The Basis of Stereochemistry.

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Within the last quarter of a century notable advances have been made in stereochemistry by the classical methods of organic chemistry. The discovery of optically active diphenyl derivatives and optically active sulphoxides—our increased knowledge of the Walden inversion and of the stereochemistry of intramolecular changes—as well as many other fine achievements—spring at once to mind.

But the advances which chiefly distinguish this period are those which have come through the application of the newer physical methods. On the one hand, these have brought the configuration of the simpler inorganic molecules into the scope of experimental investigation; on the other, they have made possible quantitative determinations of bond-lengths and intervalency angles, and have thus yielded a more definite picture of molecular configurations than the older methods alone could have given.

Now that we know the valency configurations of the greater number of the elements, a surprising fact which emerges is the frequency with which these arrangements depart from the arrangements of maximum symmetry. Thus, in bivalent elements, angular arrangements are more common than linear, and in tervalent elements, pyramidal occur more frequently than planar configurations.

These departures from maximum symmetry must clearly have their origin in the electronic structure of the atoms, and one of the most interesting advances of recent years is the progress that has been made in our understanding of the relations between atomic structure and valency configuration. These relations form the theoretical basis of stereochemistry, and I will attempt to give some account—using only simple considerations—of a method by which they can be elucidated.

We know that the electron has a wave aspect and that this wave aspect of the electron supplies the mechanism through which chemical combination is effected. Extensive mathematical knowledge is of course needed for a full comprehension of the development of the theory of valency based on the wave nature of the electron, and on this account many chemists—especially those whose study of stereochemistry has proceeded along the lines of classical organic chemistry—have been deterred from following the progress that has been made towards the establishment of stereochemistry on a theoretical basis.

But since the equations which describe the behaviour of an electron under the influence of a positively charged nucleus are similar in form to those which describe the vibration of certain mechanical systems, an elementary knowledge of the characteristics of the vibration of mechanical systems enables us in a large measure to infer the corresponding characteristics of electronic waves. By means, therefore, of very simple considerations it should be possible to gain some insight into the manner in which directed valency arises and some understanding of the causes which determine the valency configuration of the simpler atoms.

Since it has been shown experimentally that electrons exhibit interference phenomena, we know that electronic waves obey the superposition law. An atomic electron therefore has to move about the nucleus so as to set up a standing wave. The possible states of the electron thus correspond with the different types of standing waves which can be formed in a central field, and we have to consider what types of standing waves can arise under these conditions.

Before considering these tridimensional wave-systems it will be helpful if we first recall the behaviour of a simple bidimensional system—the uniform circular membrane. We know that when the membrane is set into vibration, though its movements are very complex, they can be analysed into a set of *normal modes*. Each normal mode corresponds with a standing wave, and normal modes can be classified by the number of nodes present in these waves. The movement of the membrane is that which would result from the superposition of standing waves of appropriate amplitudes in the different normal modes.

There is first the *fundamental mode* of the membrane. Here, as in the violin string sounding its fundamental note, there is no node: the whole membrane rises and falls together [Fig. 1 (*a*)]. Next, there are normal modes in which, as in the violin string sounding its first harmonic, one node is present. In place of the nodal *point* of the vibrating string the membrane will have a nodal *line* and an important point is, that, as is fairly evident, the nodal line can take two forms [Fig. 1 (*b*)]. The membrane can form a standing wave with a *circular node* concentric with the periphery; but it can also form a wave with a *rectilinear node* passing through the centre. In the mode with the circular node the motion is symmetrical; in that with the rectilinear node it is unsymmetrical.

There is a further point of difference between these two modes. The position of the nodal circle is uniquely determined (its radius is 0·436 times the radius of the membrane) but that of the nodal diameter is not. Any one of the infinite number of diameters of the circle can function as a node. If now we take any two diameters at right angles, it is clear from symmetry considerations that a standing wave having one of these diameters as a nodal line is independent of a wave for which the other is a node. The two standing waves with nodal diameters at right angles to one another are in independent modes. A vibration in the one mode has no component in the other. Any pair of diameters at right angles can be selected to define the two normal modes and a standing wave having any other diameter as a node can be obtained by the superposition of waves of appropriate relative amplitudes in the two normal modes.* There are accordingly three normal modes of the circular membrane having one nodal line. In one of these the nodal line is circular; in the other two it is rectilinear, and the nodal lines of these two modes must be mutually perpendicular.

From this consideration of the simplest modes of a bidimensional system we may pass to standing waves in three dimensions. Here we shall naturally find in place of nodal lines nodal *surfaces*. In place of the nodal circles of the bidimensional system there will be nodal *spheres*, and in place of the rectilinear nodal lines there will be nodal *planes*.

The tridimensional system consisting of an electron moving in the field of a positively charged nucleus must have first a fundamental mode—the mode in which the standing wave has no nodal surface.

In this mode, just as in the corresponding mode of the circular membrane, the wave is completely symmetrical about the centre, that is to say, about the nucleus. The relevant solution of the wave equation shows that the amplitude has its maximum value at the nucleus and falls off rapidly according to the same exponential law in every direction. It is not easy to give a physical interpretation of the amplitude of the electron wave. In wave motion, however, the square of the amplitude gives the intensity of the wave, and in an electron wave the intensity at a point is taken to be the charge density there. An atomic electron can accordingly be visualised as a little cloud whose density is everywhere proportional to the square of the amplitude of the wave. If over an element of volume dv the amplitude is ψ, ψ^2dv represents the average charge contained in that volume, and the sum of these charges taken over the whole wave (which theoretically extends throughout space) must be equal to the charge of the electron. Taking this as 1 we get:

$$\int \psi^2 \mathrm{d}v = 1$$

the integration being over the whole of space.

The way in which the amplitude (ψ) falls off with the distance (r) from the nucleus is shown in Fig. **3** (*a*). An indication is also given of the form of the corresponding electron cloud [Fig. **3** (*b*)]: it is spherically symmetrical with maximum density at the centre. When in the fundamental mode, the electron is in its one-quantum state.

We have next to consider the normal modes in which the standing wave has one nodal surface. These are the modes in which the electron is in a two quantum state.

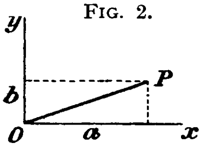
We have seen that nodal surfaces may be spherical or planar. There must therefore be a normal mode in which the electron wave has a spherical nodal surface, and it is evident that in this the wave form will be spherically symmetrical—the amplitude (ψ) of the wave at any point will be determined solely by the distance (r) from the nucleus and will be independent of direction. It is not difficult to see in a general way how the amplitude will vary along a line through the nucleus [Fig. **3** (*c*)]. Comparison with the fundamental mode indicates that the amplitude will have its greatest value at the nucleus. It will fall to zero at a distance from the nucleus equal to the radius of the nodal sphere. At this point, since displacements must be of opposite sign on either side of the node, the ψ–r curve will cross the axis to reach a maximum negative value and then re-approach the axis exponentially, the amplitude becoming negligibly small at distances greater than, but of the same order of magnitude as, the atomic radius. The electron cloud will thus consist of a central spherical portion and an outer zone, the two being separated by the nodal sphere [Fig. **3** (*d*)].

