

THE PATH TO MOLECULAR ORBITAL THEORY

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ABSTRACT

The early history of the development of molecular orbital (MO) theory is reviewed. Aided by analogies to atomic spectra and based on evidence from molecular spectra in connection with the old quantum theory, a classification of electronic states of many diatomic molecules was effected early in 1926. This classification was clarified and extended with the advent of quantum mechanics, using the new concept of molecular orbitals (not so named until 1932): Hund, Mulliken. The bonding power of electrons in MOs was discussed, and with the help of the LCAO approximation, MOs were classified as bonding or antibonding. Herzberg proposed that one half the number of bonding less half the number of antibonding electrons is equal to the number of chemical bonds in not too polar diatomic molecules. As an alternative to the use of general or non-localized MOs, Hund showed the usefulness of localized σ and π MOs in describing the structures of single and multiple chemical bonds. The close correspondence of a pair of electrons in a localized MO to G. N. Lewis's earlier concept of an electron-pair bond is pointed out. The 'semi-united-atom' MO concept, e.g. for N_2 and CO, is related to Langmuir's earlier description of the structure of these molecules. The description of the structures of polyatomic molecules using non-localized MOs, the criterion of maximum overlap in MO theory, the electronegativity scale, and the prediction of MO ionization potentials are discussed briefly.

In a discussion of 'Fifty Years of Valence Theory', I feel it is necessary to go back a few years further to the chemical theory of valence¹ developed by G. N. Lewis in 1916. The essential features of this theory still to a considerable extent form a useful framework for understanding the role of electrons in chemical bonding. Lewis's theory spanned the previously unbridged gap between ionic valence and the kind of valence that is typical of carbon compounds. This he accomplished by using the idea of pairs of electrons shared either equally or unequally between two atoms, permitting each atom either by transfer or by sharing to be surrounded by a completed electron shell, usually of two or eight. *Figure 1* summarizes the relations of Lewis's theory to earlier valence theories and to Bohr's theory of atomic structure, and points to its relations to the subsequent quantum-mechanical theories of molecular electronic structure.

Lewis's theory showed electrons distributed in pairs shared by two atoms, and in unshared 'lone pairs'. As I have discussed elsewhere², molecular orbital (MO) theory provides close counterparts to Lewis's shared pairs and

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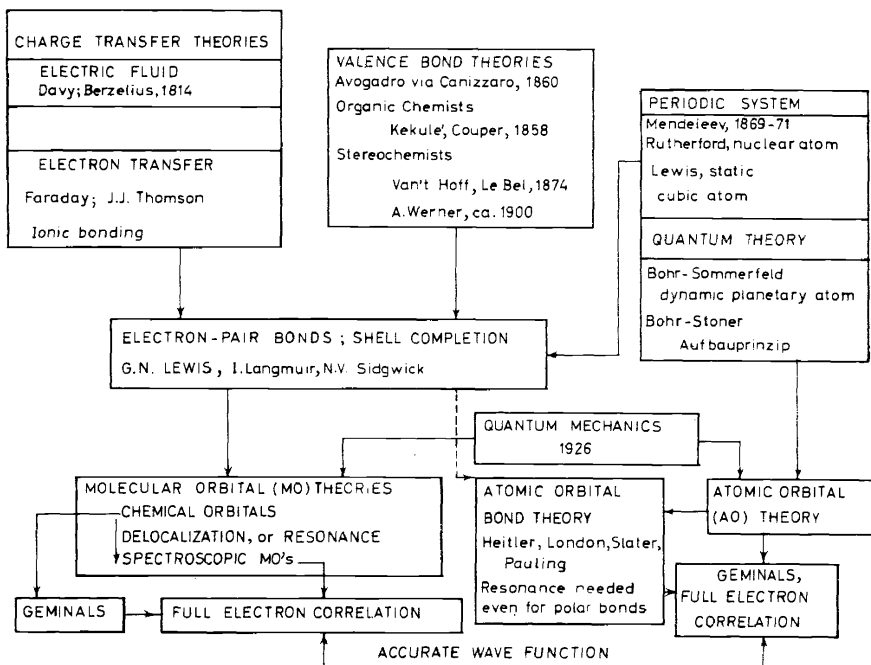


Figure 1. Historical flow diagram of ideas leading to MO and AO theories of molecular electronic structure, and on to accurate wave functions.

lone pairs if we use *localized* MOs or *chemical orbitals*, as I have called them. To be sure, MO theory is more general, in that pairs are not required. The fact that electrons occur in pairs in all but a few stable chemical compounds is explained in MO theory by the fact that the Pauli principle, taken in connection with the existence of electron spin, permits and encourages two electrons to occupy any MO. Molecules (usually radicals) with an odd number of electrons thus tend to react chemically in such a way that new molecules are formed in which the numbers of electrons are even, and each MO is occupied by two electrons. This process usually results in molecules with all electrons in MO closed shells; exceptional cases such as O₂ are satisfactorily explained by MO theory using degenerate MOs. It was at first thought that valence bond (VB) theory, in which electron pairs are formed by the exchange interaction of odd electrons of two atoms or radicals which come together, is the proper counterpart of Lewis's pair theory. However, VB theory lacks the flexibility that MO theory has, and which Lewis's theory also possesses, in accounting for pairs of electrons in polar molecules.

