ON THE PAIR BOND THEORY OF VALENCY.

BY H. LESSHEIM
AND
R. SAMUEL,

Muslim University, Aligarh.

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The method of molecular orbitals has been interpreted as leading to a single-electron bond theory of valency. This involves the assumption that in a covalent molecule the nuclear fields are almost degenerated and that the effect of the complete degeneracy due to the equality of the electrons is negligible. This implies at the same time a relation of the strength of the linkage to the polarity of the bond. It is proposed to show that, contrary to the above, chemical union is mainly an effect of the degeneracy due to the electrons. Such an interpretation of the method of molecular orbitals is mathematically equivalent to the previous one and does not require the above assumptions (Sections I to VII); it leads to an electron pair bond theory of valency. Spectroscopic evidence appears to favour the present view and to contradict the above relation between polarity and energy of linkage (Sections II, VIII to XI). The single-electron bond theory of valency requires the Octet Rule or its extensions to explain the phenomenon of saturation of valences and therefore the existence of different varieties of non-electrostatic linkage. Such a description of chemical evidence is not possible without introducing various additional hypotheses (Section XII). All this is not necessary in a pair bond theory of valency in which chemical linkage is produced by the degeneracy due to the equality of the electrons whereas the degeneracy of the nuclear fields is reduced to an effect determining the polarity (Sections XIII to XV).

I.

In this paper it is proposed to show that the results of Band Spectroscopy and the experimental facts as presented by Chemistry can be satisfactorily expressed in terms of an electron-pair bond theory of valency. During the last three or four years the method of molecular orbitals appears to have been interpreted as a single-electron bond theory of valency, which in a way has been responsible for an antagonism towards the pair bond theory. From this point of view we shall discuss the principles underlying the wave-mechanical treatment of the process of formation of molecules, although a critical analysis of the various methods has already been given before by several authors.1,2,3

The wavefunction of a molecule may be constructed in two ways:—

Method A, which has first been developed by Heitler and London4 investigates the interaction of the atoms constituting the molecule. This
can be done in two different ways; one can either form complete wavefunctions for each of the interacting atoms and then construct the wavefunction of the molecule by combining them. Confined to s-states, this view leads to the theory of spin valency and has been developed by London, Heitler, Born, Heitler and Rumer, Weyl.6 Or one can construct the wavefunction of the molecule from those of single-electron pairs representing one link each. Such a link is accordingly localised between two particular ones of the constituent atoms contributing one electron each to the pair. (Kemble and Zener, Bartlett, Slater, Pauling, Penney and others.6)

Method B, generally termed the method of molecular orbitals, considers each single electron in the completed molecule, i.e. in the field of all the nuclei or cores concerned, a core in this case consisting of the nucleus and all those electrons which for practical purposes can be considered as localised about it and not participating in the formation of the molecule (Lennard-Jones). The wavefunction of the molecule is then a combination of those of its constituent electrons. We owe the development of this method to Hund, Mulliken, Herzberg and Lennard-Jones.1,7,8,10,11,12

For a theory of valency the essential point is the transition between the system of the separated atoms and the molecule, i.e. in the field of all the nuclei or cores concerned, a core in this case consisting of the nucleus and all those electrons which for practical purposes can be considered as localised about it and not participating in the formation of the molecule (Lennard-Jones). The wavefunction of the molecule is then a combination of those of its constituent electrons. We owe the development of this method to Hund, Mulliken, Herzberg and Lennard-Jones.1,7,8,10,11,12

On the other hand method B is especially designed to describe the conditions at those internuclear distances which prevail in the completed molecule. Without considering the interaction between the single electrons this method is of course unable to give the amount of the energy of dissociation and unable, furthermore, to distinguish between the attractive and the repulsive terms of a system of two or more centres. On taking into consideration the interaction between the electrons up to sufficiently high approximations the method should also be able to determine the energy of the molecule and to follow the process of dissociation.

It is evident from the above that, if it is intended to use method B, the ideal manner of calculating the transition from the molecule to the separated atoms would be a combination of the two methods, commencing with method B in the molecule and changing gradually to method A, as the
Internuclear distance increases. This procedure presents, however, the greatest mathematical difficulties. Therefore the simple correlation table is generally adopted to describe the transition to the separated system. This procedure yields already in zeroth approximation a description of the term system of the molecule, but only a qualitative picture of the change of the term order, and gives us neither an idea of the absolute increase or decrease of energy in the process of dissociation nor even an idea as to whether a particular term means attraction or repulsion. The correlation table tells us only whether a particular electron of the molecule was an s, p, or d electron in the separated atoms, but it does not give any direct information as to which atom it originates from. Therefore, as is well known, the resulting ratio of the probabilities of the different products of dissociation is incorrect. Such procedure in $\text{H}_2$ for instance gives 50% atoms and 50% positive and negative ions. This is a direct result of the neglect of the mutual interaction* of the electrons, and shows that this approximation is not sufficient for a description of the process of dissociation. Just the process of dissociation is more important from the point of view of a theory of valency than a description of the term system of the completed molecule. The introduction of the mutual interaction of the electrons in the next approximation is already an approach to the view of method A.

The method of molecular orbitals contains already in zeroth approximation the degeneracy of the nuclear fields which, where it exists, results in a bonding effect. It has been assumed that this bonding effect is generally the cause of chemical linkage. It is proposed to show that in general this effect is too weak to produce chemical combination, and that in order to find its actual cause, we have to introduce also here the next approximation, i.e., the interaction of the electrons, which owing to the degeneracy of the system due to the equality of the electrons produces a strong bonding effect. This results in the formation of electron pairs, which is also an approach to method A, where they appear already in zeroth approximation but in a slightly different way. The two methods are of course ultimately bound to merge, but in general we are not able to calculate as far as this.

II.

It is true that mostly the orbital method has been interpreted as a single-electron bond theory of valency. Certain of the arguments for

* It is here particularly referred to that part of the interaction of two electrons, which cannot be represented by a simple screening effect, but involves the use of integrals containing the wavefunctions of both of them. Evidently it is just this part of the interaction that the symmetry properties of the total wavefunction depend upon.
this interpretation are connected with the discussion on localised and non-localised bonds which are dealt with in Section VI. Here we intend to discuss this interpretation as far as it is concerned with the energy of formation of a molecule.

Chemical union means liberation of energy on decreasing internuclear distance. There remain only two possibilities which coincide in the case of the H₂ molecule and accordingly allow of two different manners of generalisation, i.e. the neutralisation of the spins of the electrons and the degeneracy of the system resulting in the splitting of the terms. Either of these features may serve as a distinguishing characteristic and may be generalised to the basic postulate of a theory of linkage.

If we postulate that chemical union occurs whenever two electrons counterbalance their spins, we arrive at the theory of spin valency which although successful in many details has proved to be unable to give a full account of chemical combination. Nowadays it is, however, generally assumed that the neutralisation of spin is rather in the nature of a consequence of Pauli's principle and that chemical linkage is brought about by a degeneracy of the system.

If in the diatomic molecule the wavefunction of a valency electron in the field of one of the atomic cores is \( \psi_a \) and the corresponding one for the other core \( \psi_b \), and if the two cores concerned are equal, the wavefunction of the electron in the combined system in zeroth approximation without the normalising factor is given by \( \psi_a(1) \pm \psi_b(1) \). With the usual definition of the signs of the wavefunction \( \psi_a(1) + \psi_b(1) \) will belong to the lower term. A second electron entering the same orbital, i.e. getting the same wavefunctions \( \psi_a(2) \pm \psi_b(2) \) will give rise to a degeneracy owing to the equality of the two electrons, thus causing the wavefunctions of the two of them to enter combinations of which

\[
\{\psi_a(1) + \psi_b(1)\} \{\psi_a(2) + \psi_b(2)\}
\]

belongs to the lowest eigenvalue, to which the linkage is ascribed.

There are two kinds of symmetrical relation in the wavefunction, one inside either bracket and one connecting the two brackets with each other. The first is due to the degeneracy of the eigenvalues brought about by the equality of the atomic fields, the second one due to that caused by the equality of the electrons. When the atomic fields grow slightly different, the normalising factors will be different too and the bonding function will be approximately given by

\[
\{a\psi_a(1) + b\psi_b(1)\} \{a\psi_a(2) + b\psi_b(2)\}.
\]

The symmetrical relation brought about by the equality of the electrons remains unchanged. It remains so until, when the gradual change of the
fields continues, every likeness disappears, when the wavefunction \( a\psi_a + b\psi_b \) gradually turns into \( \psi_a \) or \( \psi_b \), whichever is the lowest. If this is \( \psi_a \), the relation eventually left is \( \psi_a(1)\psi_a(2) \), which still retains its symmetry as to the electrons and thus represents ionic linkage, both the electrons being with the same nucleus. It will be seen later on, how the gradual change of the wavefunction actually displays the growing polarity of the bond thus manifesting the transition from covalent to electrovalent linkage.

The correlation table provides only a qualitative scheme of the rearrangement of the terms on formation of the molecule and accordingly shows, whether a particular electron will be bound to the molecular system with more energy or less than another one. In the molecule a premoted orbital is higher than a corresponding unpremoted one, but the correlation table is unable to indicate whether the two together are higher or lower than the correlated ones in the atom. To provide a quantitative relation between the right and left hand sides of the table Mulliken fixes the energy difference between the lower ends (1s\(\sigma \) — 1s\(\sigma \)) by referring to \( H_2^+ \), when the single electron present passes from 1s of the atom in the separated system to 1s\(\sigma \) of the molecule ion. In this manner, showing that in the case of \( H_2^+ \) the lowest level of the molecular system is considerably below the correlated atomic level, Mulliken infers that in general unpremoted electrons are bonding and therefore premoted ones, being bound with lesser energy, are generally anti-bonding. This argumentation involves the consideration of one electron only, which accordingly can act as bonding or anti-bonding already by itself without the interference of a second one. If, however, as in the case of \( H_2 \) two electrons are present and come into the same bonding orbital, the energy of formation will be the sum of the bonding energies of either of them, in the next approximation modified rather than actually influenced by the energy of interaction. Experimental evidence for this is found in the actual existence of \( H_2^+ \) with one electron only.

