrt{3}$ along the y and z axis, respectively. From Rule 5 we conclude that *p electrons will form stronger bonds than s electrons*, and that *the bonds formed by p electrons in an atom tend to be oriented at right angles to one another*.

The second conclusion explains several interesting facts. Normal oxygen, in the state $2s^2 2p^4 {}^3P$, contains two unpaired p electrons. When an atom of oxygen combines with two of hydrogen, a water molecule will result in which the angle formed by the three atoms is 90° , or somewhat larger because of interaction of the two hydrogen atoms. It has been long known from their large electric moment

that water molecules have a kinked rather than a collinear arrangement of their atoms, and attempts have been made to explain this with rather unsatisfactory calculations based on an ionic structure with strong polarization of the oxygen anion in the field of the protons. The above simple explanation results directly from the reasonable assumption of an electron-pair bond structure and the properties of tesseral harmonics.

It can be predicted that H_2O_2 , with the structure $\begin{array}{c} :\ddot{O}:\ddot{O}: \\ \text{H} \quad \text{H} \end{array}$ involving bonds of p electrons, also consists of kinked rather than collinear molecules.

Nitrogen, with the normal state $2s^2 2p^3 {}^4S$, contains three unpaired p

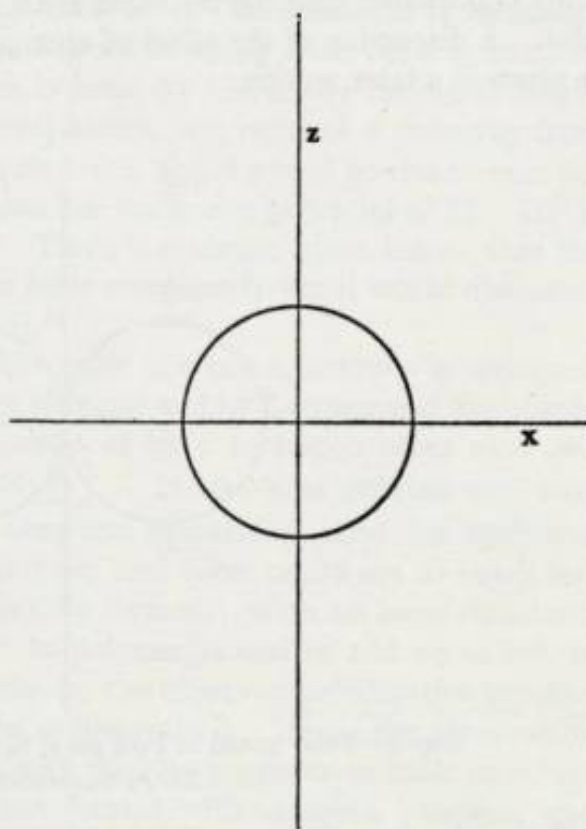


Fig. 1.—Polar graph of 1 in the xz plane, representing an s eigenfunction.

electrons, which can form bonds at about 90° from one another with three hydrogen atoms. The ammonia molecule, with the resulting pyramidal structure, also has a large electric moment.

The crystal skutterudite, $\text{Co}_4^{3+}(\text{As}_4^{4-})_3$, contains As_4^{4-} groups with a square configuration, corresponding to the structure $\left[\begin{array}{cc} \ddot{\text{As}} & \ddot{\text{As}} \\ \vdots & \vdots \\ \ddot{\text{As}} & \ddot{\text{As}} \end{array} \right]^{4-}$. This complex has bond angles of exactly 90° .

In the above discussion it has been assumed that the type of quantization has not been changed, and that s and p eigenfunctions retain their identity. This is probably true for H_2O and H_2O_2 , and perhaps for NH_3 and As_4^{4-} also. A discussion of the effect of change of quantization on bond angles is given in a later section.

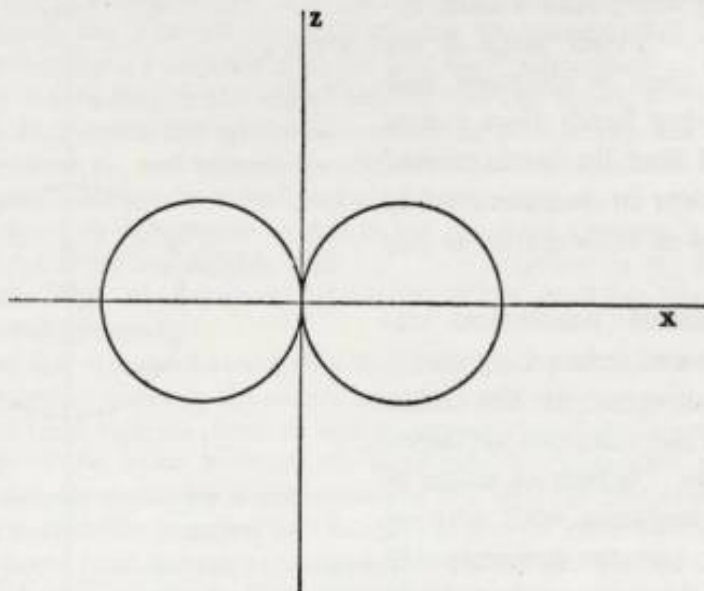


Fig. 2.—Polar graph of $|\sqrt{3} \sin \theta|$ in the xs plane, representing the p_x eigenfunction.

Transition from Electron-Pair to Ionic Bonds. The Hydrogen Bond.—In case that the symmetry character of an electron-pair structure and an ionic structure for a molecule are the same, it may be difficult to decide between the two, for the structure may lie anywhere between these extremes. The zeroth-order eigenfunction for the two bond electrons for a molecule MX (HF , say, or NaCl) with a single electron-pair bond would be

$$\Psi_{\text{MX}} = \frac{\psi_{\text{M}}(1) \psi_{\text{X}}(2) + \psi_{\text{M}}(2) \psi_{\text{X}}(1)}{\sqrt{2 + 2S^2}} \quad (3)$$

in which $S = \int \psi_{\text{M}}(1) \psi_{\text{X}}^*(1) d\tau_1$. The eigenfunction for a pure ionic state would be

$$\Psi_{\text{M}^+\text{X}^-} = \psi_{\text{X}}(1) \psi_{\text{X}}(2) \quad (4)$$

In certain cases one of these might approximate the correct eigenfunction

closely. In other cases, however, it would be necessary to consider combinations of the two, namely

$$\Psi_+ = a \Psi_{MX} + \sqrt{1-a^2} \Psi_{M^+X^-}$$

and

$$\Psi_- = \sqrt{1-a^2} \Psi_{MX} - a \Psi_{M^+X^-} \quad (5)$$

For a given molecule and a given internuclear separation a would have a definite value, such as to make the energy level for Ψ_+ lie as low as possible. If a happens to be nearly 1 for the equilibrium state of the molecule, it would be convenient to say that the bond is an electron-pair bond; if a is nearly zero, it could be called an ionic bond. This definition is somewhat unsatisfactory in that it does not depend on easily observable quantities. For example, a compound which is ionic by the above definition might dissociate adiabatically into neutral atoms, the value of a changing from nearly zero to unity as the nuclei separate, and it would do this in case the electron affinity of X were less than the ionization potential of M. HF is an example of such a compound. There is evidence, given below, that the normal molecule approximates an ionic compound; yet it would dissociate adiabatically into neutral F and H.¹³

But direct evidence regarding the value of a can sometimes be obtained. The hydrogen bond, discovered by Huggins and by Latimer and Rodebush, has been usually considered as produced by a hydrogen atom with two electron-pair bonds, as in $[\ddot{F}:H:\ddot{F}]$. It was later pointed out¹ that this is not compatible with the quantum mechanical rules, for hydrogen can have only one unpaired 1s electron, and outer orbits are so much less stable that strong bonds would not be formed. With an ionic structure, however, we would expect H^+F^- to polymerize and to add on to F^- , to give H_2F_2 and $[F^-H^+F^-]^-$; moreover, the observed coordination number 2 is just that predicted¹⁴ from the radius ratio 0. Hence the observation that hydrogen bonds are formed with fluorine supports an ionic structure for HF. Hydrogen bonds are not formed with chlorine, bromine, and iodine, so that the bonds in HCl, HBr, and HI are to be considered as approaching the electron-pair type.

Hydrogen bonds are formed to some extent by oxygen ($(H_2O)_x$, ice, etc.) and perhaps also in some cases by nitrogen. The electrostatic structure for the hydrogen bond explains the observation that only these atoms of high electron affinity form such bonds, a fact for which no explanation was given by the older conception. It is of interest that there is considerable

¹³ There would, however, be a certain probability, dependent on the nature of the eigenfunctions, that actual non-adiabatic dissociation would give ions rather than atoms, and this might be nearly unity, in case the two potential curves come very close to one another at some point. See I. v. Neumann and E. Wigner, *Physik. Z.*, 30, 467 (1929).

¹⁴ Linus Pauling, *THIS JOURNAL*, 51, 1010 (1929).

results from the fact that the interaction of one electron with the nucleus and other electrons can be represented approximately by a non-Coulombian central field, so that the wave equation can be separated in polar coördinates r , θ , and φ , giving rise to eigenfunctions involving tesseral harmonics such as those in Equation 1. The deeper penetration of s electrons within inner shells causes them to be more tightly bound than p electrons with the same total quantum number. If an atom approaches a given atom, forming a bond with it, the interaction between the two can be considered as a perturbation, and the first step in applying the perturbation theory for a degenerate system consists in finding the correct zeroth-order eigenfunctions for the perturbation, one of which is the eigenfunction which will lead to the largest negative perturbation energy. This will be the one with the largest values along the bond direction. The correct zeroth-order eigenfunctions must be certain normalized and mutually orthogonal linear aggregates of the original eigenfunctions. If the perturbation is small, the s eigenfunction cannot be changed, and the only combinations which can be made with the p eigenfunctions are equivalent merely to a rotation of axes. But in case the energy of interaction of the two atoms is greater than the difference in energy of an s electron and a p electron (or, if there are originally two s electrons present, as in a normal carbon atom, of twice this difference), hydrogen-like s and p eigenfunctions must be grouped together to form the original degenerate state, and the interaction of the two atoms together with the deviation of the atomic field from a Coulombian one must be considered as the perturbation, with the former predominating. The correct zeroth-order bond eigenfunctions will then be those orthogonal and normalized linear aggregates of both the s and p eigenfunctions which would give the strongest bonds according to Rule 5.

A rough criterion as to whether the quantization is changed from that in polar coördinates to a type giving stronger bond eigenfunctions is thus that the possible bond energy be greater than the s - p (or, if d eigenfunctions are also involved, s - d or p - d) separation.²⁰

This criterion is satisfied for quadrivalent carbon. The energy difference of the states²¹ $2s^2 2p^2 \ ^3P$ and $2s 2p^3 \ ^3P$ of carbon is 9.3 v. e., and a similar value of about 200,000 cal. per mole is found for other atoms in the first row of the periodic system. The energy of a single bond is of the order of 100,000 cal. per mole. Hence a carbon atom forming four bonds would certainly have changed quantization, and even when the bond energy must be divided between two atoms, as in a diamond crystal, the criterion is sufficiently well satisfied. The same results hold for quadrivalent

²⁰ This criterion was expressed in Ref. 1.