In the Lewis theory, electrons in shared pairs are bonding electrons, those in lone pairs are non-bonding. In Lewis's description of coordination compounds, pairs which are initially lone pairs become shared pairs. In such compounds, as also in all polar bonds, there is unequal sharing between two atoms; the same thing is true of electrons in two-centre localized MOs.

THE PATH TO MOLECULAR ORBITAL THEORY

Langmuir in 1919 in extending Lewis's theory introduced the term isostere to designate molecules which have the same number of electrons and are believed to have essentially the same electronic structure as judged by their properties³. As examples Langmuir gave, among others, N₂, CO, CN⁻; CO₂, N₂O, N₃⁻, NCO⁻. In particular, N₂ and CO have very similar physical properties in spite of their very different atomic composition and their very different structure in terms of early ideas of valence bonding. In retrospect, we may find here a strong hint of the need for a new type of molecular description such as MO theory now gives. For in terms of MOs, isosteric molecules do indeed have closely related structures, in a way which is not readily seen from VB theory.

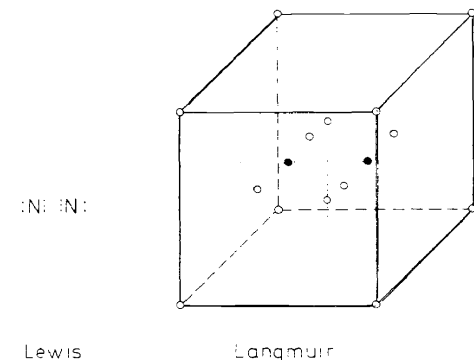


Figure 2. Models of the N₂ molecule (CO similar).

Langmuir described the structure of N₂ and CO as consisting of two *K* shells surrounded by an atom-like valence octet, plus what he called an 'imprisoned pair'⁴. Langmuir's picture of the structure of N₂ differs considerably from Lewis's (see Figure 2). In NO, there is an additional imprisoned electron⁴. Langmuir's picture of N₂ can nowadays be translated into orbital language by writing the electron configuration shown by item (1) in Figure 3, corresponding to a 'semi-united atom', with 3*dσ*² as the imprisoned pair. I shall discuss this identification later. In NO, an imprisoned 3*dπ* electron is added.

Let us now turn to Bohr's quantum theory of atomic structure and spectra in terms of electron orbits—as further developed by Sommerfeld,

(1) Semi-united atom :	$(1s)^2(1s)^2(2s)^2(2p\sigma)^2(2p\pi)^4(3d\sigma)^2$
(2) United-atom :	$(1s\sigma)^2(2p\sigma)^2(2s\sigma)^2(3p\sigma)^2(2p\pi)^4(3s\sigma \text{ or } 3d\sigma)^2$
(3) Lennard-Jones*	$(1s)^2(1s)^2(2s)^2(2s)^2(2p\pi)^4(2p\sigma)^2$
(4) Rough LCAO†	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$
(5) Semi-empirical :	$(kz\sigma)^2(ky\sigma)^2(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2$
(6) Formal MO :	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$

* Lennard-Jones's 2*ππ* and 2*pσ* mean the same as *π_u2p* and *σ_g2p*.

† Mutual hybridization modifies *σ_g2s* and *σ_g2p*; likewise *σ_u2s* and *σ_u2p*.

Figure 3. Electron configuration of N₂.

Main Smith, Stoner, Pauli, Landé, and others. Although this theory met with great success in explaining atoms and the periodic system of the elements, it did not help in understanding valence except in ionic molecules. Here Kossel made important contributions. Bohr's early papers⁵ included some pictures of pairs of electrons circulating in orbits to form chemical bonds, for example in H_2 and in CH_4 , but these pictures led to no progress in understanding non-polar valence.