It has been pointed out by Hund that such a bonding power based on the degeneracy of the nuclear fields is exerted by a single electron already, when the fields short of being identical are only approximately degenerated. The bonding wavefunction, which in the rigorously degenerated case of equal nuclei is given by \( \psi_a + \psi_b \), changes in almost equal fields into \( a\psi_a + b\psi_b \), where \( a \) is slightly different from \( b \). This difference increases with growing inequality of the fields, the degeneracy and along with it the bonding power gradually decreasing and eventually vanishing, when \( a >> b \) or \( b >> a \) and the electron actually belongs to one of the nuclei.
only. If therefore a theory of valency is solely based on this degeneracy, it is bound to meet with difficulties. One such difficulty results from the existence of LiH along with the non-existence of (LiII)+. LiH is a well-known stable chemical compound; bands due to it have been measured. (LiH)+ has never been known to exist; wave-mechanical considerations showed it to be incapable of existence, and furthermore, if it existed nevertheless, we should all the more expect HeH made up of unexcited He and H atoms to exist, because it has the same electrons, but a much smaller repulsion of the nuclei. When Li and H combine to form LiH, we should find an LiH with one bonding 2s\sigma and one anti-bonding 2p\sigma electron; their effects would more or less cancel each other and if we obtain a linkage at all, it would be a very weak one, which contradicts physical evidence showing a dissociation energy of about 2.5 electron volts. An attempt to explain this by considering the anti-bonding electron as nearly non-bonding (slight promotion only) and ascribing a bonding power of about 3 volts to the bonding electron would fail, since Li\(_2\) with two bonding electrons of the same kind, with lesser repulsion of the nuclei, and with the additional bonding power of the rigorous degeneracy of the eigenvalues on account of the two cores being equal, displays a dissociation energy of 1.1 electron volts only. LiH can then be explained only by means of a generalisation of Lennard-Jones's manner of denumerating the orbitals, i.e. by starting afresh on the outside of each core with the main quantum number 1. In this case either of the electrons would be a bonding one; but then the theory would fail to explain the non-existence of the ions (LiH)+, (NaH)+, (KH)+ and so on which would still possess a bonding electron. The corresponding neutral molecules are all of them stable compounds. This becomes even clearer, when we note that molecules like Li\(_2\), Na\(_2\), K\(_2\), LiK, NaK and so on are spectroscopically known, but not a single one of their ions. It is also significant, that in the second group the hydrides both neutral and ionised are capable of existence (BeH, BeH+; MgH, MgH+; ZnH, ZnH+; etc.).

The rigorous degeneracy due to completely equal cores results doubtless in a bonding power. But that this is a proportionately weak one as compared with that produced by the equality of electrons, becomes evident from the fact that H\(_2\)+ is the only existing instance. As soon as we substitute anything else for the hydrogen nucleus, viz. a nucleus of higher charge (He+++) or a core of larger dimension (Li+), the bonding power of this degeneracy is too weak to overcome the enlarged repulsion of the nuclei or the enlarged distance between the cores. Since already Li\(_2\)+ with its rigorous degeneracy of its eigenvalues is not
capable of existence,* and since this bond is further weakened, when the

eigenvalues are, if at all, only almost degenerated, it would be difficult
to understand how molecules with different nuclei could possibly exist, if
there was no effect other than the degeneracy of the fields.

The above discussion shows clearly that already in the simplest cases
and before entering into a discussion of finer details objections can be
raised against the interpretation of the method of molecular orbitals as a
single-electron bond theory. To our mind all these difficulties and others
that will be pointed out below are due only to an unnecessary restriction
as to the bonding effects of a degeneracy. There is no reason to consider
the interaction of several electrons on the same orbital as more or less
negligible and to prefer the incomplete degeneracy of the nuclear fields to the
degeneracy due to the equality of the electrons, which also results in a splitting
of the terms and accordingly in a bonding effect. This degeneracy is
always rigorous and remains so, even if the degeneracy of the fields disappears
completely, i.e. when the molecular orbital changes gradually into an atomic
orbital, or in other words the bond changes from covalency to electrovalency.
Accordingly we feel compelled to regard the interaction between the electrons
as the principal cause of chemical union and to conclude that the effect of
degeneracy of the electrons predominates over the effect of degeneracy of
the nuclear fields. Thus we are led to an interpretation of the orbital
method as a pair-bond theory of valency. From this point of view H2+
and perhaps the Helium molecule ions are the only possible instances of a
single-electron bond, whereas in general chemical linkage is due to the
formation of pairs of electrons on the same orbital to which two different
atoms contribute one electron each. We remark here only and shall discuss
more fully in Section VI that in the case of polyatomic molecules this does
not involve a strict localisation of the bonds.

Mathematically this view is fully equivalent to that of the single-
electron bond and it does not require the additional assumption of approximate
degeneracy for unequal fields. We are even of opinion that experimental evidence is in favour of the pair bond view. The above
examples show that only those molecules exist which have at least two
electrons. Thus the existence of the neutral molecules and the non-existence
of their ions in the first group and the existence of either kind in the second

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* Note added in proof.—In his paper on the molecule Li2+, James shows that
Pauling's estimate for the dissociation energy of Li2+ made by reference to the situation
with H2 and H2+ taken to be analogous systems, cannot be considered to be conclusive.
His own variational method is essentially the same as that applied by him in the case
of Li2 where it yields only half the experimental value.
group is easily explained in a pair bond theory of valency. The phenomenon of premotion then finds its place automatically in the electron-pair bond theory as an additional effect, i.e. only as incidental one caused by the change of the order of terms and superposed on the bonding effect, thus increasing or decreasing the energy of linkage.

III.

Independently of the above just the conditions in $\text{H}_2^+$ are very instructive as regards the premotion being able to govern the linkage. Teller's calculation\textsuperscript{18} throws light on the question whether particular orbitals can be considered as either bonding or anti-bonding. The degeneracy due to the equality of the nuclei brings about a linkage only, if the electron is in an $\Sigma$ orbital; all the other terms, whether premoted or non-premoted, are repulsive except the term $3\sigma(2p)\dagger$ which has a flat minimum at a large internuclear distance, and just this orbital is a highly premoted one, which ought to be anti-bonding, if the premotion alone was decisive.

Hund assumes that a linkage occurs only, if the electrons enter an unpremoted orbital, whereas an electron pair in a premoted one acts repulsively. When combining two atoms with one $s$ electron each we get the following wavefunctions:—

\[
\begin{align*}
\{a\psi_a(1) + b\psi_a(1)\} \{a\psi_a(2) + b\psi_a(2)\} \\
\{a\psi_a(1) + b\psi_a(1)\} \{c\psi_u(2) - d\psi_u(2)\} - \{a\psi_u(2) + b\psi_u(2)\} \{c\psi_a(1) - d\psi_a(1)\} \\
\{a\psi_a(1) + b\psi_a(1)\} \{a\psi_a(2) - d\psi_a(2)\} + \{a\psi_u(2) + b\psi_u(2)\} \{c\psi_a(1) - d\psi_a(1)\} \\
\{a\psi_a(1) - d\psi_a(1)\} \{c\psi_u(2) - d\psi_u(2)\}
\end{align*}
\]

In the case of equal nuclei ($a=b$, $c=d$) they belong to the terms $\sigma_g$, $\Sigma_u$, $\pi_u$, $\pi_u$, $\Pi_u$, $\sigma_u$, $\pi_u$, $\Pi_u$, $\Pi_u$, $\Sigma_u$. According to Hund only the first of these would be a bonding one, whereas the last one is not bonding, though it represents also the entry of both the electrons into the same orbital, which, however, does not satisfy the additional condition of non-premotion. The experimental evidence at present available is not enough to decide whether or not this additional imposition is necessary, because in the well-known lighter molecules there is no term known which can serve to decide this question. Since the premoted groups lie higher in the molecule, the number of p-electrons becomes sufficient to fill one of them only when a linkage is already established in an unpremoted one. The cases of $\text{H}_2$ and $\text{H}_2^+$ are not capable of generalisation.

\textsuperscript{1} This orbital is in fact $3\sigma(2p)$ as also quoted by Teller. Due to the correlation in the one-electron-system being somewhat different from that in other cases, this orbital is highly premoted, whereas the corresponding orbital $3\sigma(2p)$ in other systems is not "premoted", though "promoted".
for this purpose. In H₂ all the above states are bonding except the triplet term. The excited terms of H₂⁺ indicate only that non-premotional alone by itself cannot possibly be responsible for the linkage. Considering that the effect of premotion only superposes itself upon the actual bonding effect of the interacting electrons, it is clear that unpremoted orbitals contribute more, premoted ones less to the energy of linkage, but it is by no means proved that an electron pair in a premoted group is really anti-bonding.* Instead of introducing the symmetrical relation of the nuclei as an additional postulate, we are rather inclined to believe, that also in the case of an electron pair in a premoted group, the interaction of the electrons exerts a bonding power, counteracted by their premotion, and that accordingly the total effect can vary from case to case, though at this stage of our knowledge it cannot be predicted as to whether it will provide a positive or negative contribution to the energy of linkage.

IV.

If two atoms possessing more than one electron each combine, e.g., one with 1 and one with 3 p-electrons which may constitute a π₄ (p) group in the molecule we get, per electron, in the lowest state a partial wavefunction of the type \(a\psi_A + b\psi_B\) which is the same for all the electrons on the same orbital. As a matter of principle each electron is in the field of both the nuclei and is accordingly to be considered as belonging to both of them in the completed molecule. The coefficients \(a\) and \(b\) with which the nuclei enter into the partial wavefunction are, however, different and are functions of the internuclear distance. If we consider the case that on dissociation of the molecule the π₄ group is broken up into 1 + 3 electrons the analytical representation of this process would be that with increasing internuclear distance \(a\) and \(b\) assume such values that the resulting probability for an electron to remain with one nucleus is three times as much as for the other nucleus. In the completed molecule the ratio between \(a\) and \(b\) is not necessarily the same as in the separated system, but still far from being equal to 1, because the two central fields, composing the molecular field, are far from being equal. The field acting upon the π₄ group—neglecting polarisation—is composed of two central fields, those of A⁺ and B³⁺, which are of course vastly different and do not give rise to an actual degeneracy. Thus the dissymmetry of the products of dissociation prevails already in the molecule and the distribution of the electrons into groups according to their origin is not lost at all, when on chemical combination they join in the same orbital.

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* The pair in the premoted group (the fourth function above) satisfies also the criterion of linkage in method A, i.e. the wavefunctions of the two electrons are overlapping.
Chemistry defines the number of valencies of a particular atom as the number of monovalent atoms which can be linked by it. If it is intended to develop a wave-mechanical conception of valency which meets the requirements of chemistry, it must be inferred that the fact of the splitting of the said $\pi^4$ group into $1+3$ electrons on dissociation and its pre-arrangement in the molecule lead us to count the linkage in question as monovalent. A convenient way of expressing this is to count for the number of bonds only those pairs which contain electrons of different atoms and to neglect for this denumeration pairs of electrons from the same atom.

This is also the manner in which Hund counts the number of valencies. Mulliken and Herzberg from the viewpoint of independent electrons count each of them as half a valency, and therefore the number of valencies is the total number of pairs of electrons in molecular orbitals, irrespective of the number of electrons contributed by each single atom. To take a particular example, the electronic configuration of CO in its ground state $^1\Sigma$ is

$$\sigma^2(2s)\ \sigma^*^2(2s)\ \pi^4(2p)\ \sigma^2(2p).$$

Whatever theory we base our considerations on, it is not necessary to take into account the two $\sigma(2s)$ groups at all. According to Mulliken and Herzberg one of them is bonding, the other anti-bonding; so their effects cancel each other. According to Hund they are not to be counted, since no electrons from different atoms join in them; one of them contains the two $s$-electrons of carbon, the other those of oxygen. So our discussion is restricted to the $\pi(2p)\ \sigma^2(2p)$ groups. Both of them are bonding (non-promoted), they contain six electrons, i.e., three pairs. Thus the linkage according to Mulliken and Herzberg is to be termed trivalent. But since two of these six p-electrons are provided by carbon and four by oxygen, there are only two pairs in which electrons from different atoms join, whereas the remaining pair belongs to oxygen alone. So according to Hund's terminology the linkage is divalent.

