

Band Spectra and Valency.*

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ELECTRONIC CONFIGURATIONS.

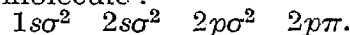
THE vibrational analysis of the band system of a diatomic molecule gives the vibrational frequency ω and the factor of anharmonicity ωx and according to the formula $D = \frac{\omega^2}{4\omega x}$ the dissociation energy D of each of the two electronic states involved. It is mostly possible also, to obtain an idea as to the character of these terms, *e.g.*, from considerations of the emitter and the number of heads each individual band possesses. The internuclear distance r_0 can also be estimated by certain empirical formulæ and this as well as the character of the terms can be definitely confirmed by the detailed rotational analysis of the bands.

In analogy with the spectra of atoms we distinguish these terms by their multiplicity and by the value of a quantum number, which represents the total orbital angular momentum along the nuclear axis of the molecule. Thus we get Σ , Π , Δ , etc., if this quantum number $\Lambda = 0, 1, 2$, etc. The multiplicity is indicated by a superscript thus $^1\Sigma$, $^2\Sigma$, $^3\Sigma$, etc., which means that the spin quantum number S has the values $0, \frac{1}{2}$, etc., the multiplicity (number of sub-levels) being given by $2S + 1$.

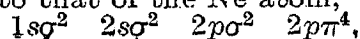
This description is not complete, but sufficient for the purpose of the present subject, which is the electronic configuration of the molecule. There are two ways to construct the wavefunction of a molecule. The first method has been developed mainly by Heitler, London, Slater, and Pauling, and is therefore known as the H.L.S.P. method.¹ This method constructs the wavefunction of the molecule from those of the separated atoms or their valence electrons and accordingly arrives at the character of the molecular electronic term from considerations of the constituting atomic terms. The second method, originated by Lennard-Jones and developed by Herzberg, Hund, and Mulliken, is called the method of molecular orbitals and starts from the very beginning with the completed molecule, *i.e.*, with the atoms at their proper internuclear distance and constructs the wavefunction of the molecule from those of its constituent electrons. The first method naturally is better suited for the description of the molecule at large internuclear distances, while the second one is so at smaller distances. Both of these have their own advantages; thus the H.L.S.P. method appears to be

superior, as far as questions of energy are involved, whereas the orbital method is more suited to the description of the electronic configuration and term scheme of the molecule. We shall therefore take up the latter view-point and base the following remarks on the method of molecular orbitals.

Accordingly, we start with the system of the two positively charged nuclei at a fixed distance and introduce into the resulting field the electrons of the molecule individually one after the other. A molecule is distinguished from an atom because its field possesses a favoured direction; this corresponds to the behaviour of an atom in a strong electric field and the quantum numbers of the electrons therefore are the same as those of the Stark effect. Each single electron is characterised by an axial quantum number λ , which shows, how much each electron contributes to that of the total angular momentum Λ and which is identical with the Stark effect quantum number m_l of the atoms. The electrons are called σ , π , δ , ... electrons, if λ is $0, 1, 2, \dots$ in analogy to the s, p, d electrons of the atoms. They form quantum groups or "orbitals" and the maximal number of electrons in a σ group is 2, that in the π group 4, because this includes the values $m_l = +1$ and -1 . In a polyatomic molecule, however, the two directions parallel and antiparallel to the field are no longer degenerated, and the π group is split into two pairs. The molecule CH, for instance, with its 7 electrons, may be considered as a N atom, whose nucleus is divided into two parts, of which one possesses 6, the other one, 1 charge, and which are slightly separated from each other. The two 1s and the two 2s electrons of N can become σ electrons only, because, for $l = 0$, $m_l = \lambda$ can have no other value but 0. The p -electrons, however, can become σ or π electrons, because for $l = 1$, $m_l = \lambda$ may have the values 0 and ± 1 . We denote by superscripts the number of electrons in each group (if more than one is present), we obtain the following electronic configurations for the CH molecule:—



Of the three p electrons, the first two have populated the $p\sigma$ group, the third, not finding a place there according to Pauli's principle, has gone into the $p\pi$ group. The order in which the orbitals are written, is an energetical order. The more we proceed towards the right-hand side, the less energy is necessary, to ionise the molecule. This way of writing gives us also the contribution of each electron to Λ . At the same time each electron contributes $\frac{1}{2}$ to the spin quantum number S . For both quantum numbers, however, we have not to pay regard to the electrons on the closed orbitals, here the first three, because all the vectors are counterbalanced, and the character of the ground term of CH is determined only by the single π -electron. Two vectorial positions of L and S are possible and the term is a $^2\Pi$ term. In the molecule HF, three electrons more are present and fill the three empty places in the $2p\pi$ orbital. Its electronic configuration is, according to that of the Ne atom,



* Presidential address, delivered in the Physical Society, Aligarh, March 26th, 1936.