Nevertheless, certain features of the spectra of diatomic molecules (for example, Rydberg series of He_2 molecule bands, and electronic doublets resembling those in the spectra of alkali metal atoms) pointed to the existence in molecules of electronic states and perhaps orbits more or less similar to those of atoms⁶. There was some discussion about the possibility of the interaction of electronic and nuclear-rotational angular momentum, and Kramers and Pauli⁷ in 1923 proposed the formula

$$E_{rot.} = B\{(m^2 - \sigma^2)^{\frac{1}{2}} - \varepsilon\}^2 \quad (1)$$

for the nuclear rotational energy. Here $mh/2\pi$ is the total angular momentum, and $\sigma h/2\pi$ and $\varepsilon h/2\pi$ are components of electron angular momentum along and perpendicular to the line joining the nuclei. Kratzer⁸ interpreted empirical features of certain band spectra in terms of an electronic quantum number $\varepsilon = \frac{1}{2}$. Also, he ascribed the paramagnetism of O_2 and some features of its band spectrum to an electronic angular momentum $\sigma h/2\pi$ around the line joining the nuclei. While these particular conclusions were incorrect, they pointed the way toward later valid developments. R. Mecke⁹ also made efforts to carry over the systematics of atomic spectra to diatomic molecular spectra.

It should be kept in mind that the foregoing developments occurred in the period 1923–25 before there was a clear understanding of the nature of the various components of electronic angular momentum even in *atoms*. In particular, it was not until late 1925 and early 1926 that Goudsmit and Uhlenbeck¹⁰ proposed that each electron has a quantized spin of $\frac{1}{2}h/2\pi$.

In 1925 I called attention to what I called 'a class of one-valence-electron emitters of band spectra', one series of which includes BeF , BO , CN , CO^+ , . . . while another includes MgF , AlO , SiN , . . .¹¹. These molecules each showed three low-energy electronic levels, and I suggested that those of the first series are analogous to the levels of a sodium atom; the middle one of the levels shows a doublet structure reminiscent of 2P of the Na atom, while the other two levels resemble 2S levels (see *Figure 4*). The analogy could be understood in terms of Langmuir's description of N_2 and CO if the 'im-

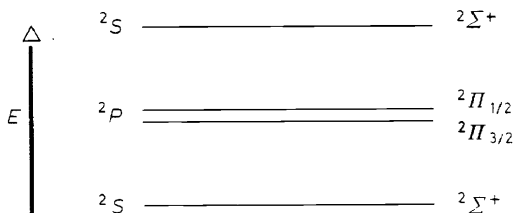


Figure 4. Electronic levels of BO . (Old notation at left; current notation at right).

prisoned pair' in these molecules is identified as analogous to the valence electrons of Mg; when there is one less electron, as in BO, CN, etc., a structure like that of Na is left. Adding one electron makes a structure like Al, with a 2P normal state; actually, NO was soon found to have a 2P -like normal state. Mecke also discussed some of these analogies and other relations of molecular to atomic electron levels¹².

R. T. Birge then proposed that 'the energy levels associated with the valence electrons of molecules agree in all essential aspects with those associated with the valence electrons of atoms', and proposed that the molecular levels should be given the same letter designations *s*, *p*, *d*, etc. as in atomic spectra.

In a systematic survey and analysis of available data on diatomic spectra beginning in 1926, I found that the electronic states involved could be classified as what are now called¹³ $^1\Sigma$, $^1\Pi$, $^1\Delta$, $^2\Sigma$, $^2\Pi$ (with sublevels $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$), $^3\Pi$ (ref. 13). At that time they were called 1S , 1P , 1D , 2S , 2P , 3P in accordance with Birge's proposal, although it was clear that the symbol *S*, *P* or *D* here referred not to an atomic quantum number *L* but to a quantum number belonging to an electronic angular momentum component directed along the internuclear axis, corresponding to σ of the Kramers-Pauli equation.

Meanwhile quantum mechanics was discovered, and Hund in 1926-27 applied it to a detailed understanding of atoms and their spectra and of major aspects of diatomic spectra (in particular, the delineation of his well-known cases *a*, *b*, *c*, *d*)¹⁴. He also discussed the general relations of separate-atom to diatomic electron states, with applications to BO, CN, N₂, etc. Somewhat later, Wigner and Witmer published their well-known group-theoretically derived rules for specifying the types of diatomic states derivable from two atomic states of given types¹⁵.

In the course of the developments outlined above, there was much semi-empirical groping, especially before quantum mechanics became available, but even after that it took a few years before things settled down to a point where all major important features were fairly well clarified.

Molecular orbitals, for diatomic molecules, first emerged clearly in 1928 in a paper by myself¹⁶ and independently in one by Hund¹⁷. In my paper, I said that 'the essential ideas and methods were those already successfully used by Hund' in earlier papers¹⁴, 'the chief difference being in the attempt to assign individual quantum numbers to the electrons' (that is, to specify electron configurations, analogous to those for atoms). The quantum number symbols used in these papers were chosen to correspond to electrons of the so-called united-atom as modified by separating the united-atom nucleus into two.

My paper originated in an attempt to explain an important defect in the analogy of the three observed states of BO, CO⁺ and CN to Na, namely this: that the $^2\Pi$ states are *inverted* (see *Figure 4*), whereas the supposedly analogous 2P state of sodium is *normal*. Careful consideration led to (2) in *Figure 3* as the most probable electron configuration† for the normal states of N₂ and CO. Although because of the 'non-crossing rule' the assignment for the last MO as $3s\sigma$ was favoured, the possibility that it is $3d\sigma$ (as suggested by the

† In the original paper, the configuration was written $(1s)^2(2s^p)^2(2s^s)^2(3s^p)^2(3s^s)^2$.