There exists doubtless a certain bonding power among these six p-electrons for which slight differences in the nuclear charges are of very little importance. It is of course impossible to try and identify particular ones of the electrons as to which of the atoms they originate from. In this sense the definition of Mulliken and Herzberg is correct. The number of valencies defined like that remains, however, unaltered, when the nuclear charges change provided the total number of p-electrons contributed by both the atoms remains six. So we would have the same trivalency in "compounds" as $N_2$, CO, BF, Be Ne. But this is clearly not the conception of valency developed by chemistry. The chemical valencies of the said combinations are 3, 2, 1 and 0 respectively. The reason for this disagreement
is that chemistry takes into account the number of electrons going to
the particular atoms on dissociation. Only then the number of bonds is
identical with the number of valencies of the atoms. Of course it is still
possible to say that in the case of Be Ne the six p-electrons do not go
any more into molecular orbitals, whereas in CO and BF the adiabatical
dissociation would lead us actually to C-+O+ and B--F++ respectively.
Such an explanation has actually been attempted by Pauling, but proved
to be inadmissible.* On the contrary the analysis of the term system of
CO is definitely in favour of an ordinary covalent linkage. It has been
shown elsewhere at greater length that this linkage is indeed a divalent one
in spite of its high energy of dissociation, high frequency of Raman effect and
low dipole moment. The recent value of the energy of dissociation of Ns
takes completely away the similarity to that of CO and therefore also all
possibility of comparing the nitrides and the oxides. In BF the assumption
of a triple link, which is the logical consequence but leads obviously to nine
links in BFs, is still less in agreement with the ideas of chemistry, and
similar consequences could be shown in many other cases. Therefore in
order to come to an agreement with chemistry, only those pairs of electrons
ought to be counted in which one electron of either partner joins. This way
of counting the linkages in a molecule has the advantage, that the number
of bonds is brought into a simple connection with the number of valencies
of the atoms concerned.

The difference between these two conceptions and the justification of
the second one can also be expressed as follows: The term system of the
molecule Ns is that of a molecule with six electrons in the molecular
orbitals

\[ \pi^6(2p) \sigma^2(2p) \]

formed by the original six p-electrons of the two N atoms. The term
system of the CO molecule will not differ very much from that of Ns, but
the different distribution of the nuclear charges will produce a different
distribution of the electric charge on the molecular orbitals. If one
considers CO to be triply linked in the same manner as the Ns molecule one
does not pay consideration to the fact that the change in the distribution of
nuclear charge on transition from Ns to CO at once involves an entirely
different correlation to the terms of the separated atoms. In either case we
have to consider two groups of atomic terms, with distributions of the six
p-electrons in 3+3 and 2+4 respectively. In Ns the groundmost level of
the separated atoms, to which also the ground level of the molecule is

* Reference No. 10, footnote on page 528, and Mulliken.
correlated, has the distribution 3+3, the lowest level of the distribution 2+4 is much higher, the difference of energy being the ionisation potential of N (14.5 volts) diminished by the electronic affinity of N, which is very small, if not negative. Therefore the terms of the N₂ molecule to be correlated to atoms with the distribution 2+4 have potential curves going to much higher atomic levels than those which are to be correlated to atoms with the distribution 3+3. Since potential curves of terms of equal race do not intersect, the lower terms of the N₂ molecule, especially the ground level 1Σ₀, belong to two nitrogen atoms with three p-electrons each.

The matter is different with the CO molecule in spite of its term system being nearly equal to that of N₂. Here the lower terms are correlated to atoms which have 2 and 4 p-electrons respectively, e.g. in their ground levels. The group of atomic terms with the distribution of electrons 3+3 is much higher, i.e. high enough not to perturb the lower terms of the molecule, since the ionisation potential of oxygen is 13.6 volts and the electronic affinity of carbon most probably negative or, if positive, negligibly small. The ground level of the molecule with the same electronic configuration, which in N₂ belongs to N+N with 3+3 p-electrons, belongs in CO to C+O with 2+4 p-electrons.

Though the change of the nuclear charges on transition from N₂ to CO does not essentially alter the term system of the molecule, it is already sufficient to cause a small perturbation, e.g. a small increase of the internuclear distance, to divide the six electrons in question into two groups of 3 electrons each in the case of N₂, but of 2 and 4 electrons respectively in the case of CO. Hence it is not correct to say that if N₂ is triply linked, CO with the same electronic configuration is also triply linked, since just a small perturbation of the said type is a decisive test. This test shows that anything working against the linkage has to work against three bonds in one case and against two bonds in the other one. If we would consider the configuration in the molecule alone without submitting it to the perturbation test, the meaning of the expressions "triply linked" or "doubly linked" would be reduced to a name only and would lose all physical meaning.

The same remarks obtain in any other case where Mulliken-Herzberg's and Hund's methods of counting the valencies differ, provided that the difference between the "ionic" and "atomic" terms of the molecule is great enough.

V.

The difference between the single-electron bond theory and the electron-pair bond theory derived from the method of molecular orbitals
can also be considered from another point of view. Hund\textsuperscript{1} has shown, as already mentioned, that even in the event of the nuclear fields being only *almost* degenerated the resonance degeneracy still prevails up to a certain extent and that accordingly a single electron may exercise a bonding power. So the distinction between the single-electron bond and the pair bond amounts to whether or not the degeneracy of the fields is almost complete in the practical cases. It is shown in Sections II and IV that the variation of the wavefunction describes the continuous transition from a molecular orbital to an atomic orbital. Since this process leads us to ions, it is clear that the variation of the ratio of the normalising factors is the analytical representation of the transition from covalent to electrovalent linkage, when we compare different molecules. Thus it is measured by the polarity of a molecule, and since this again is measured by the dipole moment, we obtain under otherwise equal conditions a direct measure of the variation of the two fields.

From this point of view we consider the construction of the wavefunction of CO by means of one-electron wavefunctions. We compose a molecular field by superposing the fields of the cores of C\textsuperscript{2+} and O\textsuperscript{4+} at a fixed distance and add successively the six p-electrons. The fields of C\textsuperscript{2+} and O\textsuperscript{4+} are entirely different and cannot possibly be regarded as almost degenerated. The two electrons introduced first will, therefore, belong considerably more to the oxygen nucleus than to that of carbon. Although this group may still be termed a molecular orbital, it appears that the physical significance of such an intermediate group is better characterised by the term atomic orbital. The fields of C\textsuperscript{2+} and O\textsuperscript{4+} are no longer so vastly different and may now be considered as more or less degenerated. The following four p-electrons belong then equally to either nucleus and thus constitute the linkage. Therefore even from the viewpoint of the single-electron bond theory the linkage of CO should be regarded only as a double bond. In CO we have selected an example particularly favourable for the single-electron bond theory, since here the two fields are rather similar, as shown also by the small dipole moment. One step further among the molecules with six p-electrons, brings us to BF\textsubscript{2}, where for the first four electrons with regard to F the same conditions prevail, as in CO for the first two with regard to O. In BF\textsubscript{2} only the two electrons added last to the molecule should be regarded as on a proper molecular orbital, since only for them the necessary condition of approximate degeneracy is perhaps satisfied. Considering other molecules we see both from the structure of the atoms concerned and from the increased dipole moment that in general the condition of approximate degeneracy does not obtain any longer. In a series as CO,
SiO, GeO, SnO, PbO, even the four bonding electrons belong more and more to oxygen, the field of the other partner growing gradually weaker. The polarity of the molecules increases step by step, the linkage striving towards electrovalency, which is fully exhibited by molecules like PbCl₂.¹⁸

At the same time the above considerations show clearly that except in the case of complete degeneracy a certain polarity is always present and even in a covalent linkage justifies the distinction between a negative and a positive partner, which for experimental reasons was introduced into chemistry long ago.¹⁹

Incidentally we note that the difference of the fields naturally decreases in a series in which the negative partner is exchanged for one from a following period; the effective charge of an ion decreases from period to period, and this change when manifested in the negative partner has an effect opposite to that in the positive one.

VI.

If in a polyatomic molecule like CR₄ the linkage is treated by method A it appears automatically in the form of electron pairs each pair localised between the central atom and a particular one of the approaching radicals. In method B, however, each electron is a priori put in a field constructed in a way as expected in the completed molecule, i.e., in CR₄ a field of tetrahedral symmetry. Accordingly each electron belongs equally to all of the five nuclei and the bonds are strictly non-localised. This is true only, if in method A the interaction of the electrons from pair to pair and in method B the interaction* of the electrons at all (zeroth approximation) is neglected and so the truth lies of course somewhere between the two extremes. This is confirmed by the investigations of Van Vleck,²⁰ who has pointed out the characteristic errors of either conception. Slater²¹ has shown this directly in the case of H₂, and it has also been discussed by Mulliken.² In the case of a diatomic molecule the bonding wavefunction of the molecule involving only one wavefunction of each atom can be written according to method A as

\[ a[\psi_A(1) \psi_B(2) + \psi_B(1) \psi_A(2)] \]

whereas method B furnishes the function

\[ \{a\psi_A(1) + b\psi_B(1)\} \{a\psi_B(2) + b\psi_A(2)\}. \]

Either function describes the dissociation incorrectly. In H₂ for instance, when \(a = b\), the Slater-Pauling function allows of course a dissociation only into normal atoms, since it is composed like that, whereas the orbital function becomes

\[ a^2 \{\psi_A(1) + \psi_B(1)\} \{\psi_A(2) + \psi_B(2)\} = a^2 \{\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)\} \]

\[ + a^2 \{\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)\} \]

* See footnote on p. 625.
On the Pair Bond Theory of Valency

and therefore yields 50% of normal atoms and 50% of ions. The truth lies in between, but obviously nearer to the result of method A, and Slater has found that the best description is given by

\[ a^2 \{ \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2) \} + \tfrac{1}{2} a^2 \{ \psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2) \} \]

i.e. by introduction of a slight hybridisation with ionic terms into method A or by a nearly complete reduction of their influence in method B. This is easily generalised for polyatomic molecules. Let \( \phi_A \) and \( \phi_B \) be two s-functions, which in this example may be taken to belong to equal atoms, \( \psi \) and \( \chi \) two p-functions of a third atom, \( \psi \) with a node in the symmetry plane perpendicular to the plane of the three atoms, \( \chi \) symmetrical to either plane. This model corresponds roughly to the case of \( \text{CH}_2 \) or \( \text{H}_2\text{O} \). The bonding wavefunction according to the method of molecular orbitals is in zeroth approximation

\[
\{a_1\psi(1) + b_1[\phi_A(1)-\phi_B(1)]\} \{a_2\psi(2) + b_1[\phi_A(2)-\phi_B(2)]\} \{a_2\chi(3) + b_2[\phi_A(3)+\phi_B(3)]\}
\]

\[
\{a_2\chi(4) + b_2[\phi_A(4)+\phi_B(4)]\}.
\]