²¹ States with the same multiplicity should be compared, for increase in multiplicity decreases the term value, the difference between $2s^2 2p^3 \ ^3P$ and $2s 2p^3 \ ^3S$ being only about 1.6 v. e., as mentioned above.

nitrogen, a nitrogen *ion* in the state $N^+ 2s2p^3 {}^4S$ forming four bonds, as in $(NH_4)^+$, $N(CH_3)_4^+$, etc. But for bivalent oxygen there is available only about 200,000 cal. per mole bond energy, and the s - p separation for two s electrons corresponds to about 400,000 cal. per mole, so that it is very probable that the oxygen bond eigenfunctions in H_2O , for example, are p eigenfunctions, as assumed in a previous section. Trivalent nitrogen is a border-line case; the bond energy of about 300,000 cal. per mole is sufficiently close to the s - p energy of 400,000 cal. per mole to permit the eigenfunctions to be changed somewhat, but not to the extent that they are in quadrivalent carbon and nitrogen.

It may be pointed out that the s - p separation for atoms in the same column of the periodic table is nearly constant, about 200,000 cal. per mole for one s electron. The bond energy decreases somewhat with increasing atomic number. Thus the energies of a bond in the compounds H_2O , H_2S , H_2Se , and H_2Te , calculated from thermochemical and band spectral data, are 110,000, 90,000, 73,000, and 60,000 cal. per mole, respectively. Hence we conclude that if quantization in polar coördinates is not broken for a light atom on formation of a compound, it will not be broken for heavier atoms in the same column of the periodic system. The molecules H_2S , H_2Se , and H_2Te must accordingly also have a non-linear structure, with bond angles of 90° or slightly greater.

Let us now determine the zeroth-order eigenfunctions which will form the strongest bonds for the case when the s - p quantization is broken. The dependence on r of s and p hydrogen-like eigenfunctions is not greatly different,²² and it seems probable that the effect of the non-Coulombian field would decrease the difference for actual atoms. We may accordingly assume that $R_{n0}(r)$ and $R_{n1}(r)$ are effectively the same as far as bond formation is concerned, so that the problem of determining the bond eigenfunctions reduces to a discussion of the θ, φ eigenfunctions of Equation 1. Arbitrary sets of θ, φ eigenfunctions formed from s, p_x, p_y , and p_z are given by the expressions

$$\left. \begin{aligned} \psi_1 &= a_1s + b_1p_x + c_1p_y + d_1p_z \\ \psi_2 &= a_2s + b_2p_x + c_2p_y + d_2p_z \\ \psi_3 &= a_3s + b_3p_x + c_3p_y + d_3p_z \\ \psi_4 &= a_4s + b_4p_x + c_4p_y + d_4p_z \end{aligned} \right\} \quad (6)$$

in which the coefficients a_1 , etc., are restricted only by the orthogonality and normalization requirements

$$\int \psi_i^2 d\tau = 1 \quad \text{or } a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1 \quad i = 1, 2, 3, 4 \quad (7a)$$

and

$$\int \psi_i \psi_k d\tau = 0 \quad \text{or } a_i a_k + b_i b_k + c_i c_k + d_i d_k = 0 \quad i, k = 1, 2, 3, 4 \quad i \neq k \quad (7b)$$

²² See the curves given by Linus Pauling, *Proc. Roy. Soc. (London)*, A114, 181 (1927), or A. Sommerfeld, "Wellenmechanischer Ergänzungsband," p. 88.

From Rule 5 the best bond eigenfunction will be that which has the largest value in the bond direction. This direction can be chosen arbitrarily for a single bond. Taking it along the x axis, it is found that the best single bond eigenfunction is²³

$$\psi_1 = \frac{1}{2} s + \frac{\sqrt{3}}{2} p_x \quad (8a)$$

with a maximum value of 2, considerably larger than that 1.732 for a p eigenfunction. A graph of this function in the xz plane is shown in Fig. 3.

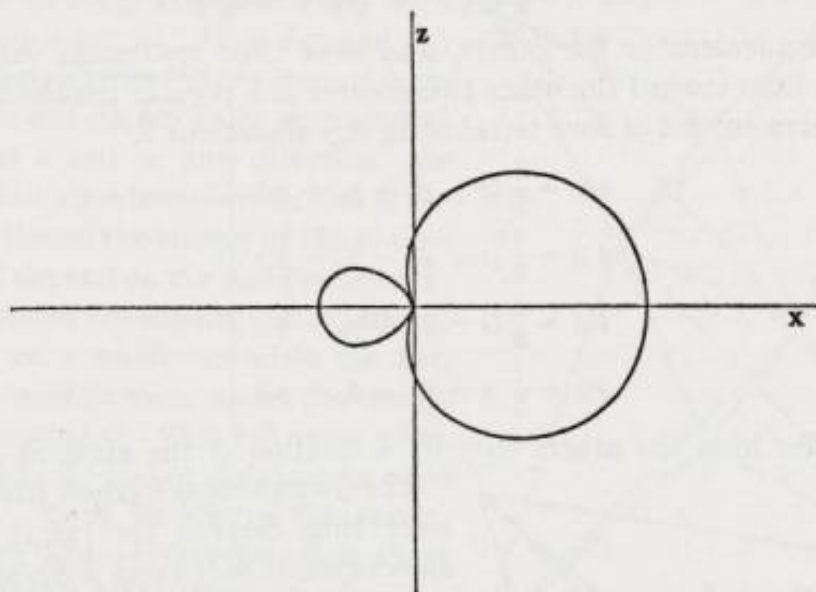


Fig. 3.—Polar graph of $|1/2 + 3/2 \sin \theta|$ in the xz plane, representing a tetrahedral eigenfunction, the best bond eigenfunction which can be formed from s and p eigenfunctions.

A second bond can be introduced in the xz plane. The best eigenfunction for this bond is found to be

$$\psi_2 = \frac{1}{2} s - \frac{1}{2\sqrt{3}} p_x + \frac{\sqrt{2}}{\sqrt{3}} p_z \quad (8b)$$

²³ It is easily shown with the use of the method of undetermined multipliers that the eigenfunction with the maximum value in the direction defined by the polar angles θ_0, φ_0 has as coefficients of the initial eigenfunctions quantities proportional to $\psi_k(\theta_0, \varphi_0)$, and that the maximum value is itself equal to $\{\sum_k [\psi_k(\theta_0, \varphi_0)]^2\}^{1/2}$. For let $\psi(\theta, \varphi) = \sum_{k=1}^n a_k \psi_k(\theta, \varphi)$, with $\sum a_k^2 = 1$. We want $\psi(\theta_0, \varphi_0) = \sum a_k \psi_k(\theta_0, \varphi_0)$ to be a maximum with respect to variation in the a_k 's. Consider the expression

$$\Delta = \psi(\theta_0, \varphi_0) - \frac{\lambda}{2} \{\sum a_k^2 - 1\} = \sum \left\{ a_k \psi_k(\theta_0, \varphi_0) - \frac{\lambda}{2} a_k^2 \right\} + \frac{\lambda}{2}$$

in which λ is an undetermined multiplier. Then we put

$$\frac{\partial \Delta}{\partial a_k} = \psi_k(\theta_0, \varphi_0) - \lambda a_k = 0 \text{ or } a_k = \frac{\psi_k(\theta_0, \varphi_0)}{\lambda}, k = 1, 2, \dots, n$$

in which λ has such a value that $\sum a_k^2 = 1$; i. e., $\lambda = \{\sum [\psi_k(\theta_0, \varphi_0)]^2\}^{1/2}$. $\psi(\theta_0, \varphi_0)$ is itself then equal to $\sum [\psi_k(\theta_0, \varphi_0)]^2 / \lambda$ or $\{\sum [\psi_k(\theta_0, \varphi_0)]^2\}^{1/2}$.

This eigenfunction is equivalent to and orthogonal to ψ_1 , and has its maximum value of 2 at $\theta = 19^\circ 28'$, $\varphi = 180^\circ$, that is, at an angle of $109^\circ 28'$ with the first bond, which is just the angle between the lines drawn from the center to two corners of a regular tetrahedron. The third and fourth best bond eigenfunctions

$$\psi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{6}}p_y + \frac{1}{\sqrt{2}}p_z \quad (8c)$$

and

$$\psi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}p_x - \frac{1}{\sqrt{6}}p_y - \frac{1}{\sqrt{2}}p_z \quad (8d)$$

are also equivalent to the others, and have their maximum values of 2 along the lines toward the other two corners of a regular tetrahedron.

An equivalent set of four tetrahedral eigenfunctions is²⁴

$$\left. \begin{aligned} \psi_{\text{III}} &= \frac{1}{2}(s + p_x + p_y + p_z) \\ \psi_{\text{II}} &= \frac{1}{2}(s + p_x - p_y - p_z) \\ \psi_{\text{I}} &= \frac{1}{2}(s - p_x + p_y - p_z) \\ \psi_{\text{IV}} &= \frac{1}{2}(s - p_x - p_y + p_z) \end{aligned} \right\} \quad (9)$$

These differ from the others only by a rotation of the atom as a whole.

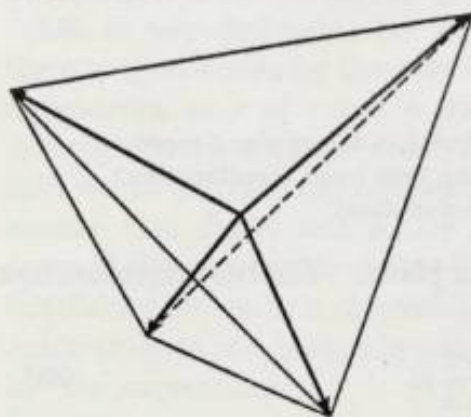


Fig. 4.—Diagram showing relative orientation in space of the directions of the maxima of four tetrahedral eigenfunctions.

The Tetrahedral Carbon Atom.—We have thus derived the result that an atom in which only s and p eigenfunctions contribute to bond formation and in which the quantization in polar coordinates is broken can form one, two, three, or four equivalent bonds, which are directed toward the corners of a regular tetrahedron (Fig. 4).

This calculation provides the quantum mechanical justification of the chemist's tetrahedral carbon atom, present in diamond and all aliphatic carbon compounds, and for the tetrahedral quadrivalent nitrogen atom, the tetrahedral phosphorus atom, as in phosphonium compounds, the tetrahedral boron atom in B_2H_6 (involving single-electron bonds), and many other such atoms.

Free or Restricted Rotation.—Each of these tetrahedral bond eigen-

²⁴ It should be borne in mind that the bond eigenfunctions actually are obtained from the expressions given in this paper by substituting for s the complete eigenfunction $\Psi_{n_0}(r, \theta, \varphi)$, etc. It is not necessary that the r part of the eigenfunctions be identical; the assumption made in the above treatment is that they do not affect the evaluation of the coefficients in the bond eigenfunctions.

functions is cylindrically symmetrical about its bond direction. Hence the bond energy is independent of orientation about this direction, so that there will be *free rotation about a single bond*, except in so far as rotation is hindered by steric effects, arising from interactions of the substituent atoms or groups.