MO diagram of H_2^+) was also considered. The electrons in $2p\sigma$, $3p\sigma$ and $3s\sigma$ were called *promoted* electrons, because they correspond to $1s$, $2s$ and $2p\sigma$ electrons of the separated atoms. The electron configurations for BO, CN and CO^+ were now explained as corresponding to line (2) of *Figure 3* less one electron from $2s\sigma$, from $2p\pi$, or from $3p\sigma$ for the normal, the first excited, and the second excited states respectively. The *key point* was that for the second excited, $^2\Pi$, state, the grouping $(2p\pi)^3$ explains the observed inverted character of that state.

Proceeding further, electron configurations for NO^+ , NO, O_2^+ , O_2 and F_2 were obtained by adding from one to four electrons in a $3p\pi$ MO. (Later it was seen that this should be $3d\pi$, not $3p\pi$.) Electron configurations for various excited states of these molecules were also assigned. The paramagnetism of O_2 was explained by the fact that *two* electrons in a π MO yield a $^3\Sigma$, a $^1\Delta$ and a $^1\Sigma$ state, of which the $^3\Sigma$ should be the lowest 'if the order of levels is as in atoms'.

The current notation σ , π , δ , \dots , $^1\Sigma$, $^2\Pi$, \dots was first introduced by Hund in his 1928 paper. The notations Σ^+ and Σ^- , σ_g and σ_u , Σ_g and Σ_u , and so on, were introduced somewhat later¹⁸, although the distinctions involved had already been recognized by Wigner and Witmer¹⁵ and by Hund.

My paper introduced the concept of the *bonding power* of electrons in MOs. *Classically*, only bonding and non-bonding electrons were distinguished. Quoting (with a few insubstantial omissions or minor changes) 'while the present work does not indicate any such sharp division, it is nevertheless possible to assign, roughly, various degrees of *bonding power* for various orbit types. For this purpose, electrons whose presence in a molecule tends to make the dissociation energy D large, or the internuclear distance r_0 small, as judged by the fact that their *removal* causes a decrease in D or an increase in r_0 , may be said to have positive bonding power, or to be bonding electrons; and conversely'. Also, 'unpromoted electrons whose "orbits" are of the order of size of r_0 show strong bonding power. Electrons in large non-penetrating orbits should be as good as ionized, and should show zero bonding power. Promoted electrons should show small or negative bonding power unless orbit size or other conditions are very favourable'. The term 'antibonding electrons' for those with negative bonding power was introduced somewhat later.

In the papers just discussed, the MO concept appeared in its general form. The usefulness of the LCAO approximation in estimating the energies and bonding power of MOs was not yet recognized. In his discussion of the resonance between HH^+ and H^+H wavefunctions in the structure of H_2^+ , Pauling¹⁹ obtained approximate wavefunctions which may be considered as the prototypes of MOs approximated in LCAO form as simple linear combinations of AOs (atomic orbitals) of the two separate atoms involved (see $\sigma_g 1s$ and $\sigma_u 1s$ in *Figure 5*). Here $\sigma_g 1s$ and $\sigma_u 1s$ are respectively unpromoted ($\sigma_g 1s \rightarrow 1s$) and bonding, and promoted ($\sigma_u 1s \rightarrow 2p\sigma$) and antibonding. Bloch²⁰ used the LCAO method for metallic MOs.

Lennard-Jones²¹ introduced the systematic use of LCAO-approximated MOs for valence electrons, but employed these only for bonding electrons; for example he described the structure of N_2 as in line (3) of *Figure 3*, where in current notation $2p\pi$ and $2p\sigma$ are written as $\pi_u 2p$ and $\sigma_g 2p$. These symbols

THE PATH TO MOLECULAR ORBITAL THEORY

refer to LCAO forms built from separate-atom AOs as shown in *Figure 5*. It is to be understood in *Figure 5* that the AOs in any LCAO expression are to be defined in such a way that *the parts which overlap* are both positive. In particular, $2p\sigma_a$ and $2p\sigma_b$ are to be defined so that that lobe of each which faces and overlaps the other is positive.

$$\text{Rough LCAO: } (\sigma_g 1s)^2 (\sigma_u 1s)^2 (\sigma_g 2s)^2 (\sigma_u 2p)^2 (\pi_u 2p)^4 (\sigma_g 2p)^p (\pi_g 2p)^q (\sigma_u 2p)^r$$

n: $\sigma_g 1s = 1s_a + 1s_b$ BB: $\sigma_g 2s = 2s_a + 2s_b$ B: $\pi_u 2p = 2p\pi_a + 2p\pi_b$ b: $\sigma_g 2p = 2p\sigma_a + 2p\sigma_b$	n: $\sigma_u 1s = 1s_a - 1s_b$ a: $\sigma_u 2s = 2s_a - 2s_b$ A: $\pi_g 2p = 2p\pi_a - 2p\pi_b$ AA: $\sigma_u 2p = 2p\sigma_a - 2p\sigma_b$
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n = nonbonding; b, B, BB = bonding; a, A, AA = antibonding. In C_2 , $p = q = 0$; in N_2 , O_2 , F_2 , $p = 2$; in O_2 , F_2 , $q = 2, 4$.