In addition to forming a wave with a spherical node, the 2-quantum electron must also be able to form a wave with a planar node. It is well known that in comparable mechanical systems, such as gas in a rigid spherical container, or a sphere of elastic solid, standing waves have nodal surfaces of these two types.

The general form of the electronic standing wave determined by the presence of a plane nodal surface is not difficult to infer. The nodal plane must evidently pass through the nucleus and, since the electron is moving in a centrally symmetrical field, the wave must be symmetrical about the normal to this plane through the nucleus—that is to say, it must have this line as an axis of symmetry. The amplitude will have its maximum values on this axis and will evidently vary along it in the kind of way shown in Fig. **4** (*a*). The amplitude will be zero at the nucleus, and it will have equal positive and negative maxima equidistant from the nucleus, and from these it will decline exponentially, rapidly becoming infinitesimal. Displacements must be equal and opposite at corresponding points on either side of the nodal plane so that the wave will be antisymmetrical about this plane. Contour lines for the amplitudes indicated in Fig. **4** (*a*) will in any section through the axis have the form represented in Fig. **4** (*b*), in which P represents the section of the nodal plane and A the axis of symmetry. A representation of the distribution of the amplitudes in space is obtained by rotating Fig. **4** (*b*) about the axis of symmetry. The corresponding electron cloud will evidently have an hour-glass shape.

When the electron wave has a spherical nodal surface and is thus spherically symmetrical, the electron is in a state which corresponds with a spectroscopic *s*-term and it is therefore described as an *s*-electron. An electron forming a wave with one plane nodal surface is in a state which corresponds with a spectroscopic *p*-term and is described as a *p*-electron.

FIG. 2.



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* These standing waves have vector-like properties and can be resolved and compounded according to the vector law (see Fig. 2). The movements of the membrane produced by a wave with maximum amplitude in the direction OP are exactly those which would result from the superposition of two waves with their maximum amplitudes along the axes x and y, these amplitudes being a and b times that of the single wave; a and b are of course the cosine and the sine of the angle which OP makes with the x-axis, so that $a^2 + b^2 = 1$. These properties are of interest, as will appear later, as illustrating analogous properties of electronic p-waves.

Fig. 1 (*a*).

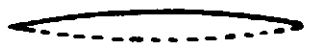


Fig. I (*b*).

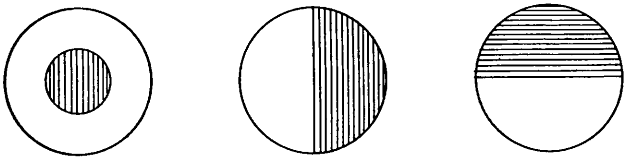


Fig. 3 (*a*).

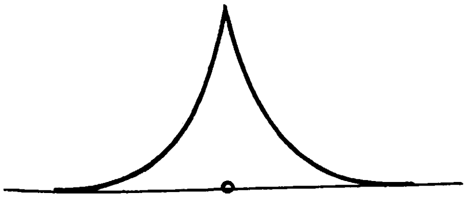
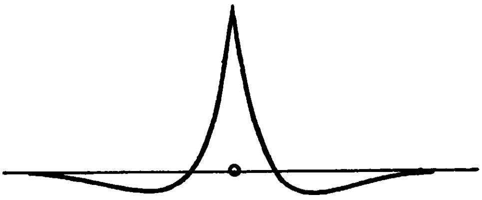


Fig. 3 (*c*).



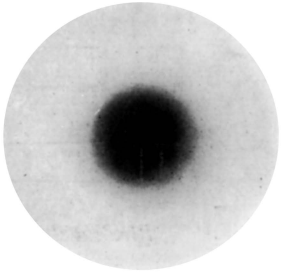


Fig. 3 (*b*).

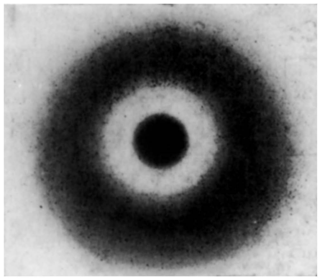
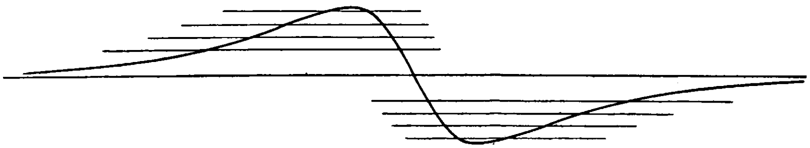


Fig. 3 (*d*).

Fig. 4 (*a*).



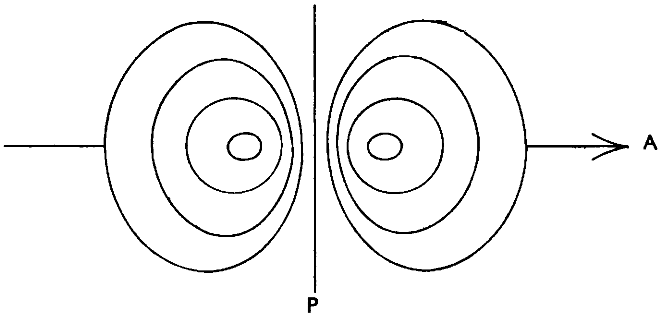


Fig. 4 (*b*).

[*To face p.* 458.

FIG. 11.

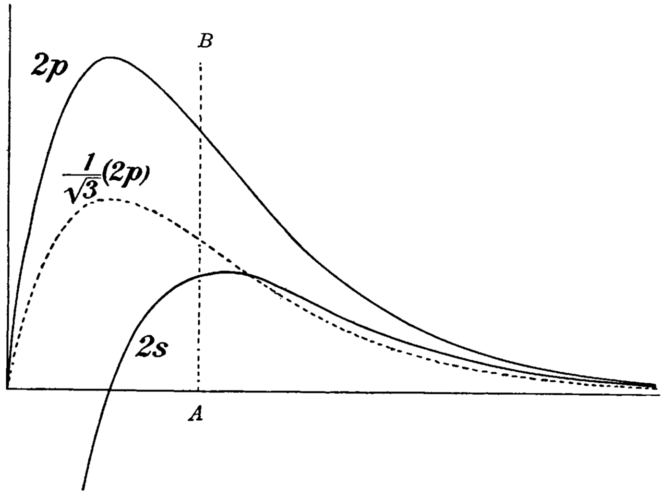


FIG. 12.