A double bond behaves differently, however. Let us introduce two substituents in the octants xyz and $\bar{x}\bar{y}z$ of an atom, a carbon atom, say, using the bond eigenfunctions ψ_{111} and $\psi_{\bar{1}\bar{1}1}$. The two eigenfunctions ψ_{111} and $\psi_{\bar{1}\bar{1}1}$ are then left to form a double bond with another such group. Now ψ_{111} and $\psi_{\bar{1}\bar{1}1}$ (or any two eigenfunctions formed from them) are not cylindrically symmetrical about the z axis or any direction, nor are the two eigenfunctions on the other group. Hence the energy of the double bond will depend on the relative orientation of the two tetrahedral carbon atoms, and will be a maximum when the two sets of eigenfunctions show the maximum overlapping. This will occur when the two tetrahedral atoms share an edge (Fig. 5). Thus we derive the result, found long ago by chemists, that there are two stable states for a simple compound involving a double bond, a *cis* and a *trans* state, differing in orientation by 180° . *There is no free rotation about a double bond.*²⁵

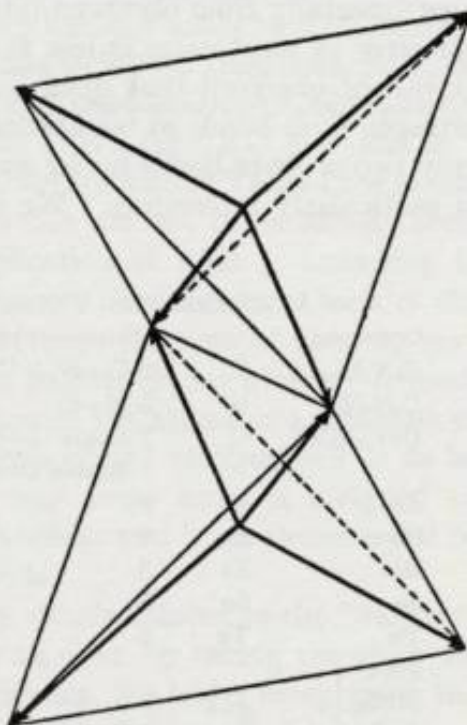


Fig. 5.—Directions of maxima of tetrahedral eigenfunctions in two atoms connected by a double bond.

The three eigenfunctions which would take part in the formation of a triple bond can be made symmetrical about the bond direction, for an atom of the type considered above, with only four eigenfunctions in the outer shell; but since the group attached by the fourth valence lies on the axis of the triple bond, there is no way of verifying the resulting free rotation about the triple bond.

The Angles between Bonds.—The above calculation of tetrahedral angles between bonds when the quantization is changed sets an upper limit on bond angles in doubtful cases, when the criterion is only approximately satisfied. For we can now state that the bond angles in H_2O and NH_3

²⁵ A discussion of rotation about a double bond on the basis of the quantum mechanics has been published by E. Hückel, *Z. Physik*, 60, 423 (1930), which is, I feel, neither so straightforward nor so convincing as the above treatment, inasmuch as neither the phenomenon of concentration of the bond eigenfunctions nor that of change in quantization is taken into account.

should lie between 90 and $109^{\circ}28'$, closer to 90° for the first and to $109^{\circ}28'$ for the second compound. The same limits should apply to other atoms with an outer 8-shell (counting both shared and unshared electron pairs). Direct evidence on this point is provided by crystal structure data for non-ionic crystals, given in Table I. Every one of the angles given in this table depends on one or more parameters, which have been determined experimentally from observed intensities of x-ray reflections. The probable error in most cases is less than 5° , and in many is only about $\pm 1^{\circ}$. It will be observed that quadrivalent carbon and nitrogen and trivalent nitrogen form bonds at tetrahedral angles, whereas heavier atoms forming only two or three bonds prefer smaller bond angles. The series As, Sb, Bi is particularly interesting. We expect, from an argument given earlier,

TABLE I
ANGLES BETWEEN BONDS, FROM CRYSTAL STRUCTURE DATA^a

Compound	Atom	Number of bonds	Angles between bonds
$C_2N_4H_{12}$	C	2 C—N, 2 C—H	112° between C—N bonds
$C_2N_4H_{12}$	N	3 N—C	108°
$(NH_4)_2CO^b$	C	2 single C—N 1 double C=O	115° between single bonds
As	As	3	97°
Sb	Sb	3	96°
Bi	Bi	3	94°
Se	Se	2	105°
Te	Te	2	102°
FeS_2^d	S ⁺⁺	1 S—S	103° between S—S and S—M bonds
MnS_2			
CoS_2		3 S—M	115° between two M—S bonds
NiS_2			
MoS_2^d	S ⁺	3 S—Mo	82°
$Co_2(As_4)_2$	As ⁻	2 As—As	90°
$CaSi_2$	Si	3 Si—Si	103° between Si—Si bonds
HgI_2	I ⁺	2 Hg—I	103°
GeI_4	Ge	4 Ge—I	109.5°
SnI_4	Sn	4 Sn—I	109.5°
As_4O_6	As	3 As—O	109.5°
	O	2 O—As	109.5°
Sb_4O_6	Sb	3 Sb—O	109.5°
	O	2 O—Sb	109.5°
$NaClO_3^c$	Cl ⁺⁺	3 Cl—O	109.5°
$KClO_3$	Cl ⁺⁺	3 Cl—O	109.5°
$KBrO_3$	Br ⁺⁺	3 Br—O	109.5°

^a Data for which no reference is given are from the *Strukturbericht* of P. P. Ewald and C. Hermann. ^b R. W. G. Wyckoff, *Z. Krist.*, 75, 529 (1930). ^c W. H. Zachariasen, *ibid.*, 71, 501, 517 (1929). ^d The very small paramagnetic susceptibility of pyrite requires the presence of electron-pair bonds, eliminating an ionic structure $Fe^{++}S_2^{--}$. Angles are calculated for FeS_2 , for which the parameters have been most accurately determined. The parameter value (correct value $u = 0.371$) and interatomic distances for molybdenite are incorrectly given in the *Strukturbericht*.

that the bond eigenfunctions will deviate less and less from pure p eigenfunctions in this order, and this evidences itself in a closer approach of the bond angle to 90° in the series. Geometrical effects sometimes affect the bond angles, as in As_4O_6 and Sb_4O_6 , where a decrease in the oxygen bond angle would necessarily be accompanied by an increase in that for the other atom, and in molybdenite and pyrite.

Many compounds with tetrahedral structures (diamond, sphalerite, wurzite, carborundum, etc.) are known, in which the four bonds have tetrahedral angles. Tetrahedral atoms in such crystals include C (diamond, SiC), Si, Ge, Sn, Cl^{3+} (in CuCl), Br^{3+} , I^{3+} , O^{++} (in Cu_2O and ZnO), S^{++} , Se^{++} , Te^{++} , N^+ (in AlN), P^+ , As^+ , Sb^+ , Bi^+ , Cu^- , Zn^- , Cd^- , Hg^- , Al^- , Ga^- and In^- .

The Valence of Atoms.—In the last paragraph and in Table I the atoms are represented with electrical charges which are not those usually seen. These charges are obtained by the application of Rule 1, according to which an electron-pair bond is formed by one electron from each of the two atoms (even though as the atoms separate the type of bonding may change in such a way that both electrons go over to one atom). Accordingly in determining the state of ionization of the atoms in a molecule or crystal containing electron-pair bonds each shared electron-pair is to be split between the two atoms. In this way every atom is assigned an electrovalence obtained by the above procedure and a covalence equal to the number of its shared electron-pair bonds.

It is of interest to note that a quantity closely related to the "valence" of the old valence theory is obtained for an atom by taking the algebraic sum of the electrovalence and of the covalence, the latter being given the positive sign for metals and the negative sign for non-metals. For example, oxygen in OH^- is O^- with a covalence of 1, in H_2O it is O with a covalence of 2, in H_3O^+ it is O^+ with a covalence of 3, and in crystalline ZnO it is O^{++} with a covalence of 4; in each case the above rule gives -2 for its valence.

Trigonal Quantization.—We have seen that an atom with s - p quantization unchanged will form three equivalent bonds at 90° to one another. If quantization is changed, the three strongest bonds will lie at tetrahedral angles. But increase in the bond angle beyond the tetrahedral angle is not accompanied by a very pronounced decrease in bond strength. Thus three equivalent bond eigenfunctions in a plane, with maxima 120° apart, can be formed

$$\left. \begin{aligned} \psi_1 &= \frac{1}{\sqrt{3}} s + \sqrt{\frac{2}{3}} p_x \\ \psi_2 &= \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y \\ \psi_3 &= \frac{1}{\sqrt{3}} s - \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y \end{aligned} \right\} \quad (10)$$

and these have a strength of 1.991, only a little less than that 2.000 of tetrahedral bonds (Fig. 6). As a result, we may anticipate that in some cases the bond angles will be larger than $109^{\circ}28'$. The carbonate ion in calcite and the nitrate ion in sodium nitrate are assigned a plane configuration from the results of x-ray investigations. In these ions the oxygen atoms are only 2.25 Å. from one another, so that their characteristic repulsive forces must be large, resisting decrease in the bond angle (the smallest distance observed between oxygen ions in ionic crystals is 2.5 Å.). But repulsion of the oxygen atoms would not be very effective in increasing the bond angle in the neighborhood of 120° , so that we might expect equilibrium to be achieved at a somewhat smaller angle, such as 118° . This would give CO_3^{2-} and NO_3^- a

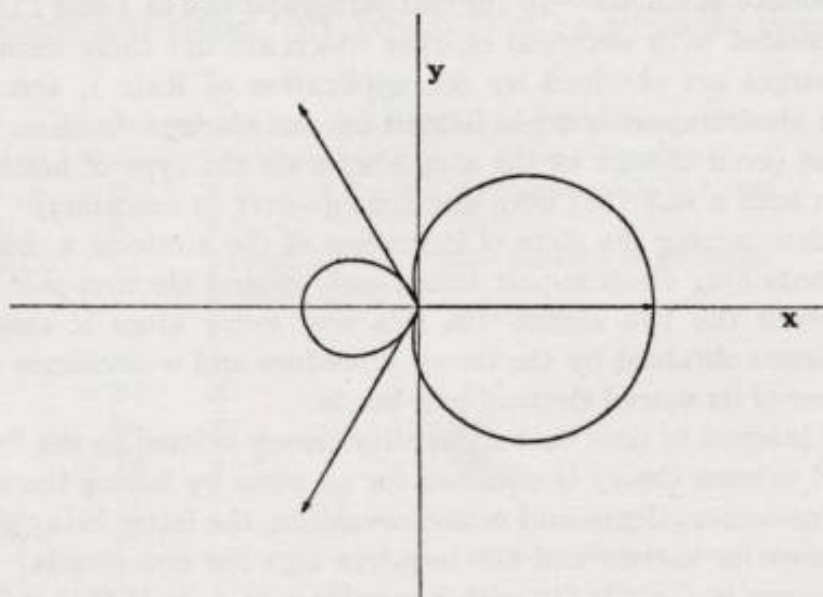


Fig. 6.—Polar graph of $\left| \frac{1}{\sqrt{3}} + \sqrt{2} \cos \varphi \right|$ in the xy plane, representing a trigonal eigenfunction. The maximum directions of the other two equivalent eigenfunctions are also shown.

pyramidal structure, like that of NH_3 . There would be two configurations possible for a given orientation of the O_3 plane, one in which the carbon (or nitrogen) atom was a short distance above this plane (taken as horizontal) and one with it below the plane. If there is appreciable interaction between these two, as there will be in case the pyramid is flat, the symmetric and antisymmetric combinations of the two will be the correct eigenfunctions, corresponding to the rapid inversion of the pyramid, with a frequency of the order of magnitude of the vibrational frequency of the complex ion along its symmetry axis. This inversion would introduce an effective symmetry plane normal to the three-fold axis, so that a pyramidal structure with rapid inversion is compatible with the x-ray observations.²⁶

²⁶ Simulation of symmetry by molecules or complex ions in crystals has been discussed by Linus Pauling, *Phys. Rev.*, 36, 430 (1930).