Figure 5. Electron configurations and bonding (homopolar molecules).

In line (4) of *Figure 3*, LCAO-MO symbols have replaced the corresponding UA (united-atom) MO symbols in line (2) of *Figure 3*[†]. Each type of symbol embodies a rough description of the forms of the MOs. The UA symbols are more nearly appropriate at small, the LCAO symbols at larger, internuclear distances. *Figure 5* brings out the important fact that MOs approximated by *additive* or by *subtractive* LCAO expressions are respectively *bonding* or *antibonding*.

Lennard-Jones avoided assigning electrons to antibonding MOs, for example by using atomic shells $(2s_a)^2(2s_b)^2$ in line (3) of *Figure 3* instead of $(\sigma_g 2s)^2(\sigma_u 2s)^2$. Where interactions between atomic closed shells are weak, as in the case of the two 1s shells in N_2 , or in general for these and for completed octet shells like the *L* shells in Na_2 , Lennard-Jones's practice has much to recommend it[‡]. However, as applied to molecules like O_2 with incomplete MO shells, it created difficulties. Further, for strongly interacting atomic shells like the 2s shells of the N atoms in N_2 , it is clearly better to replace them by corresponding MO shells containing antibonding $\sigma_u 2s$ and bonding $\sigma_g 2s$ MOs. Then, as proposed by Herzberg^{2,2}, 'It seems sensible to define the number of bonds in a molecule such as O_2 or F_2 as half the difference in the number of electrons which tighten the bonding and the number which are working in the opposite direction'. In other words, half the difference in the numbers of bonding and antibonding electrons.

The electron configurations of C_2 , N_2^+ , N_2 , O_2^+ , O_2 and F_2 are all of the form given in *Figure 5*. [Instead of $(\sigma_g 1s)^2(\sigma_u 1s)^2$, the atomic-closed-shell expression $(1s_a)^2(1s_b)^2$ can be substituted.] The σ_g and π_u MOs, of additive LCAO-approximate form, are bonding, the σ_u and π_g MOs, of subtractive form, are antibonding. (The *K* shell MOs of course are essentially non-bonding.) Herzberg's rule then gives for the number of bonds 2, $2\frac{1}{2}$, 3, $2\frac{1}{2}$, 2 and 1 in the respective molecules.

[†] As later became clear, $\sigma_g 2s$ and $\sigma_g 2p$ are strongly modified by mutual interaction (hybridization). likewise $\sigma_u 2s$ is modified by interaction with the unoccupied $\sigma_u 2p$.

[‡] However, for systematic all-electron self-consistent-field MO calculations as now carried out, it is necessary to use MOs for *all* the electrons.

Herzberg's rule glosses over the fact that, especially because of hybridization (see footnote†, page 209), different bonding or antibonding MOs differ considerably in their bonding or antibonding power, as indicated in *Figure 5*, for example $\sigma_g 2s$ is very strongly bonding but $\sigma_g 2p$ only weakly bonding, while $\sigma_u 2p$ is only weakly antibonding. In general, especially when we come to the MOs in heteropolar and in polyatomic molecules, the general concept of bonding power perhaps has advantages over a sharp division into bonding and antibonding MOs.

$$\text{General: } (1s_a)^2(1s_b)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)^p(\pi^* 2p)^q(\sigma^* 2p)^0$$

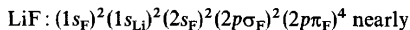


Figure 6. Heteropolar molecules.

Herzberg's rule can be applied not only to homopolar molecules but also to moderately heteropolar molecules, e.g. NO and CO with configurations as shown in the first line of *Figure 6*, where $p = 2$, $q = 0$ for CO and $p = 2$, $q = 1$ for NO, giving three bonds in CO and two and a half in NO. However, if we go to successively more polar molecules—consider for example the series C_2 , BN, BeO, LiF—covalent bonding in the MOs becomes very weak, and in LiF (where, also, $\sigma^* 2s$ is replaced by $\sigma 2p$, see *Figure 6*) the bonding is largely ionic. In any event, however, additive and subtractive LCAO forms $a\chi_a + b\chi_b$ and $a'\chi_a - b'\chi_b$ respectively (with $a > b$ and $a' > b'$ if a is the more electronegative of the two atoms) remain qualitatively well correlated with positive or negative bonding powers of MOs.