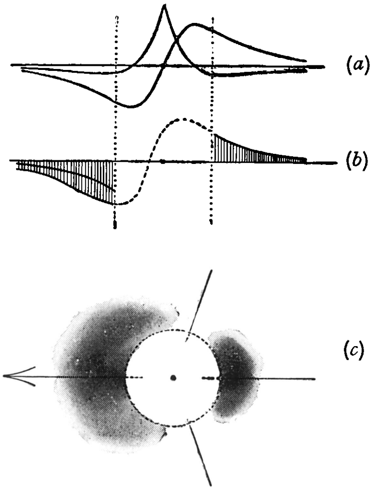
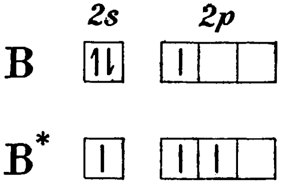


FIG. 14.

Ground state.



Tervalent state.

FIG. 15.

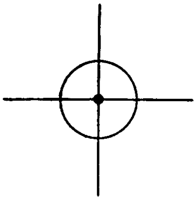
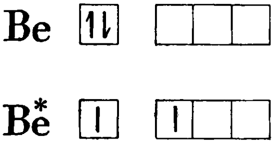


FIG. 16.

Ground state.



Bivalent state.

FIG. 17.

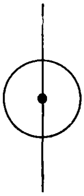


FIG. 19.

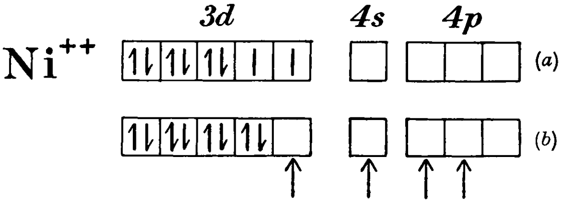


FIG. 21.

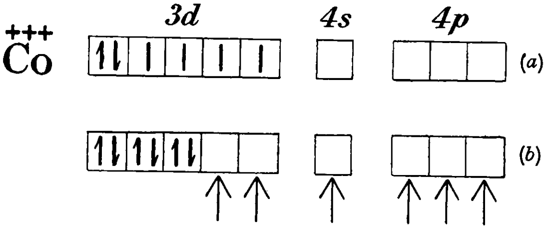


FIG. 20.

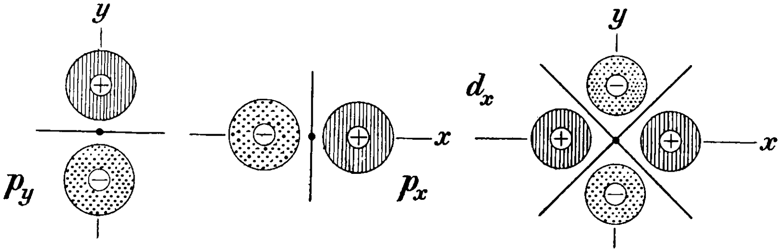
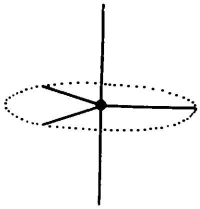


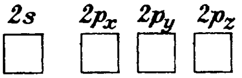
FIG. 22.



When the nodal surface is spherical, the radius of the sphere is evidently uniquely determined : there can only be one 2*s*-orbital. It is otherwise when the nodal surface is a plane. We saw that in the vibrating circular membrane, modes with one rectilinear node were independent when they were at right angles. A corresponding principle holds for electronic standing waves. Normal modes with one nodal plane are independent when their nodal planes are at right angles. Hence, since a tridimensional system accommodates three planes at right angles to one another, an atomic electron has three normal modes with a nodal plane. That is to say there are three 2*p*-orbitals. The mutually perpendicular axes of symmetry of these three normal modes may be taken as the co-ordinate axes, and the corresponding orbitals can then be conveniently described as $2p_x$, $2p_y$, and $2p_z$ orbitals.*

The *s*-mode and the three *p*-modes represent the four normal modes of a single 2-quantum electron. But since the Pauli exclusion principle allows of the existence in an atom of only two electrons (of opposite spin) in any one mode, the number of independent modes for a single electron of given quantum number determines the possible number of electrons of that quantum number in an atom (see Fig. 6). There are therefore one 2*s*- and three 2*p*-orbitals in an atom, and the axes of symmetry of the latter are mutually perpendicular.

Fig. 6.



Wave forms corresponding with a higher quantum number *n* will have $(n - 1)$ nodal surfaces and these may be all spheres, or all planes, or spheres and planes in combination. Nodal surfaces can also take the form of a double cone with its apex at the nucleus.

When all the nodal surfaces are spheres, the electron is in an *s*-state, and since the radius of each sphere must be uniquely determined there can only be one *s*-orbital for each principal quantum number. Wave forms in which one nodal plane is combined with one or more spheres correspond with *p*-states of the electron. It will be clear from the foregoing that each of these forms, having only one plane node, will give rise to three normal modes differing only in the orientation of the nodal plane, the nodal planes (and therefore also the axes of symmetry of the corresponding waves) being mutually perpendicular.

The simple facts that for each principal quantum number beyond the first there are one *s*- and three *p*-orbitals—facts which derive from such simple geometrical principles—play, as is well known, a major part in shaping the periodic table. But also—and this more particularly concerns our present purpose—the fact that the axes of symmetry of the three *p*-orbitals are at right angles to one another is the basis of most of our stereochemistry and ultimately determines the configuration of the majority of chemical compounds.

We have now to see how valency directions are determined by the characteristics of *s*- and *p*-electrons.

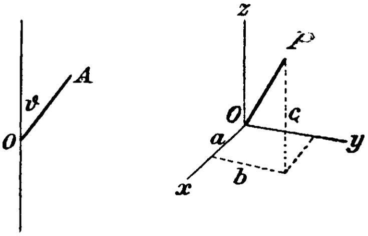
To an *s*-electron, with its spherically symmetrical wave-system, all directions are alike. Hence, if an *s*-electron acts as a valency electron it can form a bond equally well in any direction. It is quite otherwise with a *p*-electron. It can be proved for simple systems—for example, a hydrogen atom linked through a *p*-electron—that the bond will tend to be formed in the direction of the axis of symmetry of the *p*-electron.

This would seem almost self-evident on the basis of Pauling's criterion of *maximum overlapping*. When two atoms combine they must tend to form the strongest bond obtainable, since this leads to the greatest fall of potential energy of the system. Now we know that a covalent bond arises through the resonance of two vibrating systems, these systems being the electrons concerned in the formation of the bond, and the resonance must be the stronger the greater the coupling between the two systems, and the coupling must clearly be the greater the greater their interpenetration. We have seen that the density of the *p*-electron cloud is greatest along its axis of symmetry and falls off gradually in all directions. There will therefore be, for a given internuclear distance, a maximum overlap of the two electron clouds when the hydrogen nucleus is on the axis of symmetry of the *p*-electron, and the bond should therefore tend to be formed in the direction of this axis.