It is strictly non-localised, but it is incorrect in so far as it involves too great an amount of hybridisation with the various possible ionic terms. The approximation is improved by reducing their influence, and since in general this influence is very small, we shall still have an improvement, when we overdo the reduction and cancel the ionic terms completely. On doing so, we obtain

\[
\begin{align*}
& a_1 b_1 a_2 b_2 \{ \phi_A(1)\psi(2)\phi_A(3)\chi(4) + \phi_A(2)\psi(1)\phi_A(3)\chi(4) + \phi_A(1)\psi(2)\phi_A(4)\chi(3) \\
& \quad + \phi_A(2)\psi(1)\phi_A(4)\chi(3) \} \\
- & a_1 b_1 a_2 b_2 \{ \phi_A(3)\psi(2)\phi_A(1)\chi(4) + \phi_A(3)\psi(1)\phi_A(2)\chi(4) + \phi_A(4)\psi(2)\phi_A(1)\chi(3) \\
& \quad + \phi_A(4)\psi(1)\phi_A(2)\chi(3) \}.
\end{align*}
\]

This function is strictly symmetrical as far as the exchange of electrons between any of the s-functions and any of the p-functions is concerned, but it is strictly anti-symmetrical as to any possible exchange of electrons between the s-functions, either direct or in a cycle involving the p-functions. This is strict localisation of the bonds. Of course when dropping the ionic terms, we have overshot the mark, but very slightly only, and this again means that ordinarily the equilibrium between localisation and non-localisation gravitates more to the side of the former one as far as questions of valency are concerned, and that for this purpose each bond, e.g. in \( \text{CR}_4 \), should be regarded as existing between the central C atom and a particular one of the radicals. Up to a certain extent, however, non-localisation of the bonds is still prevailing. Physically the linkage is due in the first instance to a strong interaction of the electrons inside the pair. In addition to this there exists, of course, an interaction of the electrons from pair to pair, which,
though smaller than the interaction inside the pairs, is not negligible. We infer that to decide questions of valency we have in general, i.e. with the exception of certain cases, to describe also polyatomic molecules in terms of diatomic electron-pair bonds.

It has sometimes been said that localisation of the bonds is a poorer approximation to the truth than non-localisation. This opinion is based on a calculation of Hund. If the incorrect hybridisation of the strictly non-localised wavefunctions is not given up, linear combinations of the original functions can be formed, which represent almost, or—when the difference between $\frac{b_2}{a_1}$ and $\frac{b_4}{a_2}$ is neglected—strictly, localised pairs of electrons. These functions are, however, not orthogonal, and on forming orthogonal linear combinations one falls back to the original non-localised wavefunctions. Therefore this way of localising the electrons has rightly been considered as a change for the worse of the approximation, but it is clear, that it is not an approach to the view of method A and is quite different from the above manner of localising the bonds.

The description of the linkage in polyatomic molecules in terms of electron-pair bonds has the advantage of great simplicity. It is not necessary to resort to the considerations based on the properties of more complicated symmetry groups, the choice of which is after all only dictated by the frame of the expected molecule, but which, though advancing a beautiful description of the molecule itself, are hardly qualified to give an exhaustive information about questions on valency.

Our considerations do not pretend to fix once for all that point, between the extremes of strict localisation and strict non-localisation, to which the physical linkage gravitates. On the contrary, conditions will differ in different cases. Bonds relating to different central atoms especially in distant parts of large organic molecules, have practically no relation at all to one another, and strict localisation without much consideration for the interaction from bond to bond will meet best the requirements of chemistry. On the other hand the special character of cyclic compounds shows that also the case of strong non-localisation, at least of a certain number of electrons, exists in nature. It appears not to be impossible that the "genuine" complex salts of Werner represent another type of strong non-localisation, but recently it has been shown that the term "co-ordination number" is used for quite different mechanisms of linkage and a theory of such compounds can be attempted only, if further experimental evidence is advanced.
Till now we have only considered the simple case, when two electrons of different atoms each represented by a single wavefunction join in the same molecular orbital, i.e. are represented by a wavefunction which in zeroth approximation is a linear combination of the original atomic wavefunctions. This occurs especially, when there is an ordinary p-p linkage and when therefore the correlation table is applicable. This obtains also in a few simple cases which have been dealt with by Hund, e.g. that of s-p linkage, where the correlation table remains hardly applicable on the grounds of the molecular wavefunctions being formed in a different manner, e.g. as a combination of an s-function of one of the atoms and a p-function of the other one. If, however, several low terms of an atom are sufficiently close so as to perturb one another, the corresponding electron is no longer represented by one wavefunction only, but by a hybrid of several ones. Hund’s q-functions, e.g. are hybrids of s- and p-functions. Whether or not hybridisation takes place, depends on the energy difference of the terms in question, which when sufficiently small causes the functions concerned to be replaced by their linear combinations. Since this difference is a function of the distance from the other atom, we have to distinguish between two different kinds of hybridisation according to whether the approach or the intersection of the potential curves occurs at such an internuclear distance as prevails in the completed molecule or at a greater distance.

The latter case is the simpler one. If the mutual perturbation of the potential curves takes place at a greater distance, i.e. at higher vibrational levels of the electronic terms in question, the zeroth approximation of the molecular function in the lower vibrational levels, i.e. in the existing molecule, is again formed by combining single atomic functions only. Extrapolation of the curve from lower levels cannot give any information about perturbation at higher levels, especially as to whether or not a point of intersection is preserved. Since we know that at and near the point of intersection the actual wavefunctions are linear combinations of the original ones, it is a matter of terminology only, whether we say that for instance an atom is linked in its p-term or it goes into the s-term avoiding the point of intersection.

A difference in the situation arises only, when the perturbation obtains at an internuclear distance not much greater than that in the molecule, so that for the construction of the molecular function it is no longer possible to describe the state of the atom by a single wavefunction. So it is possible that in particular cases an s-electron shows already properties of a p-electron.
Hund originally supposed that, more or less, all linkages proceed like that, if one of the partners belonged to the first or second group of the periodic system, i.e., had s-electrons only to match the gaps in the p-shell of the other partner. This could for instance be imagined in a molecule like BeO. Be has two electrons outside the K shell, O has two gaps in its p-shell, so everything would be suitable for a divalent linkage, if the two electrons of Be were not s-electrons and an s-shell was not incapable of undergoing any linkage at all. The linkage becomes possible, if the p-term is close enough to perturb the s\(^2\) configuration, and by a hybridisation of the configurations s\(^2\) and sp a double link should be capable of existence. We shall see in section IX that as far as molecules like BeO or BeF are concerned, experimental evidence shows clearly that the linkage does not occur in this way. The adiabatic dissociation leads us definitely to the conclusion that these cases have nothing whatever to do with any q-bond and originate from those excited terms in which the Be atom possesses the necessary number of actual p-electrons. Be with the configuration sp undergoes in fact a single link with oxygen and is capable of a divalent linkage only from the anomalous term p\(^2\) 3P. Apart from the difficulties which the assumption of hybridisation finds in explaining the single bond of BeO in its ground-state and the crystal structure, a perturbation of the lowest vibrational levels, if it existed, would have been observed in the band-spectrum and would also have destroyed any possibility of a reasonable extrapolation. At higher vibrational levels, where the unperturbed repulsive curve originating from s\(^6\) and the unperturbed attractive curve from sp would intersect, we have of course linear combinations of the wavefunctions, and here the molecule may well pass from one of the curves to the other.

In other words, we can say that already in the atoms of the second group the p-term is too far distant from the s-term to bring about the perturbation necessary for the q-bond. We expect that in the following groups where the energy difference between the s- and p- terms in question increases the occurrence of a q-bond becomes more and more improbable. This is also of interest with reference to the so-called lone pair of nitrogen etc. To our mind the q-bond is restricted to hydrogen compounds on account of their small internuclear distances, compounds of atoms of the first group with others and highly excited terms of compounds of other atoms. Hybrids of d-functions with others, similar to the q-functions, can be expected in some of the heavier elements.

Another striking example is the case of CO\(_2\) which shows also clearly that in normal cases no q-bond occurs at all and that the number of
p-electrons required for an ordinary p-p bond is simply provided by excitation of the s-electrons.\textsuperscript{20} The constants measured in the infra-red spectrum of CO\textsubscript{2} permitted an exact calculation of the energy of adiabatic dissociation,\textsuperscript{25} and it could be seen, that in spite of all attempts to explain the CO\textsubscript{2} linkage either from the excited sp\textsuperscript{3} state of C or from the ground level s\textsuperscript{3}p\textsuperscript{3} (Mecke, Herzberg, Lennard-Jones\textsuperscript{*}) the carbon atom proved to possess four equivalent p-electrons\textsuperscript{16} and thus to be linked from the anomalous term p\textsuperscript{4} 3P. PbO\textsubscript{2} seems to be linked in the same manner.

There is another effect which passes also under the name of hybridisation. If in a particular atom different kinds of valency electrons are present, e.g. in the configuration sp\textsuperscript{3}, the resulting bonds are in general not different in different directions, say one s bond and three p bonds, but we obtain a number of equivalent bonds formed by electrons whose wavefunctions are hybrids of the different available types of simple functions. This obtains particularly in non-linear polyatomic molecules the treatment of which has actually been made possible only by this view. On the other hand, the linkage of O=\textsuperscript{\textcolor{red}{C}}=O is brought about by regular p—p bonds, whereas in the above case of linkage from the sp\textsuperscript{3} 3P term of the atoms of the second group our considerations cannot decide, whether the bonding function is a p-function or a hybrid of s and p, though the fact that only a single bond is formed is in favour of the latter possibility. We meet here again with the distinction between localisation of the electron pairs and localisation of the bonds. As shown in the preceding section the electrons of the central atom are indistinguishable but not those of the atoms linked to it. That type of hybridisation, which involves several terms of the central atom, leads to non-localisation in polyatomic molecules, whereas the other type leads to localisation of the bonds; and only this type occurs in molecules formed by atoms of the second group as central atoms.

The discussion of the linkage of CO\textsubscript{2} has shown further that the carbonyl radical is a CO molecule excited by 7·34 volts in which the original two s-electrons of the carbon are transferred to the \(\pi\) (2p) group. A carbon atom, in which the two s-electrons have been transferred to the p-shell cannot link the two O atoms simultaneously, because in spite of the four equivalent p-electrons no more than three different wavefunctions can be formed. Therefore the formation of carbon dioxide is bound to proceed in two steps. After linking the first O atom, a carbonyl radical results, which has two free \(\pi\) (2p) electrons and accordingly exhibits two more free electrons.

\textsuperscript{* Cf. reference 3 and literature quoted in reference 16.}
valencies. Practically the formation or dissociation will take place along one of the intersecting repulsive curves, involving only a moderate activation of the CO molecule.

VIII.