A comprehensive view of the forms and binding energies of MOs as a varying function of the particular nuclei involved and of the internuclear distance is obtained by use of so-called correlation diagrams. These were first introduced in simple form by Hund to show correlations between the limiting cases of united atom and two separated atoms. *Figures 7* and *8* reproduce some more elaborate correlation diagrams taken from a review paper²³. These figures show, besides the united-atom and LCAO notations, a semi-empirical notation [see line (5) in *Figure 3*] which has the advantage that it can be used equally for homopolar and heteropolar molecules (e.g. N_2 and CO, or C_2 and BeO), and can also be extended to corresponding valence-shell MOs of molecules whose atoms belong in higher rows of the periodic system. Line (6) in *Figure 3* shows still another notation introduced more recently, one that is now used in connection with systematic theoretical computations. Here the MOs of each different group-theoretical species (e.g. σ_g , σ_u , π_u) are numbered in order of decreasing binding energy.

I have now presented a variety of viewpoints and symbolisms for describing the structures of N_2 and other diatomic molecules. Let us now return to the 'semi-united atom' viewpoint on N_2 as expressed in line (1) of *Figure 3*. First of all, in (2) or (4) of *Figure 3* the first two MO shells can very nearly exactly be replaced by $(1s_a)^2(1s_b)^2$; in (2) of *Figure 3*, $2p\sigma$ is only incipiently promoted. Next, because $2p\sigma$ in (2) of *Figure 3* is essentially unpromoted, $3p\sigma$ in (2)

THE PATH TO MOLECULAR ORBITAL THEORY

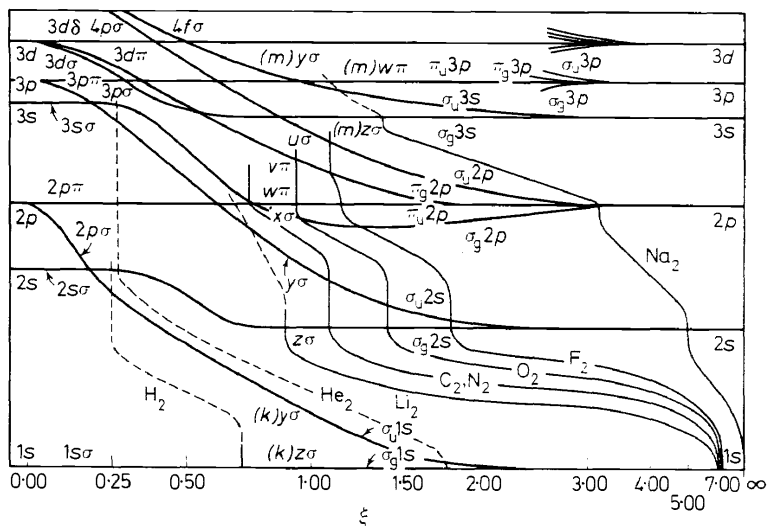


Figure 7. Binding scheme of electron orbits for molecules whose nuclei are of the same element. Neither the abscissas ξ (distance between nuclei divided by mean diameter of electron orbit) nor the ordinates (negative energy of ionization of the electron) are plotted on a uniform scale, as will be seen from the figure. Also, from the nature of the figure, it is not possible for either ordinates or abscissas, especially the former, to have a quantitative significance. The ordinates on the right are, however, proportional to the logarithms of the binding energies of electrons in the N atom, except for the 2s level which has been arbitrarily shifted downward. Those on the left, except 2s, are proportional to a function of the logarithms of the binding energies of electrons in the Si atom, which is the united-atom corresponding to N_2 . Thus the diagram is especially suited to the N_2 molecule, but is also satisfactory in a somewhat more qualitative way for other molecules. The thin lines going upward and to the left indicate roughly for various molecules the actual ξ values of various orbits, for stable molecular states. From these lines, the qualitative order of binding of orbit-types in each molecule can be seen, and at least a rough idea can often be obtained of the relative energy-differences between different orbit-types.

or $\sigma_u 2s$ in (4) of Figure 3 has a form which when laid out in a graph is seen to resemble closely a $2p\sigma$ rather than a $3p\sigma$ AO. Similarly the form of $2s\sigma$ of line (2) of Figure 3 or $\sigma_g 2s$ of (4) of Figure 3 after allowance for hybridization (see footnote†, page 209) is found when laid out to resemble a 2s (or equally an enlarged 1s) AO. Further, $2p\pi$ of (2) or $\pi_u 2p$ of (4) of Figure 3 actually rather strongly resembles in form a $2p\pi$ AO. The last MO, $\sigma_g 2p$ of line (4), the MO occupied by Langmuir's 'imprisoned pair', after allowance for hybridization, is found strongly to resemble a shrunken $3d\sigma$ AO†. All these resemblances have been determined by Huzinaga²⁴ in a comparison between the actual forms of the MOs, as determined from computer calculations, and the AOs of an atom. Further, the MO $\pi_g 2p$ in O_2^+ or O_2 in Figure 5—correspondingly $\pi^* 2p$ in NO—shows an obvious strong resemblance to a shrunken $3d\pi$ AO.