On this basis provisional explanations can be given of the non-planar configuration of the ammonia molecule and the angular configuration of the molecule of water.

The configuration of ammonia could be thought of as brought about in the following manner. If the five electrons which compose the *L*-shell of the nitrogen atom were introduced in succession, then we know that, in accordance with the general rules which have been found for the relative energies of sub-levels, the first two would fall into the 2*s*-orbital and the other three would go one into each of the three 2*p*-orbitals, so that the shell would have the constitution indicated in Fig. 7. The ground state of the nitrogen atom arises from this electron configuration through resonance between the three unpaired *p*-electrons. The tervalent state differs from the ground state in that the spins of the *p*-electrons are free of one another. The unpaired *p*-electrons

Fig. 5.



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* If *p* is the amplitude of a 2*p*-electron wave at a point *A*, the nucleus being at *O* (see Fig. 5), the appropriate solution of the wave equation shows that *p* is given by the relation $p = R\cos\theta$, where θ is the angle between *OA* and the axis of symmetry of the wave and *R* is an expression which depends only on the distance of *A* from the nucleus. It follows from this that *p*-electrons have vector-like properties, and a 2*p*-wave having *OP* as axis of symmetry is exactly reproduced by the superposition of three 2*p*-waves of *a*, *b*, and *c* times the normal amplitude having the co-ordinate axes as their axes of symmetry : *a*, *b*, and *c* are the direction cosines of *OP* and thus $a^2 + b^2 + c^2 = 1$.

Any three mutually perpendicular directions can therefore be taken to define the normal modes so long as there is nothing to disturb the spherical symmetry.

then function as valency electrons, and each could bind a hydrogen atom. The hydrogen atoms would be most strongly attracted in the directions of the mutually perpendicular axes of symmetry of these p-electrons. These directions would not, however, be exactly those of the resulting bonds, since the hydrogen atoms would have resultant positive charges (as is shown by the electric dipole associated with the hydrogen–nitrogen bond) and would repel one another. Their mutual repulsion would therefore widen the intervalency angle to a value somewhat greater than 90°. The observed value of the intervalency angle in ammonia is 107°, requiring a deflection of each valency through an angle of 13·5° from the rectangular configuration towards the trihedral axis of the molecule.

FIG. 7.

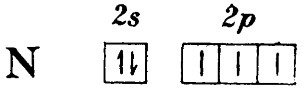

FIG. 8.

FIG. 9.

FIG. 10.

Similar considerations can be applied to the water molecule. The ground state of the oxygen atom is derived from an L-shell of the structure shown in Fig. 8. The formation of the water molecule could then be regarded as taking place through the binding of two hydrogen atoms by the two unpaired electrons. These have their axes of symmetry at right angles, so that, if there were no repulsion between the hydrogen atoms, the intervalency angle would be 90°. The repulsion actually existing would widen this angle somewhat, but the actual widening is considerable, the observed intervalency angle being 106°, which requires a deflection of each valency through 8° from the rectangular direction.

When these simple methods of consideration are applied to carbon, however, difficulties are encountered. The normal configuration of the carbon atom, $(1s)^2(2s)^2(2p)^2$, provides only two unpaired electrons, and in this state therefore the atom cannot be more than bivalent (Fig. 9). The quadrivalent atom results through the promotion of one of the $2s$-electrons to the $2p$ state (Fig. 10), a process requiring a considerable amount of energy which can be supplied from that liberated in the formation of the bonds.

The formation of methane would then be regarded as taking place in the following manner. The three p-electrons give three directed bonds at right angles to one another, and the s-electron gives a non-directed bond. The three directed bonds would bind three hydrogen atoms forming a methyl radical with a configuration resembling that of ammonia. The fourth hydrogen atom, linked through the non-directed bond, would be free to assume its preferred position, which would naturally be on the trigonal axis of the methyl radical so as to be placed as far as possible from the other three hydrogen atoms.

Such a view, differentiating one valency from the other three, is manifestly unsatisfactory. A solution of the difficulty was given by Pauling in 1928. In considering bond-formation one must look for the strongest bonds which the atom is capable of forming, since these are the bonds which will actually come into play. Pauling showed that the strongest bonds which the carbon atom can form are yielded, not by electrons in pure $2s$- or $2p$-orbitals, but by electrons in what are known as *hybrid orbitals*.

An atomic electron in its wave aspect is a vibrating system having a series of independent normal modes and somewhat like a mechanical system such as a bell is capable of vibrating simultaneously in more than one mode. The resultant vibration arising from the superposition of vibrations in different normal modes—provided these modes represent states of equal energy of the electron—is in a new mode described as a hybrid orbital.

If in the carbon atom we neglect the screening effect of the two 1-quantum electrons, regarding them as simply cutting down the nuclear charge to 4, the $2s$- and $2p$-modes of the electron would represent states of equal energy, and hybrid orbitals could be formed from them. These hybrid orbitals would represent standing waves which could be described as resulting from the superposition of waves of the appropriate amplitudes in the two normal modes. If s and p represent expressions giving the amplitudes of the $2s$- and $2p$-waves at any point in space (s will be a function of r only, where r is the distance of the point from the nucleus, and p a function both of r and of the angular co-ordinates of the point), then the amplitude of the electron wave at that point when the electron is in the hybrid orbital will be given by an expression of the form $as + bp$. The coefficients a and b may of course have any relative magnitude, but they are subject to the relation $a^2 + b^2 = 1$: * it follows from this that the proportion in which a normal mode participates in a hybrid orbital is given by the square of its coefficient in the expression for the orbital.

* We have seen that the charge density at a point is given by the square of the amplitude of the electron wave there, so that the integral $\int \psi^2 \, dv$ taken over all space is equal to the electronic charge (which we may put equal to 1). Applying this to the s-, the p-, and the hybrid wave, we have :

$$\int s^2 . dv = \int p^2 . dv = 1 \quad \ldots \ldots \quad (1)$$

$$\int (as + bp)^2 dv = 1 \quad \ldots \ldots \quad (2)$$

We have now to consider how the relative bonding power of different orbitals can be assessed.

Although $2s$- and $2p$-electron waves have a very different form near the nucleus, the curves showing the relation between the wave-amplitude and the nuclear distance show a considerable correspondence in the outer part of the atom. Now the innermost region of the atom is of relatively little importance to the chemist; the outer zone is the chief seat of the valency forces—and it is in this that he is mainly interested. In Fig. 11 the curve $2p$ shows how the amplitude of the $2p$-wave varies with distance from the nucleus along the axis of symmetry of the wave; $2s$ is the curve for the $2s$-wave. [The curves are drawn for a simplified carbon atom in which the two K-electrons are regarded as simply cutting down the nuclear charge to 4. The line AB marks a somewhat arbitrary division into the " inner " and " outer " part of the atom.]