Thus the x-ray data do not decide between this structure and a truly plane structure. Evidence from another source is at hand, however. A plane CO_3^{2-} or NO_3^- ion should show three characteristic fundamental vibrational frequencies. These have been observed as reflection maxima in the infra-red region. But two of the maxima, at 7μ and 14μ , are double,²⁷ and this doubling, which is not explicable with a plane configuration, is just that required by a pyramidal structure, the separation of the components giving the frequency of inversion of the pyramid.²⁸

In graphite each carbon atom is bound to three others in the same plane; and here the assumption of inversion of a puckered layer is improbable, because of the number of atoms involved. A probable structure is one in which each carbon atom forms two single bonds and one double bond with other atoms. These three bonds should lie in a plane, with angles $109^\circ 28'$ and $125^\circ 16'$, which are not far from 120° . Two single bonds and a double bond should be nearly as stable as four single bonds (in diamond), and the stability would be increased by the resonance terms arising from the shift of the double bond from one atom to another. But this problem and the closely related problem of the structure of aromatic nuclei demand a detailed discussion, perhaps along the lines indicated, before they can be considered to be solved.

The Structures of Simple Molecules.—The foregoing considerations throw some light on the structure of very simple molecules in the normal and lower excited states, but they do not permit such a complete and accurate discussion of these questions as for more complicated molecules, because of the difficulty of taking into consideration the effect of several unshared and sometimes unpaired electrons. Often the bond energy is not great enough to destroy s - p quantization, and the interaction between a bond and unshared electrons is more important than between a bond and other shared electrons because of the absence of the effect of concentration of the eigenfunctions.

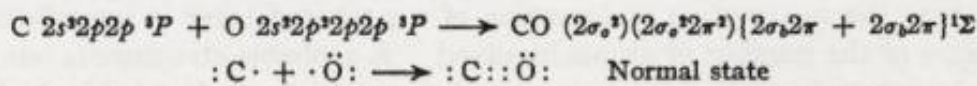
Let us consider an atom forming a bond with another atom in the direction of the z axis. Then p_z and s form two eigenfunctions designated σ , p_x and p_y two designated π (one with a resultant moment of $+1$ along the z axis, one with -1). If s - p quantization is not broken, the strongest bond will be formed by p_z , and weaker ones by π . If s - p quantization is broken, new eigenfunctions σ_b and σ_o will be formed from s and p_z . In this case the strongest bond is formed by the σ_b eigenfunction, which extends out toward the other atom, weaker ones are formed by π_+ and π_- , and an extremely weak one, if any, by σ_o . We can also predict the stability of

²⁷ C. Schaefer, F. Matossi and F. Dane, *Z. Physik*, **45**, 493 (1927).

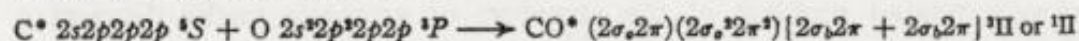
²⁸ The normal states of these ions are similar to certain excited states of ammonia, which also show doubling. The frequency of inversion of the normal ammonia molecule is negligibly small.

unshared electrons; σ_o , involving s with its greater penetration of the atom core, will be more stable than π .

As examples we may discuss CO, CN, N₂ and NO. CO might be composed of normal or excited atoms, or even of ions. A neutral oxygen atom can form only two bonds. Hence a normal carbon atom, 3P , which can also form two bonds, is at no disadvantage. We can write the following reaction, using symbols similar to those of Lennard-Jones²⁹ and Dunkel,³⁰ whose treatments of the electronic structure of simple molecules have several points of similarity with ours

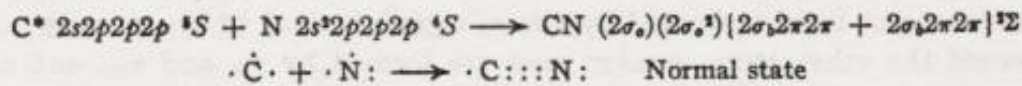


Here symbols in parentheses represent unshared electrons attached to C and O, respectively, and those in braces represent shared electrons. An excited carbon atom 5S lies about 1.6 v. e. above the normal state, but can still form only a double bond with oxygen, so that the resultant molecule should be excited. We write



The resultant states are necessarily Π , for σ_b and one π are used for the bond, leaving on C σ_o and π . These two electrons may or may not pair with one another, giving $^1\Pi$ and $^3\Pi$, respectively. Of these $^3\Pi$ should be the more stable, for the two electrons are attached essentially to one atom, and the rules for atomic spectra should be valid. This is substantiated; the observed excited states $^3\Pi$ and $^1\Pi$ lie at 5.98 and 7.99 v. e., respectively. Another way of considering these three states is the following: to go from $:\text{C}::\ddot{\text{O}}:$ to $\cdot\dot{\text{C}}::\ddot{\text{O}}:$ we lift an electron from the more deeply penetrating σ_o orbit to π ; about 6–8 v. e. is needed for this, and the resultant state is either $^3\Pi$ or $^1\Pi$. This viewpoint does not necessitate the discussion of products of dissociation.

CN is closely similar. The normal nitrogen atom, $2s^2 2p^2 \text{ } ^4S$, can form three bonds, and more cannot be formed by an excited neutral atom (with five L electrons), so that there is no reason to expect excitation. But a normal carbon atom can form only a double bond, and an excited carbon atom, only 1.6 v. e. higher, can form a triple bond, which contributes about 3 v. e. more than a double bond to the bond energy. Hence we write

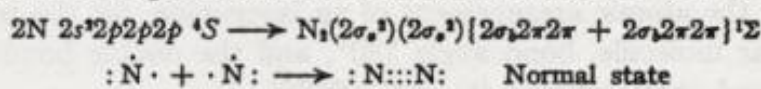


The first excited state of the molecule, $:\text{C}::\dot{\text{N}}:$, is built from normal atoms, and has the term symbol $^3\Pi$. It lies 1.78 v. e. above the normal state.

²⁹ J. E. Lennard-Jones, *Trans. Faraday Soc.*, 25, 668 (1929).

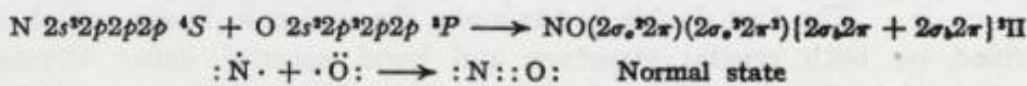
³⁰ M. Dunkel, *Z. physik. Chem.*, B7, 81 (1930).

Two normal nitrogen atoms form a normal molecule with a triple bond.



All other states lie much higher.

A normal oxygen atom and a normal nitrogen atom form a normal NO molecule with a double bond.



This treatment sometimes fails for symmetrical molecules. Thus $:\ddot{O}::\ddot{O}: \ ^1\Sigma$ would be predicted for the normal state of O_2 , whereas the observed normal state, $^3\Sigma$, lies 1.62 v. e. below this. It seems probable that the additional degeneracy arising from the identity of the two atoms gives rise to a new type of bond, the *three-electron bond*, and that in normal O_2 there are one single bond and two three-electron bonds, $:\ddot{O}::\ddot{O}: \ ^3\Sigma$; a definite decision regarding this question must await a detailed quantum-mechanical treatment. Evidence regarding the oxygen-oxygen single bond is provided by O_4 , with the square structure $\begin{array}{cc} \ddot{O} & \ddot{O} \\ \ddot{O} & \ddot{O} \end{array}$. The 90°

bond angles are expected, since quantization in s and p eigenfunctions is not changed. The equality in energy of O_4 and $2O_2$ leads to an energy of 58,000 cal. per mole per single bond in O_4 ; the difference between this value and that for a carbon-carbon single bond (100,000 cal.) shows the greater bond-forming power of tetrahedral eigenfunctions over p eigenfunctions. Ozone, which very probably has the symmetrical arrangement

$\begin{array}{c} \ddot{O} \\ \ddot{O} : \ddot{O} \end{array}$, has 60° bond angles, and this distortion from the most favorable bond angle of 90° shows up in the bond energy, for the heat of formation of $-34,000$ cal. per mole leads to 47,000 cal. per mole per single bond, a decrease of 11,000 cal. over the favored O_4 bonds.

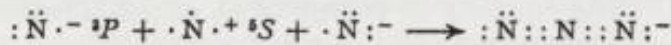
For some polyatomic molecules predictions can be made regarding the atomic arrangement from a knowledge of the electronic structure or *vice versa*. Thus $\cdot C::N: \ ^2\Sigma$ can form a bond through the unpaired σ_o electron of carbon, and this bond will extend along the CN axis. Hence the molecules $H:C::N:$, $:N::C:C::N:$ and $:\ddot{Cl}:C::N:$ should be linear. This is verified by band spectral data.¹¹ The isocyanides, RNC, such as H_3CNC , may be given either a triple or a double bond structure: $R:N::C:$ or $R:\ddot{N}::C:$. The first of these is built of the ions $N^+ \ ^4S$ and $C^- \ ^4S$, which may be an argument in favor of the second structure, built of normal

¹¹ Private communication from Professor Richard M. Badger of this Laboratory, who has kindly provided me with much information concerning the results of band spectroscopy.

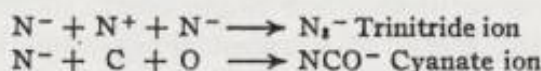
atoms.³² A decision between the two alternatives could be made by determining the atomic arrangement of an isocyanide, for the triple bond gives a linear molecule, bond angle 180° , and the double bond a kinked molecule, bond angle between 90 and $109^\circ 28'$.