¹ References of the theoretical investigations will be found more or less complete in the following papers: J. H. Van Vleck and A. Sherman: *Rev. Mod. Phys.*, 1935, 7, 167; R. S. Mulliken, *J. Chem. Phys.*, 1935, 3, 375; H. Lessheim and K. Samuel, *Proc. Ind. Ac. Sci.*, (Bangalore), 1935, 1, 623. For experimental results *cf.* W. Jevons, Report on Band Spectra, London, 1932, and H. Sponer, *Molekuel'spektren*, Berlin, 1936.

The number of papers which are connected with this subject, is very large and only a few having a direct bearing on the controversial points are quoted in detail,

This configuration is only made up of closed groups and the quantum numbers are $\Lambda = 0$ and $S = 0$, the resulting state is a $^1\Sigma$ term.

In this description, treating CH as N and HF as Ne, we have used the conception of the "united atom", i.e., we have assumed, that the two nuclei are so close to each other, that they nearly coincide. It is assumed, that the field still resembles a central field as in an atom, so much so that the quantum numbers n and l of the atom retain their significance. This is true among the hydrides because they possess particularly small internuclear distances, the proton having no dimensions in the ordinary sense. We are thus able, to use these known quantum numbers to determine the unknown ones of the molecule. Generally, however, the field does not possess an approximately central character, but has only axial symmetry. Then it is not possible, to imagine the distance between the two nuclei shortened more and more, till the molecule becomes a "united atom" because the quantum numbers of the latter one have lost their significance for the actual molecule. In this case we have to determine the values of λ from the quantum numbers of the separated atoms. In the symbols $1s\sigma$, etc. just as we have written the quantum numbers n and l of the "united atom", before the λ of the molecule, so we shall now write the corresponding n and l values of the separated atoms behind λ and get for the lowest orbitals, again in energetical order,

$\sigma(1s) \sigma(1s) \sigma(2s) \sigma(2s) \pi(2p) \sigma(2p) \pi(2p) \sigma(2p)$
 The configuration of the ground state of the molecule NO, in which we have two $1s$ groups, two $2s$ groups and together seven p -electrons, is $\sigma^2(1s) \sigma^2(1s) \sigma^2(2s) \sigma^2(2s) \pi^4(2p) \sigma^2(2p) \pi(2p)$ and the term, exactly as that of CH, is a $^2\Pi$ term. The two groups $\sigma(1s)$, i.e., the K shells of N and O, remain for all practical purposes localised in the neighbourhood of their own nuclei and form so called "atomic orbitals". The configuration proper of the molecule is formed by the following electrons of the L shell, which in this case are on "molecular orbitals". From this distinction the whole method has received its name.

PREMOTED AND NON-PREMOTED ELECTRONS.

From the above it will be seen that the energetical order of the electronic groups in the molecule is different for the two methods of interpolation, viz., from the view-point of the "united atom" and from that of the separated system. For small internuclear distances we obtained the order $\sigma\sigma\sigma\pi\sigma\sigma\pi\dots$, for bigger ones $\sigma\sigma\sigma\sigma\pi\sigma\dots$. The reason for this is the operation of Pauli's principle. Two separated atoms like C and O possess each a completed K shell, i.e., together four $1s$ electrons. But the corresponding united atom, in this case Si, can have only one $1s^2$ group. If we consider the CO molecule as an interpolation between the two extreme cases, and shorten the distance between the two atoms more and more, two of the four $1s$ electrons have to find during this process a place somewhere else in the electronic configuration of the two centre system. As a matter of fact, these two electrons will of course remain as σ electrons, but will form the group $2p\sigma$ in the united atom. In other words, if we have the two nuclei stripped of all electrons and fixed once at a small and once at a large internuclear distance and let in the electrons now being re-

captured by them, we get different configurations. If the distance is large (the field of axial symmetry) the third electron becomes a $1s$ electron. If the distance is small (approximate central symmetry), the third electron will go into the group $2s$. Similar considerations apply to other groups, and this rearrangement of the groups can be seen, if we write the electronic configuration of a molecule with all quantum numbers, namely those of the "united atom" as well as those of the separated system. That of NO may serve as an example:

$$1s\sigma^2(1s) \ 2p\sigma^{*2}(1s) \ 2s\sigma^2(2s) \ 3p\sigma^{*2}(2s) \ 2p\pi^4(2p) \\ 3s\sigma^2(2p) \ 3d\pi^*(2p).$$