To the right of AB there is an evident approximate proportionality between the ordinates of the two curves. The dotted curve $1/\sqrt{3}\,.\,(2p)$, drawn at $1/\sqrt{3}$ times the height of the $2p$ curve, shows that to a fair approximation we may take, on the p-axis in the valency region, $s = p/\sqrt{3}$.*

That the p-wave has, on its axis of symmetry, a greater amplitude than the s-wave arises of course from the fact that, in any spherical shell centred on the nucleus, the s-electron cloud is equally distributed, but that of the p-electron is concentrated towards its axis.

It seems evident that a greater concentration of the electron cloud in the direction of the bond must lead to a stronger bonding interaction. The strength of a bond which an electron can yield should accordingly be related to the amplitude of the electron wave on the direction of this bond. Pauling and Sherman showed (*J. Amer. Chem. Soc.*, **1937**, **59**, 1450) that the energy of a bond is, in fact, roughly proportional to the product of the magnitudes of the bond orbitals of the two atoms in their angular dependence. Towards a given atom, for example hydrogen, the relative strengths of a bond formed by a 2-quantum electron in its s- and p-states would thus be as $1 : \sqrt{3}$.

A hybrid orbital formed from a $2s$- and a $2p$-orbital will evidently give maximum amplitudes on the p-axis. To find the orbital of maximum bonding energy which can be thus formed, we have therefore to find the maximum value of the expression $as + bp$, given that $p = \sqrt{3}s$ and $a^2 + b^2 = 1$. The maximum value is found to be attained when $a = \frac{1}{2}$ and $b = \sqrt{3}/2$—*i.e.*, when the hybrid orbital consists of a combination of one-quarter of the s-orbital with three-quarters of the p-orbital.

If we make, as above, the approximation that in the carbon atom the screening effects of the K-electrons and the mutual action of the L-electrons are neglected, so that the L-electrons are considered to be moving in a Coulomb field, the $2s$- and $2p$-normal modes would correspond with states of equal energy, and standing waves in these modes would have equal frequencies. They could therefore combine to form a new standing wave.

The general form of the standing wave corresponding with the hybrid orbital of maximum bonding energy can be easily inferred. It will clearly have the p-axis as an axis of symmetry. Its amplitudes along this axis are found by superposing a $2p$-wave of $\sqrt{3}/2$ times normal amplitude on a $2s$-wave of $\frac{1}{2}$ normal amplitude. These components are shown separately in Fig. 12 (*a*) and the result of their superposition in Fig. 12 (*b*). The intermediate curve on the left of Fig. 12 (*b*) reproduces the form of the curve on the right. It is drawn to show more clearly the relative amplitudes on the two sides.

The displacements due to a p-wave are always of opposite sign on either side of its nodal plane, while those due to an s-wave (outside the nodal sphere) are at any instant all of the same sign. Hence, if the s- and p-waves are in the same phase on one side of the p-nodal plane, they will be in opposite phases on the other side. On the one side of this plane the resultant amplitude will then be the sum, and on the other the difference, of the amplitudes of the component waves.

It can therefore be seen that, at corresponding points on either side of the nucleus, amplitudes will be in the ratio of $(1{\cdot}5 + 0{\cdot}5)$ to $(1{\cdot}5 - 0{\cdot}5)$, *i.e.*, as 2 to 1, and the densities of the electron cloud as 4 to 1. It is thus clear how the maximum extension in one direction, characteristic of this orbital, is brought about. Compared with the relative bonding strengths 1 and $\sqrt{3}$ of the $2s$- and $2p$-orbitals, that of the hybrid orbital is 2.

The standing wave will have a conical nodal surface, the external angle between the cone and the axis being 109·5°. This can be seen by replacing p in the expression for the hybrid orbital by its approximate value $\sqrt{3}s$. The amplitude becomes zero when $\cos\theta = -\frac{1}{3}$, so that θ is the tetrahedral angle. The form of the electron cloud is indicated in Fig. 12 (*c*).

Squaring the expression in the bracket in (2) we get

$$\int (a^2s^2 + b^2p^2)\mathrm{d}v = 1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

the cross-term $\int sp\,.\,\mathrm{d}v$ being equal to zero. (This is a general property of independent normal modes—the " orthogonal " property—it is evidently the case here since the p-wave is antisymmetrical about its nodal plane.) Comparison of (3) with (1) shows at once that $a^2 + b^2 = 1$ as stated above.

* There is a reason for choosing this particular value for the approximate ratio. The forms of the $2s$ and $2p$ waves obtained from the wave equation are

$$s = R;\; p = (\sqrt{3}\cos\theta)R'$$

where R and R' are expressions whose value depends only on the nuclear distance of the point at which the respective amplitudes are s and p. Hence, putting s equal to $p/\sqrt{3}$ on the p-axis is equivalent to assuming that, in the valency region, the radial parts, R and R', of the wave-functions are equal.

For the hybrid orbital of maximum bonding strength to have the simple form $\frac{1}{2}s + (\sqrt{3}/2)p$, the co-ordinate axes must be chosen so that the z-axis coincides with the axis of the p-wave. The general form of this orbital is clearly

$$\tfrac{1}{2}s + bp_x + cp_y + dp_z$$

the coefficients b, c, and d determining the direction of its axis relatively to the co-ordinate axes and being subject to the condition $b^2 + c^2 + d^2 = \frac{3}{4}$.

We have now seen that a hybrid orbital of the foregoing form represents. in our simplified carbon atom. the state in which a 2-quantum electron has maximum bonding power. We have next to enquire whether it is possible for a set of four 2-quantum electrons to co-exist when each is in this form.

There are two conditions to be satisfied. First, the sum of the contributions which any one mode, say p_x, makes to the four hybrid orbitals must equal unity. Secondly, the four orbitals must be mutually independent. Pauling showed that a set of four of these hybrid orbitals satisfied these conditions provided that their axes had the relative inclinations of the four (trihedral) axes of the regular tetrahedron.*

We have thus seen that in order to obtain four equal bonds for the quadrivalent carbon atom—that is, to derive mutually equivalent states for the four valency electrons from the combination $(2s)(2p)^3$—it is necessary to distribute the $2s$ mode equally between four hybrid orbitals. This requires that the coefficient of s in each of the hybrid orbitals shall be $\frac{1}{2}$. But this proves to be also the condition that each electron shall be in the state in which it has its maximum bonding strength (and this is the state which it must assume in taking part in a bond). Further, it determines that the four bonds must be tetrahedrally arranged.

These are very remarkable results. The theory correlates so naturally the essential conditions which the quadrivalent carbon atom must fulfil that its essential correctness can hardly be doubted.