The molecules and complex ions containing three kernels and sixteen L electrons form an interesting group. Of these CO_2 , formed from excited carbon 5S and normal oxygen atoms, would have the structure $:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$. The two double bonds make the molecule linear, which is verified by both crystal structure and band spectral data. Crystal structure data also show N_2O to be linear, although it is not known whether or not the molecule has oxygen in the middle or at one end, as first suggested by Langmuir³³ and supported by the kernel-repulsion rule.³⁴ The known linear arrangement eliminates structures built of neutral atoms, $:\ddot{\text{N}}:\text{O}:\ddot{\text{N}}:$ and $:\ddot{\text{N}}::\ddot{\text{N}}::\ddot{\text{O}}:$, for these have bond angles between 90 and 125° . The structures $:\ddot{\text{N}}::\ddot{\text{N}}::\ddot{\text{O}}:$ and $:\ddot{\text{N}}::\text{O}::\ddot{\text{N}}:$, built from $\text{N N}^+ \text{O}^-$ and $\text{N}^- \text{O}^{++} \text{N}^-$, respectively, would both be linear, and so compatible with the known arrangement. An *a priori* decision between them is difficult, although previously advanced arguments favor the unsymmetrical structure. Band spectra should soon decide the question.

The trinitride, cyanate, and isocyanate ions, the first two of which are known³⁵ to be linear, no doubt have identical electronic structures.



or



The fulminate ion, CNO^- , probably has a structure intermediate between $:\ddot{\text{C}}::\text{N}::\ddot{\text{O}}:^-$ and $:\text{C}::\text{N}::\ddot{\text{O}}:^-$; for since these two bond types have the same bond angles and term symbols ($^1\Sigma$), they can form intermediate structures lying anywhere between the two extremes. Which extreme is the more closely approached could be determined from a study of the bond angles in un-ionized fulminate molecules, such as AgCNO or ONCHgCNO , for the first structure would lead to an angle of 125° between the CNO axis and the metal-carbon bond, the second to an angle of 180° .

Bonds Involving d -Eigenfunctions.—When d eigenfunctions as well as s and p can take part in bond formation, the number and variety of bonds which can be formed are increased. Thus with an s , a p and a d subgroup as many as nine bonds can be formed by an atom. It is found from a

³² Thus W. Heitler and G. Rumer, *Nachr. Ges. Wiss. Göttingen, Math. physik. Klasse*, 7, 277 (1930), in a paper on the quantum mechanics of polyatomic molecules, discuss only the second structure.

³³ I. Langmuir, *THIS JOURNAL*, 41, 1543 (1919).

³⁴ Linus Pauling and S. B. Hendricks, *ibid.*, 48, 641 (1926).

³⁵ S. B. Hendricks and Linus Pauling, *THIS JOURNAL*, 47, 2904 (1925).

consideration of the eigenfunctions that all cannot be equivalent, but six equivalent bonds extending toward the corners of either a regular octahedron or a trigonal pyramid, four extending toward the corners of a tetrahedron or a square, etc., can be formed; and the strength and mutual orientation of the bonds are determined by the number of d eigenfunctions involved in their formation.

There are five d eigenfunctions in a subgroup with $l = 2$ and with given n . They are

$$\left. \begin{aligned} d_z &= \sqrt{5/4} (3 \cos^2 \theta - 1) \\ d_{y+z} &= \sqrt{15} \sin \theta \cos \theta \cos \varphi \\ d_{x+z} &= \sqrt{15} \sin \theta \cos \theta \sin \varphi \\ d_{x+y} &= \sqrt{15/4} \sin^2 \theta \sin 2\varphi \\ d_x &= \sqrt{15/4} \sin^2 \theta \cos 2\varphi \end{aligned} \right\} \quad (11)$$

or any set of five orthogonal functions formed by linear combination of these. These functions are not well suited to bond formation. d_{y+z} , d_{x+z} and d_{x+y} , which are similarly related to the x , y and z axes, respectively, have the form shown in Fig. 7. Each eigenfunction has maxima in

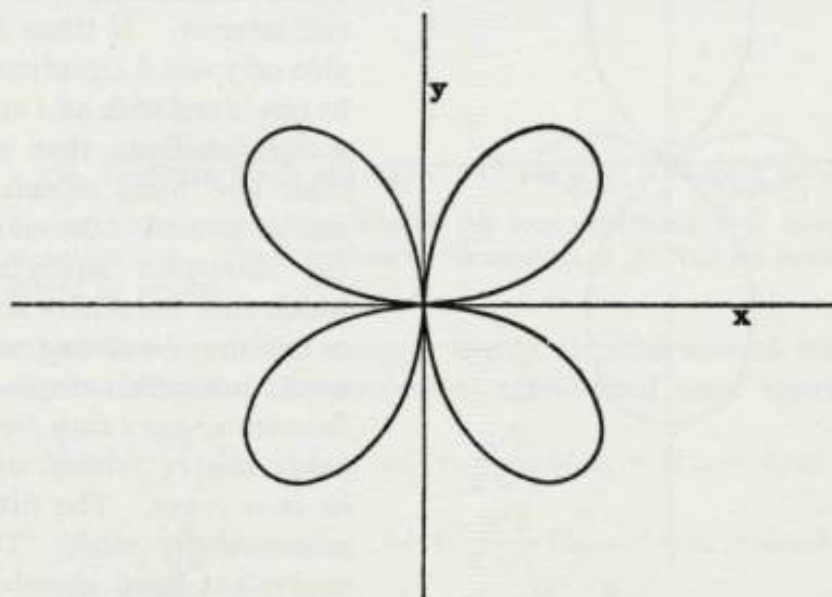


Fig. 7.—Polar graph of $\left| \frac{\sqrt{15}}{2} \sin^2 \theta \sin 2\varphi \right|$ in the xy plane, representing the d_{x+y} eigenfunction.

four directions. d_x is similar in shape, differing from d_{x+y} only in a rotation of 45° about the z axis. d_z , shown in Fig. 8, has two maxima along the z axis, and a girdle about its waist.

Assuming as before that the dependence on r of the s , p and d eigenfunctions under discussion is not greatly different, the best bond eigenfunctions can be determined by the application of the treatment already applied to s and p alone, with the following results.

The best bond eigenfunction which can be obtained from s , p and d is

$$\frac{1}{3}s + \frac{1}{\sqrt{3}}p_z + \frac{\sqrt{5}}{3}d_z$$

and has a strength of 3. The best two equivalent bond eigenfunctions involving one d eigenfunction

$$\frac{1}{2\sqrt{3}}s + \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z \quad \text{and}$$

$$\frac{1}{2\sqrt{3}}s - \frac{1}{\sqrt{2}}p_z + \frac{\sqrt{5}}{2\sqrt{3}}d_z$$

are oppositely directed and have a strength of 2.96.

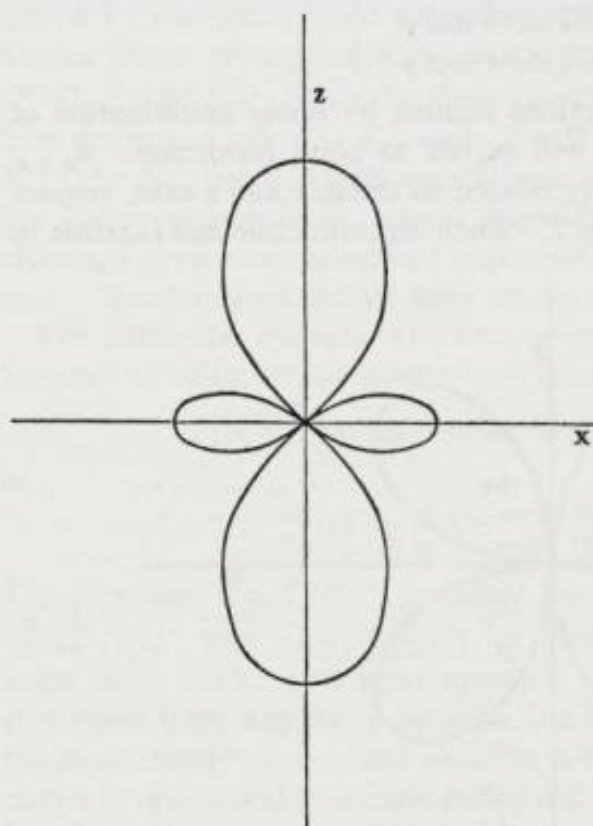


Fig. 8.—Polar graph of $\left| \frac{\sqrt{5}}{2} (3 \cos^2 \theta - 1) \right|$ in the xz plane, representing the d_z eigenfunction.

The atoms of the transition elements, for which d eigenfunctions need to be considered, are of such a size as usually to have a coordination number of 4 or 6, so that four or six equivalent bond eigenfunctions are here of especial interest. If there is available only one d eigenfunction to be combined with an s and three p eigenfunctions, then no more than five bond eigenfunctions can be formed. One may have the maximum strength 3, in which case the others are weak; or two may be strong and three weak; but *with a single d eigenfunction no more than four strong bonds can be formed, and these lie in a plane.* The fifth bond is necessarily weak. The four equivalent bond eigenfunctions formed from s , p and one d eigenfunction are

$$\left. \begin{aligned} \psi_1 &= \frac{1}{2}s + \frac{1}{2}d_z + \frac{1}{\sqrt{2}}p_x \\ \psi_2 &= \frac{1}{2}s + \frac{1}{2}d_z - \frac{1}{\sqrt{2}}p_x \\ \psi_3 &= \frac{1}{2}s - \frac{1}{2}d_z + \frac{1}{\sqrt{2}}p_y \\ \psi_4 &= \frac{1}{2}s - \frac{1}{2}d_z - \frac{1}{\sqrt{2}}p_y \end{aligned} \right\} \quad (12)$$

One of these is shown in Fig. 9. These all have their maxima in the xy plane, directed toward the corners of a square. The strength of these bond eigenfunctions, 2.694, is much greater than that of the four tetrahedral eigenfunctions formed from s and p alone (2.00). But if three d

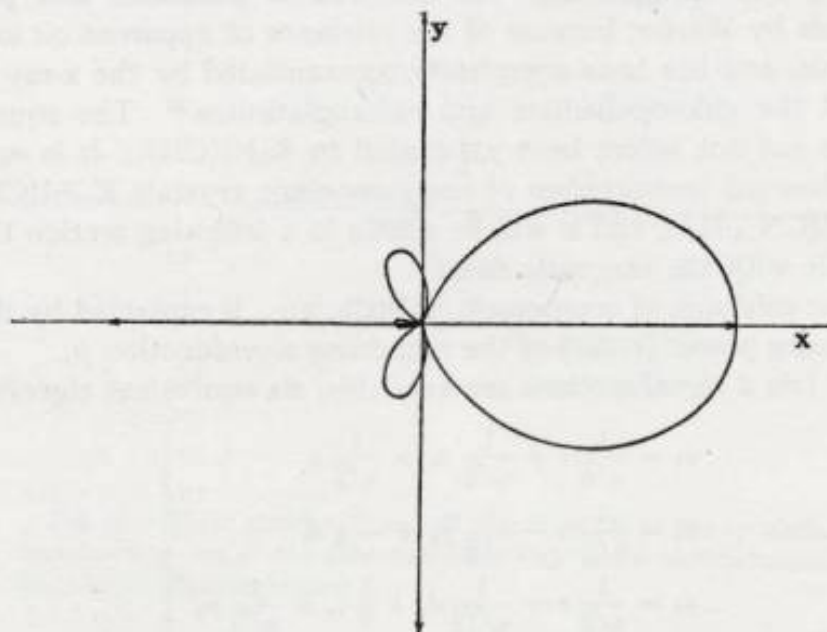


Fig. 9.—Polar graph of $\left| \frac{1}{2} + \frac{\sqrt{3}}{2} \cos \varphi + \frac{\sqrt{15}}{4} \cos 2 \varphi \right|$ in the xy plane, representing one of the four equivalent dsp^3 bond eigenfunctions. The directions of the maxima of the four are represented by arrows.