Among the electronic groups there are three (marked by asterisks), which on increasing internuclear distance go into higher orbitals, from $1s$ to $2p$, from $2s$ to $3p$, from $2p$ to $3d$ respectively. Such electrons are called "premoted" the other ones non-premoted. The energetical relation between the orbitals at various values of r was first calculated for H_2^+ and later generalised for other molecules by Hund, and is shown in the diagram of Figure 1. This correlation table

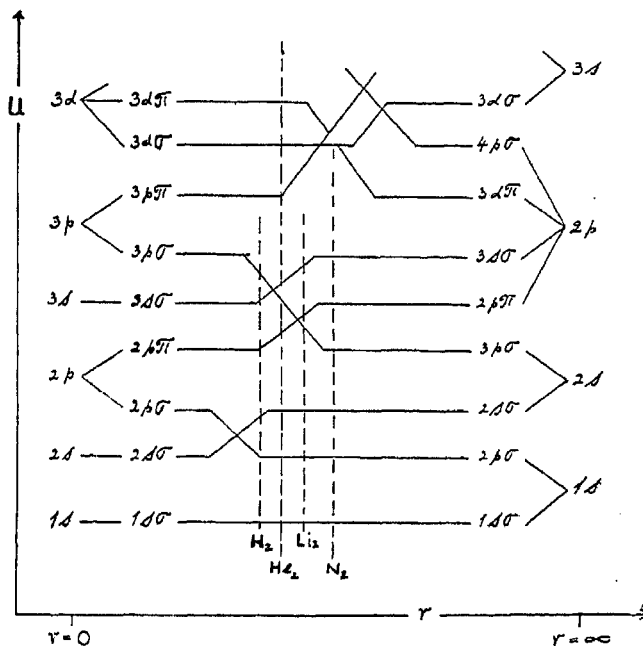


Fig. 1.

indicates the energetical order of the molecular orbitals for any internuclear distance from $r = 0$ to $r = \infty$. For a number of molecules the probable value of r is indicated and going along the dotted line, we can read off the series of electronic groups. At the same time the different heights of the groups above the abscissa indicates the energy. It can be seen that the energy to tear off the electrons generally decreases with increasing quantum numbers and, furthermore, that on decreasing internuclear distance the system of two atoms loses energy by the process of premotion and gains energy by the non-premoted groups. A premoted group is bound with less energy than the corresponding non-premoted one.

THE PROCESS OF DISSOCIATION.

From the character of the term we construct such electronic configurations, which yield the required S and Λ values. The energies of excitation and dissociation (calculated from the harmonic and anharmonic constants) indicate, from which

term of the atoms in question the level of the molecule arises and gives us the quantum numbers of the electrons in the separated atoms. In this way it is mostly possible to select the true electronic configuration from among the possible ones.

In the case of a diatomic molecule we know that its potential energy can be expressed as a function of the internuclear distance between its constituent atoms. We thus obtain, as Franck pointed out first, the potential energy curve, which runs parallel to the axis of the internuclear distance so long as the system represents two separated atoms. This curve will show a minimum if the two atoms enter into chemical combination to form a molecule, but it will have no minimum in the case of an elastic impact of the two atoms, which does not lead to chemical linkage. If one or both of these atoms are excited from the very beginning of molecular formation, then the horizontal part of the curve is higher by an amount which is given by the excitation energy of the atom or atoms concerned. If now the atoms combine to form a molecule, we obtain the curve of potential energy of an excited electronic level which again may or may not exhibit a minimum. In this way we may obtain a number of potential energy curves for a molecule which represent the various electronic levels of the molecule in different electronic configurations. The potential energy curves which do not show a minimum also come under this category.