We have to bear in mind, however, that this theory rests on very considerable approximations. The energy difference of the $2s$- and $2p$-electrons of the actual carbon atom, as well as the differences between the radial parts of the s- and p-wave functions, are neglected. These approximations can, however, be justified, so long as the energy set free by the formation of the bonds is sufficient to equalise the differences.

The recognition that in the carbon atom the strongest bonds are formed by electrons in tetrahedral orbitals makes it necessary to consider the possibility that the bonds of the tervalent nitrogen atom are derived from electrons in an analogous state. The five electrons of this atom might conceivably be in four hybrid orbitals of the tetrahedral form $s/2 + (\sqrt{3}/2)p$, one of the orbitals being doubly occupied by the " lone pair " of G. N. Lewis and the other three singly occupied by the three valency electrons. This would entail $\frac{3}{4}$ promotion of one s-electron to the $2p$-state. The energy required to bring the atom from its ground state into the tetrahedral condition would have to be supplied from that made available by the formation of the three bonds.

Since the experimental determination of the configuration of the ammonia molecule has shown that the intervalency angle is *less* than the tetrahedral angle it would appear that the tervalent nitrogen atom in ammonia is not wholly derived from the tetrahedral state. Though this state should yield the strongest bonds, it may be that its full production may require more energy than the formation of three bonds could supply, the actual state of the atom being intermediate between this and the condition in which the three unpaired electrons are in pure p-states.

Similar considerations apply to the bivalent oxygen atom in water and compounds of the water type.

We have now considered carbon and the two elements, nitrogen and oxygen, which follow it in the periodic table, and have seen how the electronic structure of the respective atoms brings about a tetrahedral disposition of the carbon valencies, imposes a pyramidal arrangement on the nitrogen valencies, and causes those of oxygen to assume an angular configuration.

We have next to consider the two elements, boron and beryllium, which precede carbon in the periodic table.

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* The following proof may be given. Any four of the eight hybrid orbitals (of the most strongly bonding type)

$$\tfrac{1}{2}s \pm \tfrac{1}{2}p_x \pm \tfrac{1}{2}p_y \pm \tfrac{1}{2}p_z$$

evidently satisfy condition (1).

Condition (2) is equivalent to the " orthogonality " condition

$$\int (as + bp_x + cp_y + dp_z)\,(a's + b'p_x + c'p_y + d'p_z)\,dv = 0$$

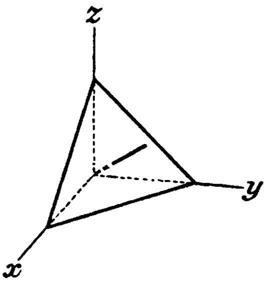
being satisfied for the several pairs of orbitals, and on multiplying out this reduces to the condition

$$aa' + bb' + cc' + dd' = 0.$$

The latter condition is easily seen to be satisfied by the set of four of the above orbitals consisting of that one in which the signs are all positive and the three in which two of the alternative signs are negative.

A p-axis whose direction is determined by equality of the coefficients b, c, and d is evidently a normal to a face of a regular octahedron (Fig. 13). The choice of signs required by condition (2) gives four alternate faces of the octahedron, *i.e.*, faces of the regular tetrahedron. The four orbitals are accordingly independent when their axes have a regular tetrahedral arrangement. The remaining four orbitals (which correspond of course with the remaining faces of the octahedron) also form a set satisfying condition (2), and their axes coincide with those of the complementary tetrahedron.

FIG. 13.



The tervalent boron atom is formed from the ground state $(1s)^2(2s)^2(2p)$ by the promotion of one of the two 2*s*-electrons to the 2*p* state. The resulting electronic configuration (Fig. 14) then has three unpaired electrons, as required for a tervalent element.

The electronic structure of the tervalent boron atom can be symbolised by Fig. 15, in which the two 2*p*-electrons are represented by their rectangular axes of symmetry, and the 2*s*-electron by the circular section of its spherical nodal surface by the plane of the axes of the *p*-electrons. This plane is evidently a plane of symmetry of the combined electron cloud formed by the three valency electrons. The cloud has a uniform maximum extension in this plane, and the strongest bonds which the atom can form must accordingly lie in this plane.

If we assume, as we clearly must, that the three valency bonds are equal, then the three valency electrons must be in three mutually independent orbitals of the same form. Three similar orbitals derived from one 2*s*- and two 2*p*-electrons must clearly be hybrid orbitals of the form $\left(\frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p\right)$.

An electron in one of these hybrid orbitals will give a standing wave closely resembling that of a tetrahedral orbital. It will be axially symmetrical. It will have a nodal surface which, except in the inner part of the atom, approximates to a cone having its apex at the nucleus, but its angle will be smaller than that of a tetrahedral orbital. The electron cloud has a maximum extension on the axis of symmetry, giving a relative bond strength of 1·99 compared with 2 for the corresponding tetrahedral orbital. The axes of symmetry of these orbitals (and therefore also the valency bonds) lie in the plane which contains the axes of the two *p*-electrons, and in order that the orbitals may be mutually independent, their axes must, as is easily shown, be inclined to one another at angles of 120°.

This planar equiangular distribution of the boron valencies, which follows so clearly from the electronic configuration of the tervalent boron atom, is in agreement with the results of experimental investigation of the halides and methides of the element.

We have now to consider beryllium. Here again the form of the element in which the chemist is interested—the bivalent form—results from the ground state of the atom by the promotion of one 2*s*-electron to the 2*p*-state (Fig. 16). The bivalent beryllium atom can be symbolised by a diagram (Fig. 17) in which the 2*s*-electron is indicated by the circular central section of its spherical nodal surface, and the 2*p*-electron by a straight line representing its axis of symmetry. Thus, whereas the tervalent boron atom was characterised by the presence of a unique plane, leading to a planar distribution of its valencies, the bivalent beryllium atom is characterised by a unique line.

The maximum extensions of the electron cloud formed by the two valency electrons evidently lie along this line, and so also must the strongest bonds which the atom is capable of forming. To yield two equivalent bonds the two electrons must be in the hybrid orbitals

$$\left(\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p\right) \quad \text{and} \quad \left(\frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{2}}p\right)$$

since these provide the only means of obtaining an equal distribution of the two modes between the two electrons.

The superposition of waves in the 2*s*- and 2*p*-modes, as has already been explained, produces a new standing wave which is symmetrical about the axis of the *p*-mode and has a maximum extension in one direction along this axis. It will be seen that changing the sign of the *p*-component reverses the direction in which the maximum extension is produced without altering the form of the wave. The two orbitals thus have their maximum extensions in opposite directions along the same axis, giving rise to two valency bonds, having a linear arrangement. The relative bond strength yielded by hybrid orbitals of this form is 1·93.