The method of molecular orbitals, as already mentioned above, is admirably adapted to the description of the completed molecule; for this purpose it is rather immaterial whether this implies a single-electron or electron pair-bond theory of valency. For the distinction between these two different views the behaviour of the molecule on dissociation is decisive. Our standpoint will lead us to distinguish in a simple manner between two different cases. Normal saturated molecules have electrons only in closed groups. In general an excitation concerns an electron in one of the groups to which the linkage is due; this group undergoes fission and the linkage is considerably weakened. Accordingly, the energy of adiabatical dissociation is smaller in the excited terms than in the groundmost one. The other case comprises mostly the unsaturated compounds. Here not all the electrons are employed to bring about the linkage. Those to which the chemical union is due are in general contained in closed electronic groups, the abundant, so-called odd ones, represent free valencies and do not form closed groups. Accordingly we have two possibilities of exciting the molecule. Either the excitation refers to an electron taking part in the linkage, then the effect is the same as with saturated compounds and the energy of dissociation decreases on excitation. Or the odd electron is excited; in this case the energy of dissociation of the excited level is greater than that of the groundmost one, i.e. the linkage becomes more stable on supply of energy.

We return to the carbon monoxide molecule as a typical case of a chemically stable compound. The ground level \(_1\Sigma^+\), as already stated above, has the electronic configuration:

\[
K_1 \quad K_2 \quad \sigma^2(2s) \quad \sigma^*2(2s) \quad \pi^1(2p) \quad \sigma^2(2p).
\]

Its energy of dissociation is 10.45 volts. The linkage depends on the last two groups. Any excitation is liable to perturb their structure, so we expect the dissociation energy of the excited terms to be considerably less than that of the ground term. As an example of an excited term we take \(a'[\Sigma^+]\) with the electronic configuration:

\[
K_1 \quad K_2 \quad \sigma^2(2s) \quad \sigma^*2(2s) \quad \pi^3(2p) \quad \sigma^2(2p) \quad \pi^*(2p).
\]

It dissociates into C in the excited \(1D\) level and O in its ground state, with an energy of dissociation of 4.58 volts. As we obtain an excited carbon atom as a product of dissociation, we infer that it was just a carbon
electron that was taken out of the \( \pi^4(2p) \) group and transferred to the \( \pi^*(2p) \) group. We further conclude that after the excitation the linkage can but rest on one group containing electrons of either partner. Hence the linkage has been reduced from a double bond to a single bond, which agrees completely with the energy of dissociation being about halved.

As an example for the other case of molecules with an odd number of electrons\(^6\) we consider the molecule NO. The ground state \(^3\Pi\) has the electronic configuration
\[
K _1 K _2 \sigma ^2(2s) \sigma ^* (2s) \pi ^4(2p) \sigma ^2(2p) \pi ^*(2p)
\]
and dissociates into \( N \, (2s^2 \, 2p^3 \, 4S) \) and \( O \, (2s^2 \, 2p^4 \, 3P) \). Of those electrons which have been \( p \)-electrons in the separated atoms six are in the closed groups \( \pi ^4(2p) \) and \( \sigma ^2(2p) \) of the molecule whereas the seventh is the odd electron in the group \( \pi ^*(2p) \). The linkage may be explained in two different ways: We may assume that of the six electrons concerned two belong to the nitrogen atom and four to the oxygen atom; in this case the odd electron belongs to the nitrogen atom and will go with the \( N \) nucleus in the case of adiabatic dissociation. Or we may assume that three of these six electrons belong to \( N \), the other three to \( O \); in this case the odd electron will belong to \( O \) and will go with its nucleus in the process of dissociation. The excited \(^2\Sigma\) state of the molecule has the configuration:
\[
K _1 K _2 \sigma ^2(2s) \sigma ^* (2s) \pi ^4(2p) \sigma ^2(2p) \pi ^*(2p) \sigma (3s).
\]
The odd electron has been transferred from the group \( \pi ^*(2p) \) to the group \( \sigma (3s) \), so this term dissociates into two atoms one of which will be excited in such a way that one electron is in the group \( 3s \) instead of in \( 2p \). If this electron belongs to the \( N \) atom, the products of dissociation of the term \(^2\Sigma\) will be \( N \, (2s^2 \, 2p^3 \, 3s \, 3P) \) and \( O \, (2s^2 \, 2p^4 \, 3P) \); if it belongs to \( O \), the \(^2\Sigma\) term will dissociate into \( N \, (2s^2 \, 2p^3 \, 4S) \) and \( O \, (2s^2 \, 2p^3 \, 3s \, 5S) \). The extrapolation of the potential curve of the \(^2\Sigma\) level indicates that one of the two atoms is excited by 9.42 volts. The values obtained by this linear extrapolation are not very accurate, and here the value of 9.42 volts agrees with the term difference \( ^4P - ^4S = 10.29 \) volts of \( N \) as well as with \( ^6S - ^3P = 9.10 \) volts of \( O \). The same excited level is, however, measured in \( PO \). If it dissociates into an unexcited \( P \) atom and an excited \( O \) atom, the extrapolation of its energy of dissociation should result again in an energy of excitation of the separated atoms in the neighbourhood of 9.10 volts. If, on the other hand, the excitation is due to the \( P \) atom, the value obtained should equal the term difference \( ^4P - ^4S \) of \( P \) which is 6.90 volts. The extrapolation of the \(^2\Sigma\) level of \( PO \) indicates a value of 6.44 volts for the excitation of the separated atoms, which figure does not agree with any term difference of the oxygen atom, but agrees very well with that of phosphorus.
Thus the odd electron of the molecules NO and PO belongs to N and P respectively. Among the other six electrons of the molecular orbitals of NO there are only two of N and four of O. In our manner of counting, this linkage has to be considered as a double bond, not a triple bond, and this agrees with the prevailing divalency of oxygen. The N atom would match the O atom best if it would possess two p-electrons only. The existence of the third p-electron of N creates a free valency in the molecule NO and produces those particular chemical properties which distinguish it from normal stable molecules. The configuration of NO is disturbed by the presence of the odd electron which does not take part in the linkage. Therefore the bond will become more and more stable, the more this electron is removed, and this is why the energy of dissociation is 6.70 volts in the ground level \( \Sigma \) of the molecule, but 10.67 volts in the excited \( \Sigma' \) level. In the case of PO the figures are 6.47 and 7.91 volts respectively.

The way in which we consider the increase or decrease of the energy of dissociation is characteristic of a pair-bond theory of valency. The phenomenon of premotion brings about an additional modification of these energies, particularly in excited terms. It is, however, evident that the premotion alone is not able to explain all the peculiar features, especially why a considerable increase of dissociation energy on excitation occurs only with such molecules as exhibit still free valencies in their ground states. A single-electron bond theory of valency, which reduces linkage to a phenomenon of non-premotion alone, appears therefore to be at a disadvantage.

IX.

Further instances are furnished by compounds of the atoms of the second group which possess a repulsive helium-like configuration of two s-electrons in a closed shell. From the configuration of the \( 3P \) term of Be and that of the ground level (\( s^2 p^2 2P \)) of the halogen we obtain for the ground level \( \Sigma \) of the BeF molecule the configuration

\[
\sigma^2(2s) \quad \pi^4(2p) \quad \sigma^*(2s) \quad \sigma^2(2p).
\]

Four of the five p-electrons of the halogen atom form a closed \( \pi^4 \) group which does not participate in the linkage, the p-electron of the excited metal atom together with the remaining electron of the negative partner forms the \( \sigma^*(2p) \) group, which represents the single bond, whereas the s-electron of the metal atom remains alone as an odd electron. If the excitation of the molecule concerns one of the electrons of the bonding group \( \sigma^4(2p) \), the energy of dissociation is smaller in the excited molecular term which dissociates into two atoms, one of which will be excited. If, however, the excitation of the molecule concerns the odd electron, the energy of dissociation is increased in the excited term, because the influence of this disturbing
electron is partly eliminated. The molecule in such a state is then formed by a metal atom in which two electrons are excited: the first one before the linkage could take place at all, the second one in the molecule itself. Therefore the products of dissociation of such an excited molecular term whose energy of dissociation is higher than that of the ground level is an unexcited halogen atom and a metal atom in the anomalous term (p^2 3P) in which both the previous s-electrons are excited to the next p-group. This prediction of the pair-bond theory could be proved in a number of cases, where the band system is analysed, e.g. BeF, MgF, CaF, SrF, and recently CdF and CaCl. In all these spectra it is not possible to correlate the levels of the separated atoms to those obtained by extrapolation of the potential curves of the molecule, except on the basis that the products of dissociation of the ground level are unexcited halogen atoms and a metal atom in the term (sp 3P), and that the metal atom in the anomalous term (p^2 3P) produces always a molecular term whose energy of dissociation is greater than that of the ground level.

Again chemical combination between atoms of the second group and oxygen does not take place, unless the repulsive group s^3 of the metal atom has undergone previous fission. The formation of such a molecule, e.g. BeO, arises from the term (2s 2p 3P) of Be. In this state Be forms a molecule with an oxygen atom in its ground state (2s 2p 3P), and the total number of s- and p-electrons gives for the ^1Σ term of BeO the configuration

\[ \text{K}_1\text{ K}_2\sigma^2(2s)\pi^4(2p)\sigma^4(2s)\sigma(2p). \]

The π^4 group contains three p-electrons of oxygen and the only p-electron of excited Be. In this state, therefore, the BeO possesses only a single link, but two free valencies and should be written as —Be—O—. When once the molecule is excited and the σ*(2s) electron is transferred to the σ(2p) group, a double bond is formed. Therefore the energy of dissociation increases very considerably on excitation of the molecule; it is 5.66 volts in the unexcited and 7.50 volts in the excited term. Since the excited electron was, so to speak, a 2s electron in the σ*(2s) group and has become a 2p electron when entering the σ(2p) group, the products of dissociation of the molecule are an unexcited oxygen atom and a beryllium atom in which both of the previous 2s electrons have become 2p electrons, i.e. a Be atom in the anomalous state (p^2 3P). The term difference 2p^2 3P — 2s 2p 3P is 4.66 volts in Be, while an extrapolation from the bands of BeO gives 4.46 volts. In the present state of knowledge we cannot yet definitely decide between the above configuration.

\[ \text{K}_1\text{ K}_2\sigma^2(2s)\pi^4(2p)\sigma^4(2s)\sigma(2p). \]
and the configuration
\[ K_1 K_2 \sigma^2(2s) \pi^3(2p) \sigma^*(2s) \sigma^2(2p). \]
The latter term is most probably slightly higher than the first one, but
everything that has been said about the bond and the free valencies of the
first one applies to it too with the only difference that the number of free
valencies has become four instead of two (\(--\text{Be}--\text{O}--\)).

The question whether this linkage can be considered as brought about
by a hybrid of the functions belonging to \(s^2 \, 1S\) and \(sp^3P\) has been dealt
with already in section VII. We have to mention here, only, that the
version of the q-bond cannot explain, why for instance a double link should
not occur already in the ground state of the BeO molecule, which would be
due to a \(q^2=p^4\) linkage, and that it leaves the strong increase of the energy
dissociation unexplained, when also the second s-electron is excited.

Our conclusions are confirmed by the properties of these molecules in
the crystalline state. Hund\(^9\) has pointed out that the high melting point
of a certain class of crystals can only be understood by free valencies
exhibited by the single unit thus making the whole of the crystal one giant
molecule. Since, however, the existence of free valencies in the ground
states of the oxides and sulphides of the atoms of the second group was not
known, he experienced a difficulty in explaining their extremely high lattice
energy. This difficulty appears now to be overcome.