Let us consider the lowest of such potential curves. Its trough represents the various vibrational energy levels that belong to the molecule and here the equilibrium position or roughly the minimum of the curve indicates the internuclear distance in that state of the molecule, where it is in its lowest vibrational level. The difference in the energy between this position and the position of the separated atoms gives the dissociation energy D'' of the molecule. If the molecule absorbs light of a certain energy ν_0 its electronic configuration is changed and we obtain an excited term. Its energy of dissociation D' correlates it with the level of the separated atoms of which now, at least in many cases, one is excited. The difference $\nu_0 + D' - D''$ equals the energy of excitation of this atom. Thus in H_2 (Fig. 2) the ground-level $1^1\Sigma$ has the electronic configuration $1s\sigma^2$ and the dissociation energy 4.47 volts. By removing one electron into an excited group, the term $1s\sigma 2p\sigma 1^1\Sigma$ obtains, ν_0 being 11.13 volts, $D' = 3.47$ volts. The difference $\nu_0 + D' - D'' = 10.15$ volts gives the energy difference of the separated system and agrees very well with the energy of the first line of the Lyman series at 1215.7 A.U. Hence the ground-level is formed by two normal H atoms both in the term 1^1S , the excited level of the molecule by one normal and one excited atom in the term 2^2S . In both states of the molecule the electrons counterbalance their spin, the two molecular states being singlet terms. If two normal H atoms approach each other the electrons having parallel spin, a $3^1\Sigma$ level results, which is a repulsive term, the $U:r$ curve not possessing any minimum. This term is the final level of the continuous emission spectrum of hydrogen.

To take another example, the above configuration of the ground state of NO contains four 2s and seven 2p electrons and therefore arises

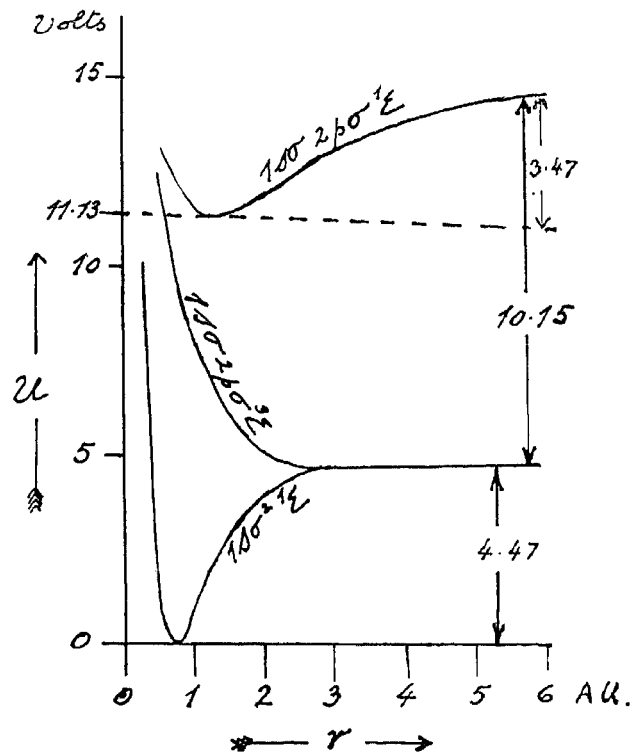


Fig. 2.

from the combinations $N(2s^2 2p^3) + O(2s^2 2p^4)$, which are those of the unexcited atoms. But

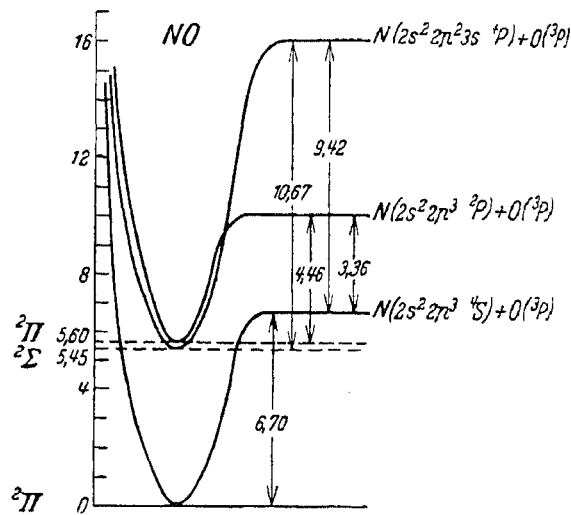


Fig. 3.