There is as yet no direct experimental evidence regarding the valency configuration of a bicovalent beryllium compound, but in compounds of other bivalent elements in which an analogous electronic structure of the valency shell is to be expected, such as mercuric bromide, it has invariably been found that the valencies have a linear arrangement.

We have now examined the causes which determine the valency configurations of the elements of the first periodic series from beryllium to oxygen. Similar relationships between the types of electrons concerned in the bond formation and the spatial arrangement of the bonds would be anticipated in the corresponding elements of the higher series. The *s*- and *p*-electrons of higher quantum number are differentiated from the *s*- and *p*-electrons of the *L*-shell by the presence of additional spherical nodes in their standing waves, but these lie deep within the atom and do not greatly alter the general form of the waves in the outer (valency) regions.

As in the *L*-shell, so in each higher shell, there are three *p*-orbitals with mutually perpendicular axes whose relative orientation ultimately determines the valency configurations. The dominant part which *p*-electrons play in fixing the relative directions of the valencies is clearly shown by the results of the experimental determinations of molecular configurations.

In the bivalent atoms of the elements of Group II the valency electrons include *one* *p*-electron only and the valencies have a unidimensional arrangement—in every case examined the two valencies have been found to lie in the same straight line.

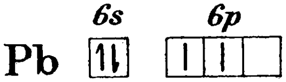
Group III elements have in their atoms three valency electrons. Of these *two* are *p*-electrons and the valencies have a bidimensional arrangement—the observations have shown in all the cases investigated that the three valencies lie in one plane.

In the quadrivalent atoms of the elements of Group IV and the tervalent atoms of those of Group V the valency electrons include *three* *p*-electrons and the valencies have a tridimensional configuration. The experimental results have shown that the arrangement is uniformly tetrahedral in Group IV and uniformly pyramidal in Group V. The reasons for the difference in the valency configurations in the two tervalent groups—planar in Group III, non-planar in Group V—are thus apparent.

In the bivalent elements of Group VI at least *two* *p*-electrons take part in the bond formation, and accordingly a unidimensional bond configuration, as is characteristic of the bivalent elements of Group II, cannot occur. For these elements in their bicovalent compounds the experimental results have without exception shown an angular arrangement of the valencies.

Another class of bicovalent atoms consists of the atoms of Group IV elements in their bivalent forms. These atoms are then presumably in electronic states exemplified by the configuration for the *P* shell of lead shown in Fig. 18. The valency electrons would thus be in pure *p*-orbitals and an intervalency angle of about 90° would be expected. Only the higher members of the group—tin and lead—can function as bivalent, since in them the bond energies (which have to be drawn upon to supply the energy required to produce the quadrivalent from the ground state of the atom) are smaller relatively to the *s*-*p* energy differences than they are in the lower members. The resulting compounds are few in number, and the experimental investigation of their valency configuration presents special difficulties. However, a definite result has been obtained for the lead bromide molecule by *X*-ray analysis of the crystal structure of ammonium and rubidium lead pentabromides (Powell and Tasker, J., 1937, 119). The angle found for the lead intervalency angle was 85½° ± 2°, in approximate accordance with these considerations.

FIG. 18.



Special interest attaches to the type of 4-covalency found in co-ordination derivatives of certain metals—chiefly bivalent nickel, palladium, and platinum—in which the four bonds, instead of being equally distributed in space, as in the tetrahedral arrangement, are concentrated in one plane with intervalency angles of 90°. The correlation of this valency type, the " square configuration " of which has been fully established by experiment, with the electronic structure of the metallic atoms concerned is one of the triumphs of the Pauling method.

Nickel being taken as representing the simplest of these elements, a typical reaction yielding a compound of 4-covalent nickel is that between the nickel and cyanogen ions yielding the complex nickelocyanide ion : $Ni^{++} + 4CN^- = [Ni(CN)_4]^{--}$. The nickel ion has the electronic configuration shown in Fig. 19 (*a*), which accords with its magnetic moment. Since in this part of the periodic system 3*d*- are more firmly bound than 4*p*-electrons, the four vacant orbitals used to link the cyanogen groups are probably those indicated in Fig. 19 (*b*), in which the nickel ion is represented in an activated form.

The nickel valency electrons would then be derived from the configuration $(3d)(4s)(4p)^2$. Four equivalent bonds derived from this configuration would have to be obtained (as can easily be seen) from hybrid orbitals of the form

$$\tfrac{1}{2}s \pm \tfrac{1}{2}d \pm \frac{1}{\sqrt{2}}p.$$

Pauling showed that four hybrid orbitals of this kind give four strong bonds of relative strength 2·694 which are co-planar and have intervalency angles of 90°. These orbitals thus provide a theoretical basis for the square valency configuration.

$$\left.\begin{matrix}\psi_1\\ \psi_2\end{matrix}\right\} = \tfrac{1}{2}s + \tfrac{1}{2}d_x \pm \frac{1}{\sqrt{2}}p_x$$

$$\left.\begin{matrix}\psi_3\\ \psi_4\end{matrix}\right\} = \tfrac{1}{2}s - \tfrac{1}{2}d_x \pm \frac{1}{\sqrt{2}}p_y$$

It may help towards a more concrete idea of the manner in which this arrangement of the valencies results if the hybrid orbitals are considered in relation to the forms of the component electronic waves. 3-Quantum electrons form standing waves with two nodal surfaces. The two surfaces may, as we have seen, either be two spheres (giving *s*-electrons), or one sphere and one plane (giving *p*-electrons); but there is evidently a third possibility, namely, two planes, and this gives *d*-electrons.

The two nodal planes, as would naturally be expected, are perpendicular to one another and pass through the nucleus. The general form of the standing wave conditioned by a nodal system of this kind is easily seen (it is shown in equatorial section in Fig. 20). It must consist of four lobes, one in each quadrant. The displacements must be of opposite signs in adjacent quadrants and the line of intersection of the nodal planes will be an axis of twofold symmetry. The equatorial plane will be a plane of symmetry for each lobe. The wave will have a maximum amplitude on four axes in the equatorial plane bisecting the angles between the nodes (the axes of *x* and *y* in the figure) and the maximum extension of each lobe will be along these axes.

There are four *d*-orbitals of this form differing only in orientation. The relation of the orientation of the

d_x- to those of the p_x- and p_y-orbitals is shown in the figure. (The fifth d-orbital has a different form, having a bi-conical nodal surface.) To obtain the form of the electron wave corresponding with the hybrid orbital ψ_1, we have first to consider the superposition of $\frac{1}{2}s$ on $\frac{1}{2}d$. In the two lobes of the d_x wave traversed by the x-axis the displacements are in the same sense as in the s-wave; in those traversed by the y-axis they are in the opposite sense to those of the s-wave. The superposition thus results in the amplification of the amplitudes in the x-lobes and their diminution in the y-lobes. When $\frac{1}{\sqrt{2}}p$ is then superposed on the resultant wave there will be a further amplification in the right-hand x-lobe, but in the left-hand x-lobe the amplitudes will be diminished, since in a p-wave displacements are in opposite senses on either side of the nodal plane. The wave finally resulting from the superposition of the three components thus has its maximum extension along the x-axis in the positive direction (*i.e.*, to the right in the diagram), and a bond formed by an electron in this state would be in that direction.