eigenfunctions are available, stronger bonds directed toward tetrahedron corners can be formed. The equivalent tetrahedral bond eigenfunctions

$$\begin{aligned}\psi_{\text{III}} &= \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x + p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} + d_{x+z} + d_{x+y}) \\ \psi_{\text{I}\overline{\text{II}}} &= \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(p_x - p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(d_{y+z} - d_{x+z} - d_{x+y}) \\ \psi_{\text{II}\overline{\text{I}}} &= \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x + p_y - p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} + d_{x+z} - d_{x+y}) \\ \psi_{\text{III}\overline{\text{I}}} &= \frac{1}{2}s + \frac{\sqrt{3}}{4\sqrt{2}}(-p_x - p_y + p_z) + \frac{\sqrt{5}}{4\sqrt{2}}(-d_{y+z} - d_{x+z} + d_{x+y})\end{aligned}$$

have a strength of 2.950, nearly equal to the maximum 3. These leave only two pure d eigenfunctions behind, however, the others being part d and part p . Thus we conclude that if there are three d eigenfunctions available, a transition group element forming four electron-pair bonds will direct them toward tetrahedron corners. Examples of such bonds are provided by CrO_4^{2-} , MoO_4^{2-} , etc. Only when one d eigenfunction alone is available will the four bonds lie in a plane. In compounds of bivalent

nickel, palladium, and platinum, such as $K_2Ni(CN)_4$, $K_2Pd(CN)_4$, K_2PtCl_4 , etc., there are eight unshared d electrons on each metal atom, which occupy four of the five d eigenfunctions. Hence the four added atoms or groups lie in a plane at the corners of a square about the metal atom. Such a configuration was assigned to palladous and platinous compounds by Werner because of the existence of apparent *cis* and *trans* compounds, and has been completely substantiated by the x-ray investigation of the chloropalladites and chloroplatinites.³⁶ The square configuration has not before been attributed to $K_2Ni(CN)_4$; it is supported by the observed isomorphism of the monoclinic crystals $K_2Pd(CN)_4 \cdot H_2O$ and $K_2Ni(CN)_4 \cdot H_2O$, and it will be shown in a following section that it is compatible with the magnetic data.

The non-existence of compounds K_2PtCl_6 , etc., is explained by the weak bond-forming power (1.732) of the remaining eigenfunction p_z .

Now if two d eigenfunctions are available, six equivalent eigenfunctions

$$\left. \begin{aligned} \psi_1 &= \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{2}} p_z + \frac{1}{\sqrt{3}} d_z \\ \psi_2 &= \frac{1}{\sqrt{6}} s - \frac{1}{\sqrt{2}} p_z + \frac{1}{\sqrt{3}} d_z \\ \psi_3 &= \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_x + \frac{1}{2} d_y + \frac{1}{\sqrt{2}} p_x \\ \psi_4 &= \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_x + \frac{1}{2} d_y - \frac{1}{\sqrt{2}} p_x \\ \psi_5 &= \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_x - \frac{1}{2} d_y + \frac{1}{\sqrt{2}} p_y \\ \psi_6 &= \frac{1}{\sqrt{6}} s + \frac{1}{\sqrt{12}} d_x - \frac{1}{2} d_y - \frac{1}{\sqrt{2}} p_y \end{aligned} \right\} \quad (13)$$

can be formed. These form strong bonds, of strength 2.923, directed toward the corners of a regular octahedron; and no stronger octahedral bonds can be formed even though more d eigenfunctions be available (Figs. 10 and 11). Hence we expect transition group atoms with six or less unshared electrons to form six electron-pair bonds. Examples of such compounds are numerous: $PtCl_6^{2-}$, $Fe(CN)_6^{3-}$, etc., although the definite assignment of an electron-pair bond structure rather than an ionic structure (as in FeF_6^{3-} , formed of Fe^{+++} and 6 F^-) can be made only after the discussion of paramagnetic susceptibility.

I have not succeeded in determining whether or not these octahedral eigenfunctions are the strongest six equivalent bond eigenfunctions which can be formed when more than two d 's are available. The known structure of molybdenite, MoS_3 , suggests that six bonds directed toward the corners of a trigonal prism are stable; but only a small increase in bond strength can possibly be obtained (from 2.923 to not over 3), and the mutual re-

³⁶ R. G. Dickinson, *THIS JOURNAL*, 44, 2404 (1922).

pulsion of the six atoms or groups will in most cases overcome this, if it does exist, and leave the octahedral configuration the stable one.

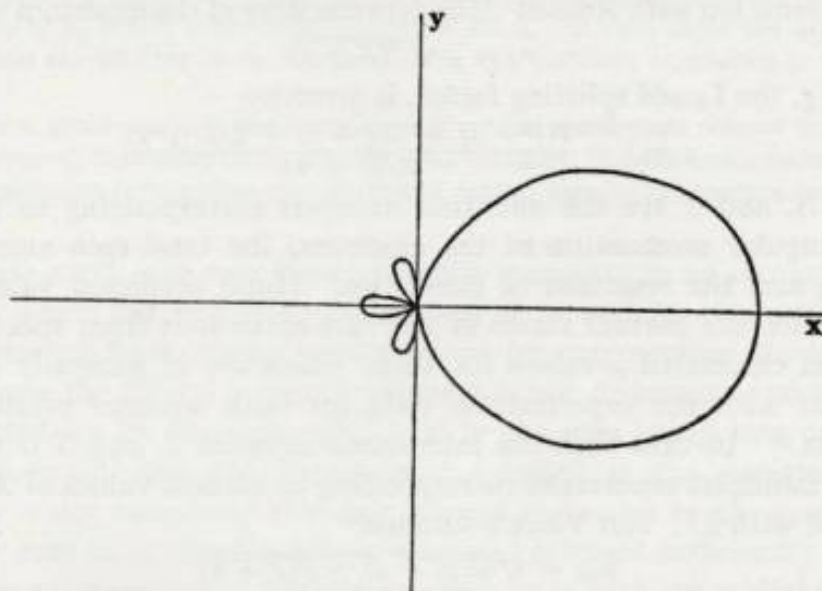


Fig. 10.—Polar graph of $|\psi_1|$ of Equation 13, in the xy plane, representing one of the six equivalent d^2sp^3 bond eigenfunctions (octahedral eigenfunctions).

II. The Magnetic Moments of Molecules and Complex Ions

The theory of the paramagnetic susceptibility of substances has been developed gradually over a long period of years through the efforts of a number of investigators. The theoretical calculation of the magnetic moments of complex molecules and ions has in particular attracted much attention recently, and both theoretical and empirical considerations have been used in developing rules applicable in various cases. The work reported in this paper provides little more than the justification and unification of previously developed rules. This finishing touch is, however, of much significance for the problem of the nature of the chemical bond; for it, in conjunction with the quantum mechanical discussion of the previous sections, permits definite conclusions to be drawn regarding type of bond in many molecules and complex ions from a knowledge of their magnetic moments, and conversely provides the basis for the definite prediction of magnetic moments from a knowledge of the type of bonds and the atomic arrangement.

The calculation of the magnetic moments of the rare-earth ions by

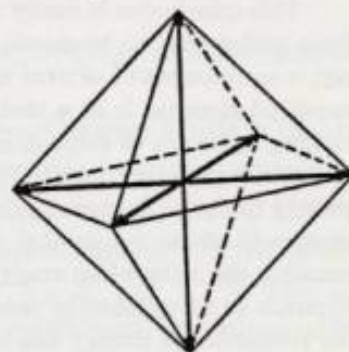


Fig. 11.—Diagram showing relative orientation in space of the directions of the maxima of the octahedral eigenfunctions.

Hund³⁷ in 1926 and of oxygen and nitric oxide by Van Vleck³⁸ in 1928 were triumphs of the theory of spectra. The magnetic moment of an atom or monatomic ion with Russell-Saunders coupling of the quantum vectors is

$$\mu_J = g \sqrt{J(J+1)}$$

in which g , the Landé splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Here L , S , and J are the quantum numbers corresponding to the total orbital angular momentum of the electrons, the total spin angular momentum, and the resultant of these two. Hund predicted values of L , S , and J for the normal states of the rare-earth ions from spectroscopic rules, and calculated μ -values for them which are in generally excellent agreement with the experimental data for both aqueous solutions and solid salts.³⁹ In case that the interaction between L and S is small, so that the multiplet separation corresponding to various values of J is small compared with kT , Van Vleck's formula³⁸

$$\mu_{LS} = \sqrt{4S(S+1) + J(J+1)}$$

is to be used.

But similar calculations for the iron-group ions show marked disagreement with experiment, and many attempts were made to explain the discrepancies. The explanation is simple: *in many condensed systems the perturbing effect of the atoms or molecules surrounding a magnetic atom destroys the contribution of the orbital momentum to the magnetic moment, which is produced entirely by the spin moments of unpaired electrons.*⁴⁰

This conclusion is easily deduced from the consideration of the nature of eigenfunctions giving rise to magnetic moments. In an atom containing unpaired p electrons, say, a component of orbital magnetic moment of $\pm(h/2\pi) \cdot (e/2mc)$ is obtained when an unpaired electron is in a state given by the eigenfunction $p_x \pm i p_y$. Now if the perturbing influence of surrounding atoms or molecules is such as to make the perturbation energy for the eigenfunction p_x or p_y or any combination of them other than $p_x \pm i p_y$ greater than the field energy, this will be the correct zeroth order eigenfunction, and the atom will show no orbital magnetic moment. In an atom with Russell-Saunders coupling the interaction energy of L and S takes the place of the field energy, so that the criterion to be satisfied in order that the magnetic moment due to L be destroyed is that the perturbation energy due to surrounding atoms and ions be greater than the multiplet separation, which for the iron-group ions is of the order of magnitude of 1 v. e.⁴¹

³⁷ F. Hund, *Z. Physik*, 33, 345 (1925).

³⁸ J. H. Van Vleck, *Phys. Rev.*, 31, 587 (1928).

³⁹ The few discrepancies have been accounted for by S. Freed [THIS JOURNAL, 52, 2702 (1930)] and J. H. Van Vleck and A. Frank [*Phys. Rev.*, 34, 1494 (1929), and a paper delivered at the Cleveland meeting of the American Physical Society, December 31, 1930].