besides the ground terms $4S$ and $3P$ respectively also other terms, i.e., $2D$ and $2P$ of N and $1D$ and $1S$ of O , have the same electronic configuration. However, NO fortunately possesses the excited electronic level 2Π and, according to the dissociation energy of this term, it arises from the combination of two atoms, one of which is excited by 3.4 volts. This agrees with the energy of excitation of the excited $(2s^2 2p^3 3p)$ term of N and proves that the ground-level of the molecule is formed by two unexcited atoms. A third term of NO , 2Σ , is interesting, because its energy of dissociation is bigger than that of the ground-level. It is correlated to $O(2s^2 2p^4 3p) + N(2s^2 2p^2 3s 4p)$. The electronic configuration of the molecule in this state is therefore (if we abbreviate the atomic orbitals of the K shells by K_1 and K_2):—
 $K_1 K_2 2s\sigma^2 (2s) 3p\sigma^2 (2s) 2p\pi^4 (2p) 3s\sigma^2 (2p) - 3s\sigma (3s)$.

We find that the partial removal of the odd $3d\pi$ ($2p$) electron increases the energy of dissociation, or in other words, if the electron, which later on remains unpaired in the molecule, is already removed to the M shell in the N atom, a molecule with an increased bond energy is formed. This interpretation, confirmed by the bands of PO, AsO and SbO, appears to be important for a theory of valency.²

In similar ways we learn that the s^2 group of the earth alkali metals acts repulsively. The ground state of the molecules of the BeO and BeF type does not arise from the combination of unexcited metal atoms in the term $s^2 1S$ with O and F, Cl, etc., but from that of excited metal atoms in the term $sp^3 P$, the helium-like s^2 group having been previously fissured. This result is of interest, because it shows, that also a non-promoted group may act repulsively. For some time, because the extrapolation of the dissociation energy is never entirely accurate, this result was doubted, but to-day it is proved in two ways. Some of the molecular terms have to be correlated to terms of atoms, in which two electrons are excited simultaneously (the so-called anomalous terms) and this shows, that already one electron was excited in the dissociation products of the ground-level. A clear decision is furthermore given by the spectrum of CdF. Here the energies of excitation of the metal are increased, Cd belonging to the sub-group of the Periodic Table and therefore the only possible correlation proves beyond doubt that the metals of the second group are chemically inert, so long as the s^2 group of electrons remains undisturbed.³

DEVELOPMENT OF THE ORBITAL METHOD TO A THEORY OF VALENCY BY THE INTRODUCTION OF NEW POSTULATES.

Proceeding from the description of the electronic configuration and term system of the molecule, to questions of valency, we shall again take up the view-point of the method of molecular orbitals. Here, however, the answers furnished by the theory are not so clear as for the problems dealt with above. Whereas these latter concerned the completed molecule, *i.e.*, the system of two atoms at small internuclear distances, for which the method of molecular orbitals is singularly adapted, questions of valency invariably involve the process of dissociation (or its converse, the process of formation) of the molecule, *i.e.*, are dealing with the same system at large internuclear distances, which is already somewhat outside the scope of the orbital method.

If two atoms undergo chemical combination, the ground state of the molecule possesses a potential curve with a minimum at a particular internuclear distance. Only by means of introduction of energy it is then possible either to increase or to decrease the distance of the two atoms and the minimum of the $U:r$ curve is therefore the necessary condition of molecular formation. Any theory of valency on the basis of band spectroscopy has therefore at first to

show, which of the curves of the possible electronic configurations possess a minimum and which not, or, in other words, which of them is an attractive curve and which a repulsive one. The next step will then be, to find out, what distinguishes the wavefunctions of the attractive terms from those which belong to the repulsive ones.

The method of molecular orbitals as such does not furnish any answer to both these questions at the present state. It is not qualified to distinguish between the attractive and repulsive curves nor to give the amount of energy of dissociation. The reasons, as we shall see, are inherent to this method; they are connected with its general inability to describe the system at larger internuclear distances and due to the same principle which brings about its advantages, *i.e.*, that the interaction of the electrons does not play any part in it. It is therefore necessary to introduce new conceptions into the method of molecular orbitals, but from the very beginning it should be emphasized, that such a procedure means the *introduction of new postulates*, and it is not on the method of molecular orbitals but on these postulates, that the theory of valency is based.