Recently the absorption spectra of a number of molecules of this type,
\textit{e.g.} ZnO, ZnS, etc. have been measured in the vapour state,\(^{29}\) and it was
found that they exhibit a continuous absorption spectrum. Obviously this
absorption spectrum represents the transition from the ground level \(1\Sigma^+\)
to the repulsive curve of the two centre system originating from unexcited
oxygen in \(3P\) and unexcited metal atoms in the term \((s^2 \, 1S)\). The curve of
the ground state of the molecule has sometimes been wrongly interpreted as
an ionic curve, but as far as experimental evidence is concerned there is no
reason\(^{24}\) for such an assumption. Its potential curve intersects the repulsive
curve originating from the unexcited states of the atoms simply because it is
formed from an excited metal atom as already shown above in the discussion
of the emission bands.

Some more examples illustrating the present view will be given in a later
publication.

X.

The previous sections deal with the comparison of the energies of
dissociation in different electronic levels of the same molecule. Attention
may now be directed to the relation of the dissociation energies of different homologous molecules in the same term. The following table gives the energies of dissociation \((D)\) of the halogen molecules in their ground states (spectroscopical values in v.e.):

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<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>2.5</td>
<td>(Cl</td>
<td>Br</td>
<td>2.2</td>
</tr>
<tr>
<td>Br</td>
<td>Cl</td>
<td>2.2</td>
<td>Br</td>
<td>2.0</td>
<td>(Br</td>
</tr>
<tr>
<td>I</td>
<td>Cl</td>
<td>2.1</td>
<td>I</td>
<td>Br</td>
<td>1.8</td>
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\(D\) decreases from period to period with increasing radius of the atoms and accordingly decreasing field-strength. It does not run parallel to increasing inequality of the nuclear fields, as is seen for instance by comparing \(\text{ICl}, \text{IBr}\) and \(\text{I}_2\), whereas the polar character of the molecule naturally increases with the inequality of the nuclei. It is well known that the hydrolysis of \(\text{ICl}\) establishes definitely the iodine atom as the positive partner of the molecule.

We have pointed out above (cf. Sections II and IV) that increasing polarity means increasing inequality of the normalising factors \(a\) and \(b\) in those wavefunctions of the molecule, which in zeroth approximation are linear combinations of those of the atoms, i.e. vanishing degeneracy of the nuclear fields. This result is not compatible with the interpretation of the method of molecular orbitals as a single-electron bond theory of valency, since in that view the phenomenon of linkage is just produced by the degeneracy of the nuclear fields and \(D\) ought to increase from \(\text{ICl}\) towards \(\text{I}_2\). According to the present interpretation the linkage is brought about in general by the exchange degeneracy of the two electrons forming the bonding pair, which remains always intact, but whose energy decreases when the distance of the two centres is enlarged.

It is a general feature throughout the periodic system, that \(D\) runs parallel to the field-strength, regardless of the polarity of the molecule. Another instance is furnished by the molecules of the following series:

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<tbody>
<tr>
<td>CO</td>
<td>SiO</td>
<td>GeO</td>
<td>SnO</td>
<td>PbO</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>10.45</td>
<td>7.3</td>
<td>7.8</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>OS</td>
<td>SiS</td>
<td>GeS</td>
<td>SnS</td>
<td>PbS</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>7.75</td>
<td>..</td>
<td>5.7</td>
<td>..</td>
<td></td>
</tr>
</tbody>
</table>

From \(\text{CO}\) to \(\text{PbO}\) the energy of dissociation decreases with increasing polarity; from \(\text{CO}\) to \(\text{CS}\) it decreases with decreasing polarity.

The same holds good in odd-numbered molecules; thus \(D\) decreases from 5.42 volts in \(\text{BeF}\) to 3.8 volts in \(\text{CaF}\) and 3.1 volts in \(\text{SrF}\), and from 6.70 volts in \(\text{NO}\) to 6.47 volts in \(\text{PO}\) and 5.93 in \(\text{NS}\). From numerous physico-chemical measurements of dipole moments, conductivity, melting point, hydrolysis, etc., it is well known that the polarity of homologous
molecules increases, if the positive partner is exchanged for a heavier atom, but decreases if the negative partner is exchanged in the same way. The energy of linkage, however, decreases always.

XI.

Several attempts\textsuperscript{10,14,15} have been made to establish a fairly constant value for the energy of dissociation per link, but even without going into details it is quite clear that any such attempt is bound to fail. Pauling, for instance, tries to establish a value of 3 volts per link for the lighter elements. It has already been pointed out that some of his assumptions are hardly admissible such as his way of considering the intersection of potential curves. Those assumptions become necessary only, because his constant value does not agree with the actual energies in a number of cases.

The preceding section has shown that the energy of formation depends on the field-strength, and therefore, a constant value valid equally well for the fluorides and for the chlorides, for the oxides and for the nitrides cannot possibly be expected. It may, however, be possible to find a certain regularity, when we confine ourselves, for instance, to the oxides of the atoms of a definite period, because then the conditions are still rather similar.

As seen above, BeO in its ground state has a single link only; its energy of dissociation is 5.66 volts. For the double bond in CO we obtain 10.45 volts. In NO we have a molecule, the linkage of which is disturbed in its ground state by an odd electron and so we have only $D = 6.70$ volts. When the disturbance is removed by excitation of the odd electron, $D$ becomes 10.67 volts for the double bond, as in CO with the same bonding electrons. In BO the correlation between the molecular levels and those of the separated atoms does not appear to be satisfactory yet, but in $(CO)^+$ with the same number of electrons, we get again 9.78 volts for the double bond in $X^3\Sigma$ and 5.37 volts for the excited and singly linked $A^2\Pi$ state. $O_2^+$ in which the same conditions prevail as in NO has also practically the same energy of dissociation (6.37 volts), whereas in $O_2$ with two disturbing electrons $D$ decreases again to 5.09 volts.

The same obtains among the oxides of the next period. The single link of MgO shows an energy of dissociation of 3.8 volts, and AlO in the singly linked ground state $X^3\Sigma$, 4.15 volts. In the state $B^2\Sigma$, AlO possesses a double link and an odd electron and an energy of dissociation of 6.15 volts. The ground level of SiO with a double bond displays 7.8 volts and the singly linked state $A^1\Pi$ 3.8 volts. The double link of PO is again disturbed by an odd electron in the ground state ($D = 6.5$ volts), but by excitation of the disturbing electron to $A^2\Sigma$ ($D = 7.9$ volts) becomes equal
to the double link of SiO with the same electronic configuration in the bonding groups.

We infer that among the oxides of the lighter atoms D is roughly 5 volts in the second and 4 volts in the third period; and for the double bond, if undisturbed, roughly 10 and 8 volts respectively.

Apparently the same value of about 4 volts, which holds for the oxides of the third period, obtains also for the sulphides of the second period, as the few examples available indicate. As we have seen in the preceding section the energy of dissociation is the same for the ground levels of SiO and CS, PO and NS. This is also valid for SnO and GeS, which are in a similar relation to each other.

These figures are not valid for the nitrides. From the triple link of N₂ and its energy of dissociation of 7.34 volts in the ground state, we obtain about 2.5 volts per link, and in the same way about 2.1 volts in the next period from the ground state of PN (D = 6.3). The molecule P₂ furnishes an energy value of 1.7 volts per link in the same manner. Thus it is not possible to deduce a constant value of the energy of the covalent link in general, not even within one period, which appears quite natural, since there is no reason why the fields of N and O should have equal effects. On the contrary, the difference of the electronic affinity of N and O makes one understand, why a link in a nitride is weaker than in the corresponding oxide.

It is interesting to see, which are the values of the energy per link, that are furnished by the single-electron bond theory of valency. From that view N₂, NO, and CO display 3, 2½, and 3 bonds respectively and accordingly the following energies per link:

\[
\begin{align*}
\text{N}_2 & \quad \text{NO (X^2Π)} & \quad \text{NO (A^2Σ)} & \quad \text{CO} \\
2.5 & \quad 2.7 & \quad 4.3 & \quad 3.5
\end{align*}
\]

Since in the single-electron bond theory the degree of degeneracy of the nuclear fields is decisive of the strength of the linkage, the energy of dissociation per bond in these molecules shows a tendency in the wrong direction, i.e. to decrease, when the degeneracy of the fields is improved.

From the present point of view there exists only one kind of non-electrostatic linkage, which occurs if two electrons belonging to different atoms join on the same orbital of the molecule. We have seen analytically in Sections II and IV that there is a continuous transition between covalent and electrovalent linkage, the degree of which is indicated by the varying polarity of the bond. The bonding effect which is caused by the degeneracy,
due to the equality of the electrons lies accordingly between the two atoms concerned in the covalent link and changes with increasing polarity directly into the wave-mechanical exchange effect, which links the electron released from the configuration of the positive partner to the electrons of the electronegative atom.

For the purpose of chemistry we have to show that the consequent application of a pair-bond theory of valency suffices to describe the experimental chemical facts without resorting to additional assumptions to explain contingent discrepancies.

This definition of the bond excludes the possibility of the existence of different kinds of non-electrostatic linkages, such as the semipolar double bond or the singlet linkage, which have been introduced to maintain the so-called "Octet Rule". The octet rule was useful, as the most important element, carbon, has just four outside electrons, which naturally compose an octet together with the valency electrons of the partners as long as it remains tetravalent. The real field of application of a theory of valency is, however, not organic chemistry, where of the 92 different atoms and their varying states of valency only a small number of combinations occur; a theory of valency has just to stand the test of being applicable to inorganic chemistry, where it has to describe the various ways in which all the known atoms enter into chemical combination in different states of valency.

The system of organic and inorganic chemistry is best described by attributing to each atom, valencies according to its different groups of outside electrons. Nitrogen then becomes simply pentavalent in \( N_2O_5 \), sulphur hexavalent in \( SF_6 \), halogen atoms heptavalent in compounds like \( Cl_2O_7 \) or \( IF_7 \) or --- to take an example from the transition elements --- osmium octavalent in \( OsO_4 \). The number of outside electrons (s- and p-electrons together) is 5, 6, and 7 in N, S, Cl respectively and that of outside d plus s-electrons is 8 for Os. Each bond being represented by two electrons, we obtain different figures for the number of electrons surrounding an atom in the molecule, the figure 8 being only one of them. Among the atoms in the first three groups, i.e. on the left hand side of carbon these figures are naturally smaller than 8, on the right hand side of carbon in the maximal valency always larger. The semipolar double bond and the singlet link are devices to enlarge or reduce these figures to eight. Yet neither are these devices nor is the octet rule itself, for the preservation of which they have been introduced, indispensable. The experimental evidence of chemistry is fully described by a pair-bond theory of valency and even contradicts the octet rule and its subsequent assumptions. The arguments collected in the last years to establish the existence of the semipolar double bond and the
singlet link are not at all conclusive. A critical analysis of these from the present point of view has already been described* by Hunter and Samuel.31

Even if it was established that AlCl₃ sometimes forms also co-ordinate compounds with NH₃ or organic molecules, we have in general to recognize its sextet as a stable electronic configuration, because the atoms of the third group are trivalent in hundreds of their most characteristic molecules. Recently, however, Ulich and his co-workers⁢² have shown that the molecular associations of the trihalides of B and Al and of the dihalides of Be are merely dipole associations without involving additional valencies. Again addition compounds like Acenaphthene-picrate were found to be mere associations⁢³; their energies of dissociation are of the order of magnitude of 0. 1 volts. Similar remarks obtain about the polymerisation of hydrogen fluoride, Fremy's double salt (BeF₂, KF) and the fluoro-borates.