The second hybrid orbital ψ_2 differs from the first in the sign of the p_x component. This change of sign is equivalent to an interchange of the two halves into which the p_x wave is divided by its nodal plane. Hence when $-(1/\sqrt{2})p$ is superposed on the resultant of $(\frac{1}{2}s + \frac{1}{2}p)$ amplitudes will be diminished in the right-hand x-lobe and correspondingly increased in the left-hand lobe. The resultant wave will have its maximum extension along the x-axis in the negative direction and this will be the direction of the corresponding bond. The orbitals ψ_1 and ψ_2 thus give two oppositely directed bonds along the x-axis.

The next pair of orbitals ψ_3 and ψ_4 differ from the first pair in two respects only: (i) the sign of the d_x component is reversed, (ii) p_x in the last term is replaced by p_y. As the diagram plainly shows, each of these changes is equivalent to a rotation of 90° in a clock-wise direction about the z-axis. This pair of orbitals, therefore, like ψ_1 and ψ_2, gives two oppositely directed bonds, but these lie along the y-axis. The set of four orbitals is thus seen to yield four mutually perpendicular coplanar bonds.

A very important stereochemical class—second in importance only to the tetrahedral 4-covalent compounds—is formed by the derivatives of elements having the covalency 6. Compounds of this type occur chiefly among the metallic co-ordination derivatives, and experimental investigation has invariably shown them to have an octahedral configuration. As an example of a metal giving 6-co-ordination derivatives cobalt may be taken, since in this element the tendency to form such compounds is especially marked. The cobaltic ion has the electronic structure indicated in Fig. 21 (*a*) but the 6-co-ordination derivatives of cobalt are presumably derived from the activated form indicated in Fig. 21 (*b*) which provides the six vacant orbitals required without going to a higher level than $4p$.

The bonding orbitals would then be derived from the configuration $(3d)^2(4s)(4p)^3$. Applying the same methods as he used in deriving the tetrahedral and the square hybrid orbitals for 4-covalent atoms, Pauling showed that from this group a set of six equivalent hybrid orbitals can be formed having the relative bond strength 2·923 (almost equal to the maximum strength 3 obtainable from s-, p-, and d-orbitals), with the bonds directed towards the corners of a regular octahedron. Thus the octahedral 6-covalent type also can be brought into relationship with the electronic structure of the atoms with which it is associated.

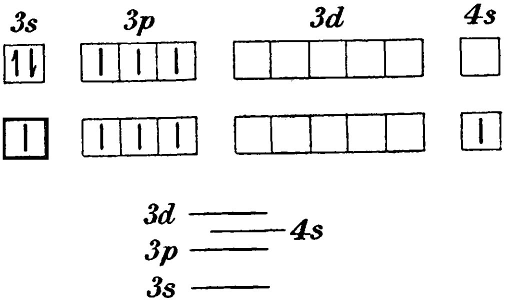
There remains now only more valency type to be dealt with—that occurring in atoms with a covalency of 5. Several compounds of 5-covalent atoms have been examined—chiefly by electron diffraction—and all found to be trigonal bipyramids. The bipyramidal arrangement places the valencies in two sets—a *triad* lying in the equatorial plane with intervalency angles of 120° and an opposed *pair* directed along the polar axis, thus making angles of 90° with the equatorial triad (Fig. 22). It would seem evident that these two sets of valencies cannot be derived from one single interequivalent set of hybrid orbitals. There is indeed some experimental evidence of a difference. Pauling ("The Nature of the Chemical Bond," 1939) states that V. Shomaker (unpublished investigation) has obtained evidence that the two chlorine atoms at the apices of the pyramids in phosphorus pentachloride are 2·11 A. from the phosphorus atom, the other three being at 2·04 A. It should be stated, however, that other investigators have discovered no measurable difference in the bond lengths either in the phosphorus pentahalides or in molybdenum pentachloride.

Taking the phosphorus pentahalides as the simplest examples of this configurational type, we have first to consider how the quinquevalent phosphorus atom arises. It must be produced from the ground state by the promotion of one of the paired $3s$-electrons to an unoccupied orbital, giving a state with five unpaired electrons, and we have to determine to which orbital the promotion will take place. It will evidently be either a $3d$- or the $4s$-orbital.

In the spectrum of un-ionised phosphorus (PI) examined by Robinson (*Physical Rev.*, **1936**, **49**, 297) terms occur derived from the combinations $(3s)^2(3p)^2(4s)$ and $(3s)^2(3p)^2(3d)$—that is, from combinations arising from the ground state by the promotion of a $(3p)$ electron in the one case to a $(4s)$ and in the other to a $(3d)$ orbital. The terms where the promotion is to a $(4s)$ orbital are lower in level by 1·7—1·8 electron-volts than those in which it is to a $(3d)$ orbital. It is hence to be inferred that the most probable structure for the quinquevalent phosphorus atom is that arising from the ground state by the promotion of a $(3s)$ electron to the $(4s)$ orbital (see Fig. 23). We should then have to form from the resulting configuration $(3s)(3p)^3(4s)$ two sets of hybrid orbitals—one for the three equatorial, the other for the two polar bonds.

We have seen in discussing the valencies of the Group III and Group II elements that three equivalent coplanar bonds can be formed from the combination $(s)(p)^2$ and two collinear bonds from the combination (*s*)(*p*). The question therefore at once arises whether the three equatorial bonds could not be formed by hybridisation of the $3p_x$, the $3p_y$ and one of the *s*-orbitals, while at the same time hybridisation of the $3p_z$ and the remaining *s*-orbital yielded the two polar bonds. From the five valency electrons mutually independent orbitals could be thus constructed which would give a set of five bonds having the correct orientation.

FIG. 23.



In this review of the chief types of bond arrangements the configurations have been considered from the point of view of the method of " localised pairs." The method admittedly does not provide rigorous explanations of valency configurations. It uses considerable approximations, it depends on rules not fully established, and its conclusions are drawn from considerations of the isolated atom.

Nevertheless, the methods and rules employed are eminently reasonable and command general assent. Their application leads simply and naturally to results which accord with the experimental facts, and the method undoubtedly provides the easiest means of approach for chemists who desire some knowledge of the causes which determine normal valency configurations.*

In preparing this lecture I have been indebted to helpful discussions on various points with Professor J. E. Lennard-Jones.

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* For multiple bonds, which lie outside the scope of this lecture, other methods have been developed.