The first postulate, introduced particularly by Herzberg and Mulliken, is, to identify promoted and non-promoted electrons with anti-bonding and bonding electrons respectively. A promoted electron of a molecule is bound with less energy than the corresponding non-promoted one. It is assumed, that a promoted or non-promoted electron tends to make the $U:r$ curve repulsive or attractive respectively. The $U:r$ curve of the particular molecule is conceived to be made up from the single terms of the single electrons, the correlation table indicates the loss or gain of energy per single electron and as a matter of principle it is assumed, that the grand total of these energy changes of the single electrons describes that of the molecule as a whole. In reality, however, the correlation table shows only that a promoted orbital is higher than the corresponding non-promoted one, but it is unable to indicate, whether both together are higher or lower than the correlated ones in the atom. This correlates a particular orbital, say $1s$, to a particular orbital in the molecule, say 1σ ($1s$) but we do not know, if the left-hand side of the table, which refers to the molecule, lies as a whole higher or lower than the right-hand side of the separated atoms. To avoid this difficulty, Mulliken fixes the energy relation of the lower ends of the two sides once for all by referring to H_2^+ . Here the potential curve of the single electron can be accurately determined, because only one electron is present. The curve of the non-promoted 1σ ($1s$) electron is that of the ground-level of this molecule ion and it is concluded, that it is attractive, *because* the orbital is a non-promoted one. In the neutral molecule H_2 a second electron is present, which finds its place in the same orbital. In He_2 , however, the third and fourth electrons populate the next orbital, on account of Pauli's principle, and this, *i.e.*, $2p\sigma$ ($1s$) is a promoted group. Thus the effect of the two first bonding electrons is counter-balanced by that of the two last anti-bonding electrons and therefore chemical combination of two He atoms is not possible.

Here the wavemechanical interaction, which is

² (a) H. Lessheim and R. Samuel, *Z. Phys.*, 1933, 184, 637; 1934, 88, 276; (b) *Phil. Mag.*, 1936, 21, 41. (c) P. C. Mahanti, *Ind. Jour. Phys.*, 1935, 9, 517.

³ (a) G. Herzberg, *Z. Phys.*, 1929, 57, 601; H. Lessheim and R. Samuel, *loc. cit.* (b) R. K. Asundi, R. Samuel and Mohd. Zaki-Uddin, *Proc. Phys. Soc.* (London), 1935, 47, 235.

due to the equality of the electrons and is the decisive bonding effect in Heitler and London's calculation, is neglected, because the whole argumentation is solely based on the conditions of H_2^+ , where only one electron is present and therefore no interaction with a second electron is possible. If linkage generally is due to this interaction, the non-existence of a stable He_2 molecule (formed by unexcited atoms[†]), will then indicate, that the orbital $1s\sigma$ ($1s$) lies still below $2p\sigma$ ($1s$) but that both the orbitals, the non-promoted one as well as the promoted one, together are higher than in the separated system, *i.e.*, they are anti-bonding, because in the He atom they form closed shells $1s^2$, and the energetical relation of the right and left-hand side of the correlation table in H_2^+ does not permit generalisation. This is corroborated by certain difficulties, which the theory encounters in the case of the molecule LiH, which possesses the same number of electrons as He_2 , but exists with an energy of dissociation of 2.5 e.v. It can be shown that there is no other explanation of this rather high energy value possible, but to accept Lennard-Jones' manner of counting by neglecting the closed shells and to consider the valence electron of Li as well as that of H as a $1s$ electron. In this case both of them are bonding electrons but then already one of them should be sufficient for the formation of a stable molecule and the molecules HeH or LiH^+ should exist too. Experimental evidence and wavemechanical calculation show, however, that they do not exist. Furthermore, experimental evidence shows, that H_2^+ is indeed the only example of a molecule with a single valence electron, that not only HeH and LiH^+ but also molecules of the type Li_2^+ or BeH^{2+} do not exist, whereas the corresponding molecules with two valence electrons are all well known spectroscopically, *i.e.*, molecules of the type LiH , Li_2 , BeH and BeH^+ .