⁴⁰ This assumption was first made by E. C. Stoner, *Phil. Mag.*, 8, 250 (1929), in order to account for the observed moments of iron-group ions.

⁴¹ Essentially the same conclusion has been announced by J. H. Van Vleck at the Cleveland meeting of the American Physical Society, December 31, 1930.

If the perturbation function shows cubic symmetry, and in certain other special cases, the first-order perturbation energy is not effective in destroying the orbital magnetic moment, for the eigenfunction $p_x \pm i p_y$ leads to the same first-order perturbation terms as p_x or p_y or any other combinations of them. In such cases the higher order perturbation energies are to be compared with the multiplet separation in the above criterion.

In linear molecules only the component of orbital momentum normal to the figure axis is destroyed, that along the figure axis being retained. In non-linear molecules with strong interatomic interactions the concept of orbital angular momentum loses its significance.

The rare-earth ions owe their magnetic moments to an incompleting 4f subshell, which lies within an outer shell of 5s and 5p electrons, and is thus protected from strong perturbations by surrounding atoms. As a consequence the orbital magnetic moment is not destroyed, and the ion is not affected by its environment. But in the iron-group ions and other transition-group ions the incompleting subshell is the outermost one. Hence it is not surprising that the solvent molecules or the surrounding atoms or ions in a complex ion or a crystal interact sufficiently strongly with these atoms or ions to destroy, in whole, or in part, the orbital magnetic moment, leaving the spin moment, with perhaps a small contribution from the orbital moment in border-line cases. We can state with certainty that the formation of electron-pair bonds will destroy the orbital moment.

This greatly simplifies the theory of the magnetic moments of molecules and complex ions. *The magnetic moment of a molecule or complex ion is determined entirely by the number of unpaired electrons, being equal to*

$$\mu_S = 2\sqrt{S(S+1)}$$

in which S is one-half that number. The factor 2 is the g -factor for electron spin.

As a matter of fact, Sommerfeld⁴³ in 1924, a year before Hund's treatment of the rare-earth ions, noticed that the observed magnetic moments of K^+ and Ca^{++} , Ca^+ (spectroscopic), Ca (spectroscopic), Cr^{3+} , Cr^{++} , Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} , Cu^{++} and Cu^+ are approximately reproduced by the above equation with $S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 2, \frac{3}{2}, 1, \frac{1}{2}$ and 0, respectively. But with the development of spectral theory he apparently gave up this simple formula because of lack of a theoretical derivation of it, and it remained for Bose⁴⁴ in 1927 to state explicitly the assumption that only S contributes to the moment in these cases, without, however, explaining why L gives no contribution, and for Stoner⁴⁵ in 1929 to supply the explanation. The comparison of calculated and observed values is given in Table I. It may be pointed out that S increases to a maximum value of $\frac{5}{2}$ when the 3d subgroup is half filled; Pauli's principle requires that succeeding electrons decrease the spin, so that μ_S is symmetrical about

⁴³ A. Sommerfeld, "Atombau," 4th ed., p. 639.

⁴⁴ D. M. Bose, *Z. Physik*, 43, 864 (1927).

this point. The agreement with experiment, while much better than for μ_J , is not perfect; ions with more than five 3d electrons are found to have moments larger than μ_S , while V^{3+} deviates in the other direction. Bose suggested that perhaps S could in some cases exceed the maximum value allowed by Pauli's principle, but the obviously correct explanation is that the perturbing effect of surrounding atoms is not sufficient completely to destroy the L moment. Hence the observed moment should lie between μ_S and μ_J , which it does in every case.

Since the interaction is not strong enough to destroy the L moment, we conclude that in aqueous solution and in some crystalline salts the atoms⁴⁴ Fe^{II} , Co^{III} , Co^{II} , Ni^{II} and Cu^{II} do not form strong electron-pair bonds with H_2O , Cl , or certain other atoms, the bonds instead being ion-dipole or ionic bonds.

The formation of a stable coordination compound involving the four tetrahedral sp^3 eigenfunctions might decrease the L contribution appreciably. It was indeed pointed out by Bose that in the compounds listed in the last column of Table II the observed moments approach more closely the theoretical values μ_S .

The Magnetic Moments of Complexes with Electron-Pair Bonds.—The peculiar magnetic behavior of some complex ions has attracted much attention. $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, for example, have $\mu = 2.0$ and 0.00, respectively, instead of the values 5.9 and 4.9 for Fe^{3+} and Fe^{++} . Welo and Baudisch⁴⁵ and later Sidgwick and Bose expressed essentially the following rule: the magnetic moment of a complex is the same as that of the atom with the same number of electrons as the central atom of the complex, counting two for each electron-pair bond. Fe^{++} has 24 electrons; adding 12 for the six bonds gives 36, the electron number of krypton, so that the diamagnetism of the ferrocyanide ion is explained. This rule is satisfactory in many cases, but there are also many exceptions. Thus $[Ni(CN)_4]^{2-}$ is diamagnetic, although the above rule would make it as paramagnetic as $[Ni(NH_3)_4]^{++}$.

The whole question is clarified when considered in relation to the foregoing quantum mechanical treatment of the electron-pair bond. For the iron-group elements the following rules follow directly from that treatment and from the rules of line spectroscopy.

1. *Bond eigenfunctions for iron-group atoms are formed from the nine eigenfunctions $3d^5$, $4s$ and $4p^3$, as described in preceding sections. One bond eigenfunction is needed for each electron-pair bond.*

2. *The remaining (unshared) electrons are to be introduced into the 3d eigenfunctions not involved in bond formation.*

⁴⁴ The symbol Fe^{II} is used for bivalent iron, etc., when the type of bond is undetermined.

⁴⁵ L. A. Welo and O. Baudisch, *Nature*, 116, 806 (1925).

TABLE II
MAGNETIC MOMENTS OF IRON-GROUP IONS*

Ion	Normal state	μ_J	μ_g	Obs. moment in aqueous soln.	Solid salts, probable coordination number 6	Solid salts, coordination number
K ⁺ , Ca ⁺⁺ , Sc ³⁺ , Ti ⁴⁺	1S ₀	0.00	0.00	0.00		
V ³⁺	³ D _{3/2}	1.55	1.73	1.7		
V ⁴⁺	³ F ₂	1.68	2.83	2.4		
V ⁺⁺ , Cr ³⁺	⁴ F _{3/2}	0.78	3.88	3.8-3.9	Cr ₂ O ₃ ·7H ₂ O CrCl ₃	3.85 3.81
Cr ⁺⁺ , Mn ⁴⁺	³ D ₅	0.00	4.90	4.8-4.9	MnCl ₂	5.75
Mn ⁺⁺ , Fe ³⁺	⁴ S _{3/2}	5.91	5.91	5.8	MnSO ₄ MnSO ₄ ·4H ₂ O Fe ₂ (SO ₄) ₃ (NH ₄) ₂ Fe ₂ (SO ₄) ₄	5.67 5.87 5.86 5.86
Fe ⁺⁺ , Co ³⁺	⁴ D ₅	6.76	4.90	5.3	FeCl ₂ FeCl ₂ ·4H ₂ O FeSO ₄ FeSO ₄ ·7H ₂ O (NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	5.23 5.25 5.25 5.25 5.25
					CoCl ₂ CoSO ₄ CoSO ₄ ·7H ₂ O (NH ₄) ₂ Co(SO ₄) ₂ ·6H ₂ O	5.04 5.04-5.25 5.06 5.00
Co ⁺⁺	⁴ F _{3/2}	6.68	3.88	5.0-5.2	NiCl ₂ NiSO ₄	3.42 3.42
Ni ⁺⁺	⁴ F ₄	5.64	2.83	3.2	Ni(N ₂ H ₄) ₂ SO ₄ Ni(N ₂ H ₄) ₂ (NO ₂) ₂ Ni(NH ₄) ₂ SO ₄ Ni(C ₂ H ₅ (NH ₂) ₂)(SCN) ₂ ·H ₂ O	3.20 2.80 2.63 2.63
Cu ⁺⁺	² D _{3/2}	3.56	1.73	1.9-2.0	CuCl ₂ CuSO ₄	2.02 2.01
Cu ⁺ , Zn ⁺⁺	1S ₀	0.00	0.00	0.00	Cu(NH ₃) ₄ (NO ₃) ₂ ⁺ Cu(NH ₃) ₄ SO ₄ ·H ₂ O	1.82 1.81

* Observed magnetic moments, other than those in the last column, are from "International Critical Tables."

3. *The normal state is the state with the maximum resultant spin S allowed by Pauli's principle.*

These rules apply also to the palladium and platinum groups, the eigenfunctions involved being $4d^5 5s 5p^3$ and $5d^5 6s 6p^3$, respectively.

There are several important types of molecules and complexes to be given separate discussion.

If the bonds are ionic or ion-dipole bonds, the magnetic moments are those of the isolated central ions, given in the first column of moments in Table III. If the complex involves electron-pair bonds formed from sp^3 alone, such as four tetrahedral sp^3 bonds, the magnetic moments are the same, for the five d eigenfunctions are still available for the remaining electrons. The hydrazine and ammonia complexes mentioned above come in this class.

If four strong bonds involving a d eigenfunction are formed (giving a square configuration), only four d eigenfunctions are available for the additional electrons. The magnetic moments are then those given in the second column of the table. Examples of such compounds are $K_2Ni(CN)_4$, $K_2Pd(CN)_4 \cdot H_2O$, K_2PdCl_4 , K_2PtCl_4 , $K_2Pt(C_2O_4)_2 \cdot 2H_2O$ and $Pt(NH_3)_4SO_4$. With eight unshared d electrons, these should all be diamagnetic. This has been experimentally verified for the first and the last three compounds; data for the others are not available. The square configuration has been experimentally verified for the chloropalladites and chloroplatinites, as mentioned before. It can be predicted that in the $[Pt(C_2O_4)_2 \cdot 2H_2O]^-$ complex the two oxalate groups lie in a plane, each attached to the platinum atom by two electron-pair bonds of the type dsp^2 . The two water molecules, if attached to the complex, are held by ion-dipole bonds.

In complexes in which the central atom forms a coordinated octahedron of six atoms or groups, the bonds may be any of several types. If they are all ionic or ion-dipole bonds, the moments are those in the first column. If four electron-pair bonds are formed, these must be dsp^2 and lie in a plane (sp^3 gives tetrahedral bonds); the $[Pt(C_2O_4)_2 \cdot 2H_2O]^-$ ion is of this type, assuming that the water molecules are part of the complex. The moments are then those of the second column. If six electron-pair bonds are formed, only three d eigenfunctions are left for the additional electrons, giving the magnetic moments of the third column. It is seen that in atoms with three or fewer unshared electrons magnetic data provide no information as to bond type with coordination number six, but that in other cases a definite statement can be made as to the type of bond when magnetic data are available. The observed magnetic moments are collected in Table IV. From them we deduce that trivalent and bivalent manganese, chromium, iron, and cobalt form six strong electron-pair bonds with cyanide groups, and in some cases with other groups, including NH_3 , Cl and NO_2 .⁴⁶ Tri-

⁴⁶ An electron-pair bond with a water molecule may perhaps be formed when induced by other strong bond-forming groups in the complex.