The discussion so far has dealt with diatomic orbitals. As we have seen,

† 'Shrunken' means that it is much smaller in size than, though of similar shape to, a $3d\sigma$ AO of an N atom. This difference, here in the semi-united atom, is explained by the fact that the MO is strongly penetrating, unlike the 3d AOs of a free atom.

diatomic MOs in general extend around both nuclei. In heteropolar molecules, however, even when we do not voluntarily prescribe replacement of inner-shell MOs by AOs, some of the MOs *automatically* become nearly the same as AOs of one atom. For example, in LiF, the special description given in *Figure 6* is rather nearly correct, although the outer-shell MOs do all extend to an appreciable degree around the Li atom. In polyatomic molecules, automatic localization occurs to a varying extent, from slight to complete, in some of the MOs. Also, while fully *non-localized* or 'best' MOs which spread at least to some slight extent over all atoms, give the most accurate electronic

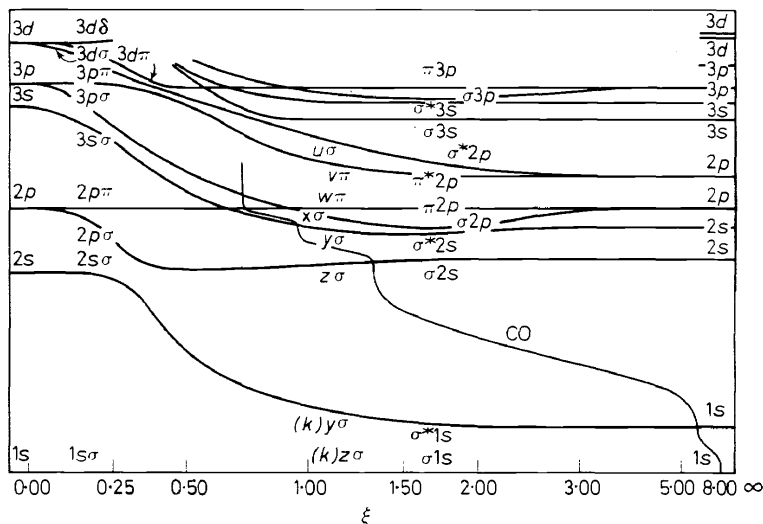


Figure 8. Binding scheme of electron orbits for molecules with nuclei of moderately unequal charge. The figure is in most respects like *Figure 7*. The ordinates on the right are proportional to the logarithms of the binding energies of electrons in the O atom (lower 1s, 2s, 2p, etc.) and in the C atom (upper 1s, 2s, 2p, etc.), those on the left correspond to the united-atom Si in the same way as in *Figure 7*. The figure is qualitatively fairly correct also for other molecules composed of atoms which do not differ too much in the numbers and nature of their outer electrons.

structure description, we can arbitrarily impose various kinds of transformations and constraints to obtain useful approximate localized MO descriptions which correlate instructively with the older valence theory. However, in conjugated and aromatic so-called π -electron molecules, as Hückel showed²⁵, the use of non-localized MOs in LCAO approximation is desirable even for approximate calculations.

Nevertheless in molecules whose bonds can be well expressed by simple classical dot or dash formulas, electrons in localized bonding MOs form a useful counterpart. This type of representation was developed by Hund²⁶. Each MO is approximated as an LCAO expression $\lambda\psi_a + \mu\psi_b$ which is applicable to polar ($\lambda \neq \mu$) as well as to homopolar bonds ($\lambda = \mu$); the ψ s here are AOs of the two atoms. I believe that the placing of two electrons in such a localized MO represents the best simple quantum-mechanical counterpart for a Lewis electron pair bond²⁷.

Hund classified these localized bond MOs under two types, σ and π . Single bonds are always σ bonds (structure σ^2), in which the AOs involved may be s , $p\sigma$ or q , where q is some s , $p\sigma$ hybrid. They are approximately cylindrically symmetrical, which accounts for 'free rotation'; in linear molecules, they are *exactly* cylindro-symmetric. Triple bonds are cylindro-symmetric, of structure $\sigma^2\pi^4$. Double bonds are of structure $\sigma^2\pi^2$ and involve a plane of symmetry which prevents free rotation. Empirically, they are never³² of structure $\sigma^2\sigma^2\ddagger$.