In this theory the bonding effect is due not to the interaction of the electrons but to the degeneracy of the nuclear fields. In H_2^+ the fields of the two nuclei are indeed completely identical and Hund has shown, that a single electron possesses bonding power also, when the nuclear fields, short of being identical, are only approximately degenerated. Such a theory of valency considers this effect based on the degeneracy of the fields as the predominating bonding effect, the formation of electron pairs in the molecule being then only incidental. Since this bonding effect is produced by the single electron, the interaction of electrons need not be considered except as a superimposed secondary effect. This conception can be made use of as a wavemechanical interpretation of those chemical theories of valency, which have been developed particularly by Langmuir, Lowry, Sidgwick *a.o.*,⁴ and in which certain types of chemical bonds are brought about by the electrons of one atom only (the "donor") without interaction with electrons of the second atom, and from the original literature it can be seen, that the interpretation of the method of molecular orbitals as a single-electron

[†] Indeed a molecule He_2 , formed by excited atoms, exists.

⁴ Cf. N. V. Sidgwick, *The Electronic Theory of Valency*, Oxford, 1927, and contributions to the *Annual Reports of the Chem. Soc. London*.

bond theory of valency has indeed been sponsored by the requirements of the theory of this school of chemical thought.

We have seen that the basic postulate of this interpretation, *i.e.*, the identification of promoted and non-promoted electrons with anti-bonding and bonding electrons has been introduced into the orbital method by fixing the energy relation of the right and left-hand side of the correlation table according to the ground state of H_2^+ . In a similar way the postulate of the second possible interpretation of the same method goes back to the neutral molecule H_2 . Here the emphasis is laid just on the second bonding effect, produced by the equality of the electrons. Since the electrons are always identical, this degeneracy remains always present and does not require the additional assumption of approximate degeneracy of so vastly different fields as, *e.g.*, C^{2+} and O^{4+} in CO or Be^{2+} and F^{5+} in BeF. So that wave-mechanical interaction is brought about and chemical linkage produced by the formation of *electron pairs* in the molecule. Accordingly it is assumed that an attractive $U:r$ curve arises, when electrons of different atoms join in the same molecular orbital, as in the ground state of H_2 . The promotion of the electrons plays the rôle of a superposed secondary effect only. Unpromoted orbitals contribute more, promoted orbitals less to the energy of formation, but if a promoted orbital is populated by a pair of electrons, one of either atom, the effect of the interaction may vastly prevail over that of promotion and the total contribution may still be positive. Thus the $^1\Sigma$ term of H_2 , which arises when the electrons of the two unexcited atoms enter the promoted orbital $2p\sigma$ ($1s$) is not only stable, but this configuration satisfies also the criterion of linkage of the Slater-Pauling theory, the wave-functions of the two electrons overlapping. Such a theory leads to the interpretation of the method of molecular orbitals as a pair bond theory of valency and approaches therefore the other wavemechanical methods of Heitler, London, Slater and Pauling. If we compare it with chemical theories of linkage, it may be considered as a wavemechanical interpretation of the pre-wavemechanical pair bond theory of Lewis and its development by Grimm and Sommerfeld.⁵

To our mind recent developments of band spectroscopy have decided more and more against the identification of bonding with non-promoted and anti-bonding with promoted electrons. We mentioned above the spectra of molecules like BeO and BeF, which clearly show that the unexcited metal atoms in the term $s^2\ ^1S$ do not undergo chemical combination. But Be ($s^2\ ^1S$) + O ($s^2p^4\ ^3P$) or + F ($s^2p^5\ ^2P$) should form a stable molecule if the above assumption were correct. The promoted and non-promoted σ groups cancel out and there remain four or five p -electrons respectively, all on non-promoted orbitals. As a matter of fact, unexcited Be + unexcited O should form a molecule BeO possessing a triplet term, but experimentally we get a singlet term as the ground level of these molecules. The further assumption, that it originates from Be (1S) + O (1D) fails, because the correlation of the molecular term to those of the separated atoms, described above, clearly indicates that

⁵ Cf. H. G. Grimm, *Handb. d. Physik*, 1933, XXIV.

the ground-level of BeO involves an excited Be atom and this is corroborated by the spectrum of BeF. This correlation has been used already for about a dozen of molecules of these two types and cannot be taken to be fortuitous. Here clearly exist two electronic configurations, which both should produce stable terms of the molecule according to the single electron bond interpretation of the method of molecular orbitals, but instable terms according to the pair bond theory of valency—and the experiment shows definitely, that these stable terms do not exist. The conclusion, that not the promoted but the odd electron weakens the chemical bond is again at once confirmed by the spectra of all the molecules of NO type, *i.e.*, NO, PO, AsO and SbO.