TABLE III
PREDICTED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS

					For ion or 4sp ² bonds	For 4 d ² sp ² bonds	For 6 d ² sp ² bonds	For 8 d ² sp ² bonds
K ^I Ca ^{II} Sc ^{III} Ti ^{IV} , etc.	Rb ^I Sr ^{II} Y ^{III} Zr ^{IV} Nb ^V Mo ^{VI}	Cs ^I Ba ^{II} —Hf ^{IV} Ta ^V W ^{VI}			0.00	0.00	0.00	0.00
					1.73	1.73	1.73	1.73
V ^{II} Cr ^{III} Mn ^{IV}	Nb ^{IV} Mo ^V Ru ^{VI}	W ^V Os ^{VI}			2.83	2.83	2.83	0.00
Cr ^{II} Mn ^{III} Fe ^{IV}	Mo ^{III} Ru ^{IV}	Os ^{IV}			3.88	3.88	3.88	
Mn ^{II} Fe ^{III} Co ^{IV}	Ru ^{III} Rh ^{IV} Pd ^{IV}	Os ^{III} Ir ^{IV}			4.90	4.90	2.83	
Fe ^{II} Co ^{III} Ni ^{III}	Rh ^{III} Pd ^{III}	Ir ^{III} Pt ^{IV}			5.91	3.88	1.73	
Co ^{II} Ni ^{II}					4.90	2.83	0.00	
Ni ^{II}					3.88	1.73		
Cu ^{II}					2.83	0.00		
Cu ^I Zn ^{II} Ca ^{III} Ge ^{IV} , etc.	Ag ^I Cd ^{II} In ^{III} Sn ^{IV} Sb ^V Te ^{VI}	Au ^I Hg ^{II} Tl ^{III} Pb ^{IV} Bi ^V Po ^{VI}			1.73			
					0.00			

valent iron apparently does not form electron-pair bonds with fluorine (in $[\text{FeF}_6 \cdot \text{H}_2\text{O}]^-$); although investigation of $(\text{NH}_4)_3\text{FeF}_6$ is to be desired in order to be sure of this conclusion. Ir^{III} and Pt^{IV} form six electron-pair bonds with Cl , NO_2 or NH_3 .

TABLE IV
OBSERVED MAGNETIC MOMENTS OF COMPLEXES CONTAINING TRANSITION ELEMENTS*

	μ		μ
$\text{K}_3[\text{Mn}(\text{CN})_6]$	3.01	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$	0.00
$\text{K}_4[\text{Cr}(\text{CN})_6]$	3.3	$[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$	.00
$\text{K}_3[\text{Fe}(\text{CN})_6]$	2.0	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	.00
$\text{K}_4[\text{Mn}(\text{CN})_6]$	2.0	$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]$	.00
$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	0.00	$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{C}_2\text{O}_4)_2$	.00
$\text{Na}_3[\text{Fe}(\text{CN})_6]\text{NH}_3$	.00		
$\text{K}_3[\text{Co}(\text{CN})_6]$	.00	$\text{K}_2\text{Ni}(\text{CN})_4$	0.00
$(\text{NH}_4)_2[\text{FeF}_6 \cdot \text{H}_2\text{O}]$	5.97	$\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$	.00
$\text{K}_4[\text{Mo}(\text{CN})_6]$	0.00	K_2PtCl_4	.00
$\text{K}_4[\text{W}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$	.00	$\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	.00
$\text{Na}_3[\text{IrCl}_6(\text{NO}_2)_4]$	.00	$\text{Pt}(\text{NH}_3)_4\text{SO}_4$	.00
$[\text{Ir}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	.00		
$[\text{Ir}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$	.00	$\text{Na}_3[\text{Fe}(\text{CN})_6\text{NO}] \cdot 2\text{H}_2\text{O}$	.00
$[\text{Ir}(\text{NH}_3)_3(\text{NO}_2)_3]$	.00	$[\text{Ru}(\text{NH}_3)_5\text{NO} \cdot \text{H}_2\text{O}]\text{Cl}_2$	.00
$\text{K}_3[\text{PtCl}_6]^-$	.00	$[\text{Ru}(\text{NH}_3)_5\text{NO} \cdot \text{Cl}]\text{Br}_2$	.00
$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	.00	$[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$	2.81
$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	.00		
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	.00	$\text{Ni}(\text{CO})_4$	0.00
$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	.00	$\text{Fe}(\text{CO})_5$	.00
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	.00	$\text{Cr}(\text{CO})_6$	.00

* Values quoted are from "International Critical Tables" or from W. Biltz, *Z. anorg. Chem.*, 170, 161 (1928), and D. M. Bose, *Z. Physik*, 65, 677 (1930). I am indebted to Mr. P. D. Brass for collecting from the literature some of the data in this table.

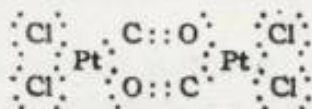
The moments of complexes containing NO offer a puzzling problem. The diamagnetism of compounds of iron and ruthenium suggests that Fe^{IV} and Ru^{IV} form a double bond with NO, making seven bonds in all, which would lead to $\mu = 0$. But this structure cannot be applied to $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$, which has a moment corresponding to a triplet state. Further study of such complexes is needed.

The observed diamagnetism of the ions $[\text{Mo}(\text{CN})_6]^{4-}$ and $[\text{W}(\text{CN})_6]^{4-}$ shows that the central atom forms eight electron-pair bonds, involving the eigenfunctions $d^4s^4p^0$ (fourth column of Table III).

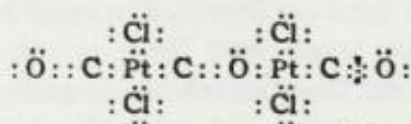
The metal carbonyls $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ are observed to be diamagnetic. This follows from the theoretical discussion if it is assumed that an electron-pair bond is formed with each carbonyl; for the nine eigenfunctions available ($3d^4s^4p^1$) are completely filled by the n bonds and $2(9-n)$ additional electrons attached to the metal atom ($n = 4, 5, 6$). The theory also explains the observed composition of these unusual sub-

stances; for the formulas $M(\text{CO})_n$, with $n = 4, 5$, and 6 , respectively, follow at once from the assumption that CO molecules add on as long as bond eigenfunctions are available. Since a single unshared electron can occupy an eigenfunction, this assumption leads to the formula $\text{Co}(\text{CO})_4$, which is known to be correct. This substance should have $\mu = 1.73$. The compounds $\text{Mn}(\text{CO})_5$ and $\text{V}(\text{CO})_5$ should also exist, and have $\mu = 1.73$. $\text{Co}(\text{CO})_4$ and $\text{Mn}(\text{CO})_5$ should form un-ionized diamagnetic cyanides, $[\text{Co}(\text{CO})_4\text{CN}]$ and $[\text{Mn}(\text{CO})_5\text{CN}]$, while $\text{V}(\text{CO})_5$ would not form a stable cyanide, since steric effects would prevent the cyanide group from forming an electron-pair bond with the vanadium atom, and ionic cyanides are formed only by strong metals. It is interesting to note the effect of the four strong bond eigenfunctions and one weak one formed from dsp^3 ; whereas nickel forms no lower carbonyl than $\text{Ni}(\text{CO})_4$, iron forms $\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ in addition to $\text{Fe}(\text{CO})_5$.

The palladium and platinum metals also form carbonyl compounds. Of the expected compounds $\text{Pd}(\text{CO})_4$, $\text{Pt}(\text{CO})_4$, $\text{Ru}(\text{CO})_5$, $\text{Os}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ only $\text{Mo}(\text{CO})_6$ has been prepared, although some unsaturated ruthenium carbonyls have been prepared. The compounds $\text{Pd}(\text{CO})_2\text{Cl}_2$, $\text{Pt}(\text{CO})_2\text{Cl}_2$, $\text{K}[\text{PtCOCl}_3]$, etc., show the stability of the four dsp^3 bonds. It would be interesting to determine whether or not each CO is bonded to two metal atoms in compounds such as $[\text{Pt}(\text{CO})\text{Cl}_2]_2$, whose structure is predicted to be



with the whole molecule in one plane. The compounds $2\text{PdCl}_2 \cdot 3\text{CO}$ and $2\text{PtCl}_2 \cdot 3\text{CO}$ probably have the structure



or one of the structures isomeric with this.

This by no means exhaustive discussion may serve to indicate the value of the information provided by magnetic data relative to the nature of the chemical bond. The quantum-mechanical rules for electron-pair bonds are essential to the treatment. Much further information is provided when these methods of attack are combined with crystal structure data, a topic which has been almost completely neglected in this paper. It has been found that the rules for electron-pair bonds permit the formulation of a set of structural principles for non-ionic inorganic crystals similar to that for complex ionic crystals; the statement of these principles and applications illustrating their use will be the subject of an article to be published in the *Zeitschrift für Kristallographie*.

Summary

With the aid of the quantum mechanics there is formulated a set of rules regarding electron-pair bonds, dealing particularly with the strength of bonds in relation to the nature of the single-electron eigenfunctions involved. It is shown that one single-electron eigenfunction on each of two atoms determines essentially the nature of the electron-pair bond formed between them; this effect is accentuated by the phenomenon of concentration of the bond eigenfunctions.

The type of bond formed by an atom is dependent on the ratio of bond energy to energy of penetration of the core (s - p separation). When this ratio is small, the bond eigenfunctions are p eigenfunctions, giving rise to bonds at right angles to one another; but when it is large, new eigenfunctions especially adapted to bond formation can be constructed. From s and p eigenfunctions the best bond eigenfunctions which can be made are four equivalent tetrahedral eigenfunctions, giving bonds directed toward the corners of a regular tetrahedron. These account for the chemist's tetrahedral atom, and lead directly to free rotation about a single bond but not about a double bond and to other tetrahedral properties. A single d eigenfunction with s and p gives rise to four strong bonds lying in a plane and directed toward the corners of a square. These are formed by bivalent nickel, palladium, and platinum. Two d eigenfunctions with s and p give six octahedral eigenfunctions, occurring in many complexes formed by transition-group elements.

It is then shown that (excepting the rare-earth ions) the magnetic moment of a non-linear molecule or complex ion is determined by the number of unpaired electrons, being equal to $\mu_S = 2 \sqrt{S(S+1)}$, in which S is half that number. This makes it possible to determine from magnetic data which eigenfunctions are involved in bond formation, and so to decide between electron-pair bonds and ionic or ion-dipole bonds for various complexes. It is found that the transition-group elements almost without exception form electron-pair bonds with CN, ionic bonds with F, and ion-dipole bonds with H_2O ; with other groups the bond type varies.

Examples of deductions regarding atomic arrangement, bond angles and other properties of molecules and complex ions from magnetic data, with the aid of calculations involving bond eigenfunctions, are given.

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