In the first and second groups of the periodic system one and two pairs of electrons respectively occur instead of octets. AgCl and CuCl in the vapour state ⁢²⁴,⁢²⁵,⁢²⁶,⁢²⁴ are covalent. The same obtains for the dihalides of Zn, Hg, etc., in the vapour as well as in the melted state.⁢altar.⁢²⁷,⁢²⁸ Already in pre-wave-mechanical theories of valency⁢³⁸ it has been shown that a complete system can be developed, if we assume that an outside electron is always able to link a monovalent atom. This renders, for instance, nitrogen pentavalent in the nitro-group, sulphur hexavalent in sulphur trioxide, and chlorine heptavalent in Cl₅O₇. Also in the case of the singlet link or the semipolar double bond one electron of the central atom links a monovalent or two electrons a divalent partner. The only difference between the theory of co-ordination and a pair-bond theory is in the manner of counting the electrons in the completed molecule. The pair-bond theory maintains the correlation between the number of valencies and the number of outside electrons; the conventional theory sacrifices this connection and preserves the octet instead. It is certainly correct that this latter way of defining valency gives also a complete description of the chemical facts; but it necessitates the introduction not only of different kinds of non-electrostatic linkage, but also of other subsidiary assumptions to explain the varying chemical behaviour of the atoms, thus rendering this description more and more artificial and unnecessarily complicated.

* In the quoted paper Hunter and Samuel⁢¹ have employed the terminology introduced by Mulliken¹ and have distinguished between the pair-bond theory of valency and the theory of molecular orbitals in the same sense, in which in the present paper the distinction is made between the terms electron-pair bond and single-electron bond theory, either of which is, as has now been shown, consistent with the method of molecular orbitals.
It has not been possible to establish any experimental proof for the assumed difference of linkage. Sulphur hexafluoride is an extremely inert and stable molecule. There is not the slightest indication of a difference in the behaviour of the two oxygen atoms in the nitro-group. On the contrary, many new experiments qualified to throw light upon the character of these linkages decide directly against the assumption of different kinds of linkage. Thus, if the oxygen atoms in the two nitro-groups in substances like p-dinitrobenzene or -44'-dinitro-diphenyl were differently linked, they should give rise to a dipole moment, which however is not present.38 Again in sulphur dioxide the infra-red spectrum establishes the equivalency of the two oxygen atoms.40 This leads again to additional assumptions; the co-ordinate link, e.g. of the nitro-group, is supposed to oscillate between the two oxygen atoms, but objections based on wave-mechanical considerations have already been raised against this hypothesis.32 Especially the valency number 7 caused difficulties, and compounds like IF7 had to be written in a bimolecular formula41 although its vapour density proves it experimentally to be monomolecular; heptavalency is, however, a direct consequence of the seven outside electrons as in Cl2O7, HClO4 or H3IO6.

Measurements of the parachor are conventionally described42 by introducing different constants for different kinds of non-electrostatic linkage and thus attempting to establish their existence. Yet it has been shown that the measurements can be described in exactly the same way,43 when different values for the parachor of the atoms according to their state of valency are introduced, e.g. different constants for P in $\text{P}^\text{III}\text{Cl}_3$ and $\text{P}^\text{V}\text{OCICO}_3$.

The so-called lone pair is represented in the majority of cases just by that closed helium-like group of s electrons, which acts repulsively only. The electrons can be utilised for the linkage only when either their wavefunctions hybridise with p-functions or when they are transferred to the p-shell. Spectroscopical evidence (of Sections VII and IX) has shown that in the known cases, for too great an energetic difference between the s and p states the former possibility is not made use of in nature and that the s-electrons in question are actually transferred to the p-shell and cannot be distinguished from the other p-electrons. This has been confirmed by chemical and physico-chemical evidence, e.g. for the nitro-group or sulphur hexafluoride as shown above. Even if the two s-electrons did not become real p-electrons but only similar to p-electrons and if therefore the linkage by hybridisation existed, the semipolar double bond does not follow from the analytical treatment, but remains an additional hypothesis. Even if for the sake of argument the fact that only pairs of electrons, one from each atom,
can exercise a bonding power in the presence of heavier nuclei is disregarded
and for the moment the view of a single-electron bond theory is assumed, it
is not correct to say that the hypothesis of the semipolar double bond and
the singlet link is based on wave-mechanical considerations. It can of course
be translated into wave-mechanical language and would then mean that the
corresponding electrons of the other partner in the linkage remain on atomic
orbitals. Though not contradictory to any already known result of wave-
mechanics, this is an additional hypothesis in it; incidentally it is difficult
to conceive, why in such cases just the closed helium-like $s^2$ group of the
central atom should become a molecular orbital, whereas the corresponding
p-electrons of the other partner should stay on an atomic orbital.

XIII.

We consider now two electrons in an unsymmetrical field, e.g. in silver
chloride. Such a molecule composed of a highly electro-positive and a
highly electro-negative atom, though still covalent in the vapour state, is
very near to that limit where the covalent linkage becomes completely
electrovalent, if the electronic affinity of the negative partner is increased,
either by additional outside forces or by exchanging the negative partner for
one with a higher electronic affinity. This follows directly from the
considerations in sections II and IV; the gradual transition from covalent
to electrovalent linkage finds its analytical expression in an increasing
dissymmetry of the orbitals.

A certain amount of dissymmetry is already exhibited by such an
apparently symmetrical molecule as $F_2$. The electronic configuration is
$\pi^4(2p)$ $\sigma^2(2p)$ $\pi^*4(2p)$. According to the single-electron bond interpreta-
tion we have six electrons in bonding, four in anti-bonding groups and
therefore one link; as each electron possesses its own bonding or anti-bond-
ing force the molecule would be completely symmetrical.

From the point of view of the electron-pair bond theory of valency the
molecule can possess already slight dissymmetry.* We have then to
interpret the electronic configuration as follows:—In $F_2$ both the fluorine
atoms possess a complete group of four $p$-electrons which do not produce any
linkage, since they originate from the same atom. The linkage itself takes
place between the two remaining $p$-electrons. Though the fluorine atoms
are completely identical in the beginning their fields influence each other
on approach in such a way as if the effective nuclear charges were different.
This is the direct effect of the splitting of the term under the influence of the

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* In a paper published just now Mulliken comes from his point of view to
similar results about the halogen molecules.
other atom, which makes four of the p-electrons go into unpremoted, four into premoted orbitals, which are bound with lesser energy. After the actual separation of these two kinds of electrons has been completed, they belong each of them to a particular atom of the two owing to the different symmetry of the wavefunctions, the premoted ones gaining an additional node. Roughly speaking, we can express this effect by saying, that the field of that atom to which the unpremoted group belongs, acts under the influence of the other approaching atom in the same way as if its effective nuclear charge was increased, the field of the other one acting as if its effective nuclear charge was decreased. In such a field the bonding electrons will distinctly belong more to the fluorine atom with the unpremoted group, thus rendering the molecule unsymmetrical, and this fluorine atom is the more negative partner of the molecule.

Such a conception of a halogen molecule explains, why only one of the two atoms is capable of exhibiting additional valencies. Indeed, of the mixed polyatomic molecules of the halogen atoms there exist only such as have a particular atom as a central atom, to which all the others are linked, e.g. IC\(_3\), IF\(_5\), IF\(_7\). Molecules of the type \(\frac{V}{V}\!\!\!\!>X<\frac{V}{V}\) originating from a symmetrical diatomic molecule are not known.

To render the linkage strictly homopolar it is not necessary that the nuclei are absolutely equal. Hund has pointed out that it is already sufficient that the sum of the energies for all the electrons on the bonding orbitals is equal for either of the nuclear fields. In the separated atoms these energies are represented by the sum of ionisation potential and electronic affinity, if we consider two electrons. In the united molecule the values will be different, but it seems plausible to assume that their values for different atoms in linkage remain in the same order in homologous molecules. For the purpose of discussing the qualitative increase or decrease of the polarity in a series of homologous molecules, in which one partner remains the same, it is sufficient to compare the values of either the ionisation potential or the electronic affinity of the changing partner instead of their sum, because both these quantities change in the same sense.

Even the same molecule may manifest different degrees of polarity under different conditions, e.g. covalent linkage in the vapour state and electrovalent linkage in the melted or crystalline state or in solution. As a first example we consider the process of dissolving gaseous potassium chloride in water. In the \(U(r)\) diagram of KCl the ionic curve intersects the atomic curve and forms the ground level of the molecule. The level of the separated ions is about half a volt above that of the separated atoms in their
ground states. As the energy of hydration for the K$^+$ ion is about 73 kcal/mol and that of the Cl$^-$ ion about 89 kcal/mol, the level of the separated hydrated ions lies about 7 volts below that of the unhydrated ones. This energy level is 2 volts below that of the combined ionic molecule, whose hydration is very small only. Therefore the ionic curve, though still the lowest of the system, is transformed into a repulsive one on dissolving and accordingly the ions separate spontaneously. If then in the vapour state a molecule like AgCl possesses an ionic curve, which is not that of the ground state, but very near above it, the ionic curve will be transformed into a repulsive curve which intersects the lowest atomic state and belongs to the lowest energy level of the system; since it is a repulsive one, the system will again separate into ions in solution. For AgCl the energies of hydration are 100 kcal/mol for Ag$^+$ and 89 kcal/mol for Cl$^-$, the level of the hydrated ions is 8.2 volts below that of the unhydrated ones, and since the energy of dissociation is 3.1 volts, the ionisation potential of Ag 7.5 volts, the electronic affinity of Cl about 3.8 volts, it is also 1.4 volts below the lowest term of the combined molecule.

So we see that external forces are easily capable of changing the bonding conditions, when a polar molecule though covalently bound is near to the limit of electrovalent linkage.

XIV.

For a brief survey of the chemical properties of the atoms with regard to their electronic configurations, we confine ourselves to the normal atoms disregarding the transition elements.

Besides the main question, whether or not in a certain case linkage occurs, the effect of changing degeneracy of the nuclear fields will also be considered in the following examples. The change of polarity is of particular interest in the first groups of the periodic system, where among homologous molecules both covalent and electrovalent linkages occur. The degree of polarity is to be recognised not only from the dipole moment, which has been employed above for this purpose, but also from other physical properties such as conductivity, melting point, hydrolysis, etc.* Although the polarity changes in a continuous manner, the said properties show a discontinuous change, when a certain degree of polarity is attained, which will take place as soon as the gradual increase of the polarity brings the ionic $U(r)$ curve below the atomic one.