The symbol π referred originally to a twofold degenerate MO in a linear (at first a diatomic) molecule; it embraces two independent MOs which may be taken in the linear case as π^+ and π^- or as π_x and π_y . In Hund's description of unsaturated and aromatic molecules, it refers to just one, say π_x , of these two orbitals. This use of the same symbol for a degenerate and for a non-degenerate MO is unfortunate. A new symbol, say τ , really should be introduced for the non-degenerate type of π .

In his papers on chemical bonding, Hund showed how the observed shapes of various molecules, for example H_2O and NH_3 , that were first explained by Slater and Pauling using valence-bond-theory, can be explained just as well in terms of MOs.

So much for the early history of MO theory. From here on I shall not attempt to discuss the further evaluation and application of the theory, but will only mention briefly a few of the earlier developments.

In a series of papers entitled 'Electronic structures of polyatomic molecules and valence'²⁸, I assigned electron configurations using non-localized MOs expressed in LCAO approximation to a considerable variety of types of molecules (especially, CH_2 , C_2H_4 , CH_4 , NH_3 , H_2O , C_2H_6 , C_2H_2 , H_2CO , CO_2 , $HgCl_2$, and derivatives and analogues of these). I proposed the name *orbital* as an abbreviation for *one-electron orbital wavefunction* in the second of these papers. Following a suggestion by Van Vleck, I used group-theoretical methods in classifying the MOs; I adopted a system of MO species symbols similar to one used by Placzek for classifying molecular vibrations. I used various other less formal symbols to indicate the approximate forms of the MOs and their relations to AOs or to MOs of constituent groups or radicals. I also gave interpretations of electronic spectra in terms of MO excitations.

I called attention to the applicability in LCAO MO theory of the criterion of maximum overlap of AOs, first used by Slater and Pauling in valence-bond theory, as a measure of the bonding power of a MO. (Later, I pursued this idea further in papers²⁹ on 'Overlap integrals and chemical binding'.)

In these and related papers³⁰, I set up and applied a new electronegativity scale. In setting up this scale, I made use of a criterion first stated by Hund[‡], also of the idea of 'valence states', first proposed by Van Vleck³¹. I applied LCAO MO theory to show the relation of this scale to Pauling's electro-

† An interesting case is that of C_2 (Figure 5 with $p = q = 0$) where the bonding is essentially π^4 (the net effect of $\sigma_g 2s^2 \sigma_u 2s^2$ is approximately non-bonding).

‡ On page 17 of ref. 25 Hund pointed out that for strongest interaction of the AOs in a localized LCAO-MO, the terms of the electrons in the two atoms should not be very different, 'and this means not that the ionization energies should be approximately equal, but that the average between atomic term and ionic term' [that is, of ionization energy and electron affinity] should be about the same for the two atoms.

negativity scale, and to give a theoretical derivation of Pauling's scale. I also set forth relations of the polarity coefficients in LCAO-MOs to charges on the atoms participating in a bond, and to dipole moments. (Later³² I developed these ideas further in a 'population analysis' which used overlap populations as measures of bonding power, and used atomic populations to yield charges on atoms.)

I made estimates of polarity coefficients as a basis for conclusions as to bonding. For example, in molecules CX_4 , the MO structure may be written as $1s_C^2[2s]^2[2p]^6 \dots$, where the dots refer to MOs largely restricted to the X atoms, and the symbols $[2s]$ and $[2p]$ refer to $2s$ -like and $2p$ -like non-localized bonding MOs. At one extreme, probably approached in Cl_4 , the $[s]$ MOs have very strong C^-X^+ polarity and so are almost unshared $2s$ carbon AOs, while the $[p]$ MOs are nearly homopolar and strongly bonding so that the four $C-X$ bonds of classical valence theory are provided almost entirely by three pairs of $[p]$ electrons. At the other extreme, as in CF_4 (better, SiF_4), the $[s]$ orbitals are nearly homopolar and give strong covalent bonding while the $[p]$ orbitals have strong R^+X^- polarity so that their bonding is to a large extent heteropolar.

I made approximate predictions of ionization potentials (I) on the basis of the specification $I > (I_a^0 + I_b^0)/2$ for two-centre bonding MOs, $I < (I_a^0 + I_b^0)/2$ for antibonding MOs, and $I \approx I^*$ for non-bonding MOs (lone-pair or nearly lone-pair orbitals, localized more or less on one atom or on a set of equivalent atoms); here I^0 and I^* refer to approximate valence-state AOs. The rules just given must be modified to allow for charge transfer. For example, in volts, for the lone-pair MOs in HI, HBr and HCl, the I^* values are 10.38, 12.28 and 13.62, the corresponding I values are 9.28, 10.55 and 11.48. In all HX, $I < I^*$ corresponding to charge transfer in the sense H^+X^- , increasing in the series from HI to HCl³³. Similar comparisons hold for CH_3X and C_2H_5X .

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THE PATH TO MOLECULAR ORBITAL THEORY

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