Furthermore, new spectra are again entirely consonant with this view. Molecules like AlO and GaO behave similar to BeO and MgO. In its unexcited configuration s^2p the metal atom forms only a single link with oxygen and the double bond comes into existence only after the original s^2 group of the metal atom has been broken up. Those excited terms, which possess a higher energy of dissociation than the ground-level on account of the double bond, therefore dissociate into oxygen and an excited metal atom in the configuration sp^2 . Again SiF and SnCl

behave like BeF, MgF, or NO; they are odd numbered and increase their energy of dissociation by the partial removal of the odd electron, which does not take part in the linkage⁶.

If we do not take into consideration hydrides, which approach the "united atom", but ordinary diatomic molecules, then we must say, that the interpretation of band spectra during the last few years has changed the whole basis for the interpretation of the method of molecular orbitals as a theory of valency. There is ample experimental proof for the conclusion, that not non-promoted electrons, but electrons, which join in the same orbital with other ones of the second atom confer stability to a molecule and that not promoted electrons disturb the linkage but the unpaired ones. These new results, obtained from new correlations and new spectra are so uniform and follow so closely the predictions of the pair bond theory, that there seems to be little or no doubt for the experimentalist. How far they may serve as the basis of the theory of valency will be seen from a more general survey.

⁶ For molecules of the type GaO and SiF, *cf.* forthcoming papers of R. K. Asundi and R. Samuel, *Proc. Ind. Ac. Sci.* (Bangalore), in press.

(To be Continued.)

Recent Advances in Sanitary Science.

THE following is the extract of an address delivered by Dr. Gilbert J. Fowler, before the Joint Session of the Association of Economic Biologists, Coimbatore, the Indian Academy of Sciences, the Indian Chemical Society (Madras Branch), the Institute of Chemistry of Great Britain and Ireland (Indian Branch), the Society of Biological Chemists, India, and the South Indian Science Association, Bangalore, held at Bangalore on 10th April 1936.

Dr. Fowler dealt with the recent researches on water purification, with particular reference to Madras, the study of sewage-sick soils and the sewage problems of Madras and Ahmedabad. Finally he spoke of recent researches and discussions on the manufacture of compost from waste materials.

Introducing the subject he thanked the President (Dewan Bahadur N. N. Iyengar) for his kind reference to the work which had been done in connection with the provision of compost for the villagers. It was a great encouragement to him that his objective towards which he had devoted a good many years of work seemed now within sight of fulfilment. He referred to a recent address by Sir George Schuster to the Royal Society of Arts in London, where Sir George had quoted Lord Bacon to the effect that money was like muck, it was no good unless it was spread. The scientific utilisation of waste materials for the use of agriculture was a true spreading of wealth. We heard that nowadays in England the distribution by Government of free milk to necessitous school children was an accomplished fact. Such a policy would have been hardly conceivable not so many years ago, yet now it was realised that the safeguarding

of the health and well-being of the future generation was the best possible investment a country could make. There was in England at the present time a movement with the object of converting the sewage works of the country into Fertiliser Factories. The economics of this question had awakened vigorous discussion. One school, supported mainly by engineers, was in favour, *e.g.*, of discharging all the sewage of London through a long tunnel into the sea. Another school, representing Biochemistry and Agriculture, was averse even to the water carriage system on account of its waste of fertilising material. In view of the large expenditure of capital on works of sanitation it was of the highest importance that the scientific foundations of the subject should be thoroughly investigated. In his (Dr. Fowler's) opinion, the true solution of the problem would only be found in a close adherence to Nature's cycle. Recent research by McCarrison, Howard and others had shown the immense importance of certain factors which must be present in the food of plants and consequently of animals if the processes of life were to function satisfactorily. It was the little extra something, be it vitamin or hormone, protein cleavage product or whatever it might be named which was characteristic of living process, which determined the health and well-being of the plant and the animal which fed thereon.

Having these considerations in mind, it was interesting to note that the largest modern sewage works, *viz.*, at Mogden (West Middlesex, England) involved a capital cost of approximately £1,700,000 which was almost the same as the capital value of the Kolar Gold Fields. The question arose, which was the more valuable, Nitrogen or Gold?