* Most of the constants quoted in this section in connection with the transition from covalent to electrovalent linkage are taken from a paper of Samuel and Lorenz and from the literature mentioned there.
The alkali metals have one single outside electron and are therefore monovalent. The ionisation potential is lower than that of the elements of any other group and varies between 5.37 volts (Li) and 3.87 volts (Cs). The polarity of their combinations with other atoms is therefore greatest. This explains why electrovalent molecules prevail. The ionisation potential, however of Cu, Ag, Au is considerably higher being 7.68, 7.54 and 9.2 volts respectively. Therefore the molecules formed by the atoms of the sub-group are closer to covalent linkage; thus the monohalides are covalent in the vapour state and become electrovalent only in the melted state or in solution. It is remarkable that silver has a lower ionisation potential than either of its neighbours in the periodic system, a fact which is connected with certain irregularities in the preceding atoms. The outside electrons of nickel form the configuration $d^8s^2$, those of palladium one of $d^{10}$ and platinum possesses the configuration $d^8s$. Only in the case of palladium the d-group is completed and as the completed configuration in Pd and Ag$^+$ when compared with Ni and Cu$^+$ or Pt and Au$^+$, is more stable, silver exhibits a more marked monovalency, whereas Cu and Au relapse easier into the condition of transition elements, showing also higher valencies.

In cases with more than one valency the polarity is determined by the sum of the ionisation potentials and electronic affinities for all the electrons concerned. As in the case of monovalency, it is sufficient to take either the sum of the ionisation potentials or that of the electronic affinities in the comparison of homologous molecules, because either of them changes in the same sense. It is further convenient to divide these sums by the number of valencies and to obtain thus a "mean ionisation potential" or a "mean electronic affinity", which render it possible to compare the polarities of particular links also in polyatomic combinations.

The elements of the second group are divalent. The arithmetic mean of the ionisation potential of both electrons together varies between 13.8 volts (Be) and 7.6 volts (Ba); for zinc, cadmium and mercury it is 13.6, 12.9 and 17.5 volts respectively. In the vapour state these elements display covalent linkages; for the oxides and sulphides this follows from the emission spectra (section IX), for some of the dihalides from the absorption spectra. Be, Zn and Hg show the highest mean ionisation potential, that of Cd is slightly lower in connection with the higher stability of the $d^{10}$ configuration of Pd. Therefore the dichlorides of Be, Zn and probably Hg are insulators in the melted state, indicating that covalent linkage prevails, whereas Cd is a good conductor in contradistinction to either of its neighbours in the periodic system. These and many other differences of behaviour could not be easily understood in a theory of polarisation of ions.
(Fajans), as the ionic radius forms a monotonous series, being 0.34, 0.83, 1.03, 1.12 A.U. respectively for Be$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$ respectively, whereas they follow directly from the irregular course of the ionisation potential.

Hydroxides are acids or bases. They are acids, when the linkage between O and H becomes electrovalent in solution, and bases, when this applies to the linkage between O and its other neighbour. This difference depends therefore on the difference of polarity of these two links; its determination amounts to a comparison between the ionisation potential of hydrogen and the mean ionisation potential of the other atom which is linked to oxygen. Since, however, the conditions in the completed molecule differ from those in the separated parts, one cannot expect this relation to be more than a qualitative indicator; but it is clear that the acidic character of the hydroxides becomes the more manifest, the higher the mean ionisation potential. Among the atoms of the second group Be and Zn have a mean ionisation potential practically equal to that of hydrogen; their hydroxides show accordingly an amphoteric character, whereas all those with a lower mean ionisation potential are bases.

In the third group the electronic configuration is s$^2$p; so for the first time we expect two different valencies, trivalence if all the three electrons are active and monovalency, if only the p-electron joins a molecular orbital together with electrons of the negative partner. All of them are trivalent and In and Tl form also monovalent derivatives.* The ionisation potential is naturally much lower for the single electron than for the two s-electrons; the first ionisation potential of In and Tl is 5.76 and 6.07 volts respectively but the arithmetic mean for the first three electrons is 17.5 and 18.7 volts respectively. Hence the electrovalent character of the linkage prevails in monovalent combinations, the covalent in trivalent ones; the boiling point of TlCl$_3$ in about 100°C., that of TlCl 306°C. TlCl exhibits a high conductivity in the melted state, TlCl$_3$ is a non-conductor. The linkage between Tl and O is electrovalent in TlOH and covalent in Tl(OH)$_3$, as can be taken from the fact that only the trichloride shows hydrolysis, but not the monochloride. The mean ionisation potential for three electrons is 23.4 volts for B, 17.5 volts for Al and 19.0 volts for Ga. Thus again In, like Ag and Cd, has a lower mean ionisation potential as both its neighbours Ga and Tl and have therefore the formula 

* Klemm and Tille$^{43}$ have shown that the dihalides of Ga and In are diamagnetic and have therefore the formula \( \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{Ga--Ga--Cl} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \), etc., the metals being trivalent.
is therefore closer to electrovalent linkage; compared with CaCl₂ and TiCl₃, InCl₃ is a better conductor in the melted state and has a higher melting point. The hydroxides of the elements of the third group exhibit mainly an amphoteric character, with the exception of boron, whose mean ionisation potential is the highest one, not only in the third group, but also of all the metals discussed before. Therefore B(OH)₃ is the first acid we meet.

The normal atoms of the fourth group, C, Si, Ge, Sn, Pb, have the electronic configuration s²p², we expect di- and tetra-valency. For carbon and silicon the mean ionisation potential for the two first electrons is 17.8 and 12.2 volts, for the first four electrons 36.9 and 25.7 volts, respectively. The values decrease with the heavier atoms (Pb 11.2 and 24 volts) and therefore the metallic character is more marked in the later periods. Also the lower state of valency is always closer to electrovalent linkage than the higher one. PbCl₂ is a typical electrovalent molecule with a conductivity of 40.7 in the melted state, a boiling point of 500°C, and showing no hydrolysis in solution. Its photo-dissociation indicates that the electrovalent character still prevails in the vapour state. PbCl₄, on the other hand, is a typical covalent molecule with a conductivity of about 10⁻⁵, a melting point of 15°C, and showing a strong hydrolysis in solution. The tetrahydrides of all the elements are volatile. Similar remarks apply to the atoms of the fifth group. Here naturally the mean ionisation potential is even higher, because we have five valency electrons. Thus the covalent character predominates still more. From the configuration s²p³ we expect tri- and penta-valency. We have dealt with examples from this group already in other sections of this paper. Lower states of valency cannot be expected in saturated compounds, because the ground state of the atoms of the fifth group is a quartet term.

In the sixth group the configuration s²p⁴ indicates the valency numbers 6 and 4. Also the valency number 2 is possible, because in the ground state s²p¹ one pair of p-electrons have their spins already neutralised and can form by themselves an electronic group in the molecule, as in H₂O or SCl₂. In the combinations of the atoms of this group with one another, two of the spins are, however, not counterbalanced and so we should expect two free valencies. Such molecules are indeed capable of utilising them, as for instance SO in SO₂ or probably O₂ in the second form of hydrogen peroxide, which process coincides then with the transition to the normal tetravalency. Why oxygen normally exists in the form of diatomic molecules, is still an open question; this is not a difficulty characteristic of the present interpretation of the theory of molecular orbitals, but confronts any theory which undertakes to explain the phenomenon of saturation.
It is, however, clear that a linear molecule $\text{O}=$ $\text{O}=$ $\text{O}$ is not capable of existence, because the repulsion between the two outer O atoms is nearly 8 volts, as can be taken from the spectrum of $\text{CO}_2$, whereas the energy of an $\text{O}=$ $\text{O}$ bond is only 5.09 volts.

As in the preceding groups the mean ionisation potential increases for each atom from lower to higher states of its valency, and for different atoms from the heavier to the lighter ones. Along with the ionisation potential, also the energy necessary to split the $s^2$ group or to excite a p-electron increases from the heavier to the lighter atoms in each group and in general also with increasing group number within a period. Those valencies to bring about which one or other of such excitations is necessary are more and more difficult to attain, when we proceed to lighter atoms within the group or to heavier atoms within the period. Therefore just the atoms N, O, and F at the end of the second period are distinguished in this manner. N is just able to exhibit the maximum valency 5 of its group, but only in particular combinations; $\text{N}_2\text{O}_3$ exists, but not $\text{NCl}_3$, whereas $\text{PCl}_5$ can easily be obtained, and F is only monovalent in contradistinction to all the other halogen atoms. In accordance with this the valency number 6 is exhibited by all the members of the sixth group except oxygen.

The halogen atoms possess seven valency electrons ($s^2$ $p^5$). Owing to their doublet term in their ground state they are monovalent; their high electronic affinity is responsible for their being generally the negative partners in chemical combinations, which are accordingly strongly polar and become easily electrovalent if the ionisation potential of the positive partner is low enough. When a halogen atom plays the role of the positive partner, it is also monovalent in the first instance; the four remaining p-electrons form a closed shell in the molecule and do not take part in the linkage, as has been discussed in the case of $\text{F}_2$ (section XIII). This $\pi^4$ group splits into two pairs on transition to polyatomic molecules; these two groups may then undergo fission and can be utilised to link further atoms, thus bringing about a tri- or a penta-valency. The same may occur to that electronic group of the molecule, which formed originally the $s$-shell of the halogen atom, the two further ensuing valencies producing a maximum valency of 7. The valencies 1, 3, 5 and 7 can easily be recognised in molecules like

$$\text{HOCI, HOOCl, HOCl}_2, \text{HOCI}_3$$

or

$$\text{ICl, ICl}_3, \text{IF}_2, \text{IF}_5.$$  

The above survey reduces the number of valencies of all atoms to the number of their outside electrons in their various electronic groups. Hund
H. Lessheim and R. Samuel

has already pointed out that the phenomenon of saturation of valencies depends on Pauli's principle, according to which it is possible to account for only two electrons in one wavefunction, and that a single odd electron represents a free valency, since in the corresponding wavefunction an electron of another atom may also be disposed of. Saturated compounds are therefore obtained, when either the total number of outside electrons or the number of p-electrons alone is made use of; often especially in polyatomic molecules, there is also a possibility of a pair of p-electrons being left unused. Thus all the saturated molecules described in the above survey have an even number of electrons. There is, however, no necessity of holding that the intermediate valency numbers are somehow impossible; on the contrary each atom will also display any number of valencies less than the maximum number. But if a single one of the outside electrons is not utilised, it represents a free valency which sooner or later undergoes a further reaction. Such chemical combinations are free radicals, including not only those which immediately undergo further combinations, but also those with a longer life-time such as NO or ClO₂ which have to be regarded as free radicals because of their characteristic properties; they are paramagnetic, exothermal and reactive.

The above survey does not claim to be an exhaustive description of all chemical facts; especially the transition elements have not been described, although the same principles apply to them too. Nevertheless the survey shows that the appropriate valencies are obtained and the characteristic features of the formed molecules described, if—as has been substantiated both theoretically and from band spectra—the degeneracy of the wavefunction due to the equality of the electrons answers for the accomplishment of molecular formation and the degeneracy of the nuclear fields for the polarity.

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