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The development of the concept of the chemical bond from hydrogen to cluster compounds

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ABSTRACT. The principal types of chemical bond have been analysed, and their ranges of applicability noted. Fields in which the concept of a localised bond is inapplicable have been indicated, and, in particular, the electronic structure of Δ-polyhedral clusters has been examined. The principle of isolobal analogy has been discussed, and its unique importance for an understanding of the structure of organometallic compounds has been demonstrated.

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I. Introduction

The present-day theory of chemical structure is based on the apparatus of quantum chemistry and the generalisation of experimental data. The methods of quantum chemistry make it possible to obtain fairly reliable information on electronic structure and to predict the physicochemical properties of both existing specific molecules and hypothetical molecules. These characteristics are usually obtained by numerical experiments using computers, and are used either to interpret experimental data or to predict the properties of chemical compounds.[1] The solution of problems of this type has applications, however. It is of no less interest to develop the general principles of the classification of chemical compounds, to describe their structure, and to establish the relationships between structure and properties.[1,2]

Structural theories in chemistry are based on the concept of the chemical bond. This concept, which appeared long before the nature of chemical bonding became clear, arose as a result of the necessity, unavoidable in chemistry, to imagine the breakdown into parts of the integral objects of chemical studies, that is molecules. It was this breakdown of molecules into a set of known parts that made possible a clear description of their structure and the prediction of a number of their physicochemical properties.

The success of the classical theory of chemical structure and its subsequent development proves the appropriateness of the description of molecules by means of chemical bonds and structural formulae. Neither structural formulae nor chemical bonds are real objects. They are theoretical constructions, or ideal formulations.[3,4] The extremely fruitful nature of these abstract imaginary objects indicates, however, that they correctly reflect the most important features of chemical reality. The present review follows the devleopment of the concept of the chemical bond as it is applied to systems of increasing complexity, and indicates the ranges of applicability of this concept.

II. The hydrogen molecule and the chemical bond

The electron in the ground state of the hydrogen atom is in the single valence orbital of this atom, the 1*s*-atomic orbital (AO), which is a function of the spatial coordinates. In a pictorial interpretation, the square of this function defines the density of the electron cloud of the hydrogen atom at a given point in space.

In the hydrogen molecule, the electrons occupy not atomic orbitals but a molecular orbital (MO), encompassing both atoms. In the MO LCAO approximation, the molecular orbitals are constructed from the atomic orbitals. The two 1*s*-atomic orbitals φ_1 and φ_2 give two molecular orbitals: a bonding MO (BMO) $\psi_+ = (\varphi_1 + \varphi_2)/N_+$ which is favourable and whose energy is lower than that of the atomic orbitals, and an antibonding MO (AMO) $\psi_- = (\varphi_1 - \varphi_2)/N_-$ which is unfavourable and whose energy is higher than that of the atomic orbitals[5,6] (Fig. 1).

The density of the electron cloud in the molecule is proportional to the square of the molecular orbital $\psi_\pm^2 = (\varphi_1^2 + \varphi_2^2 \pm 2\varphi_1\varphi_2)/N_\pm^2$. In the expression obtained, the terms φ_1^2 and φ_2^2 correspond to the electron clouds of the atoms, but the most interesting term in it is the so-called interference term $2\varphi_1\varphi_2$. As a consequence of the existence of this term, the density of the electron cloud in the molecule is not equal to the sum of the densities of the atomic orbitals, that is the cloud is deformed.

In the case of the BMO, an excess of electron density arises between the atoms. The negative cloud attracts the positive nuclei. A two-electron two-centre chemical bond is formed.

In the case of the AMO, on the other hand, the interference term decreases the electron density between the atoms. The nuclei are as it were uncovered, their repulsion is not compensated by the attraction of the electrons, and in this state the molecule breaks apart.[7] This is of course a very crude description. Its value can be examined.

Progress in computer technology has provided extremely refined methods of calculation even for fairly complex systems. While they are of undoubted value in quantum chemistry, however, these studies provide comparatively little for its users. Fig. 2 helps to explain why this is so.[8] It gives the potential curves for the hydrogen molecular ion, characterising the change in energy with increase in the distance between the nuclei. Curve *1* was obtained in the approximation just described. The presence of the minimum on this curve reflects the fact that a bond is formed. The depth of this minimum correctly reflects the order of magnitude of the bond energy, and its position the bond length. The method of calculation can be improved. Thus if account is taken of the possible change in the effective charge of the atomic orbital, curve *2* is obtained for the optimum value of the effective charge. If account is also taken of the fact that in the field of a neighbouring nucleus the atomic orbital is polarised, losing its spherical symmetry, the result is curve *3*, part of which is shown in Fig. 2.

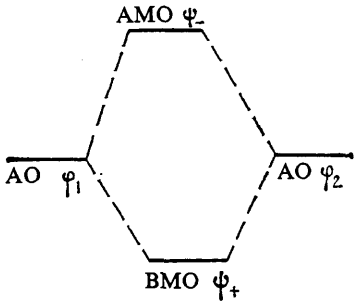


Figure 1. Correlation diagram for the H_2 molecule.

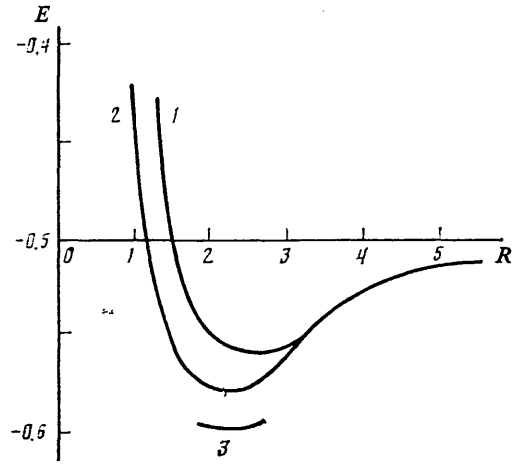


Figure 2. Potential curves for H_2^+ (in atomic units), obtained in different approximations of the MO method: *1*, molecular orbital constructed as a linear combination of the atomic orbitals of the hydrogen atoms; *2*, optimisation of the effective charge of the atomic orbitals carried out; *3*, a polarisation correction to the atomic orbitals introduced.

It is possible to improve the method of calculation even further, to expand the basis set, to abandon the MO LCAO approximation completely, and to proceed to an exact calculation. The results will be increasingly accurate, but this cannot be shown in Fig. 2, since the curves obtained coincide with curve *3*.

This situation is fairly general: the principal qualitative conclusions of greatest importance for chemistry are obtained even in the most approximate calculations. It is not accidental that Nobel Laureate R Hoffman, who has generated the most important theoretical concepts of the last quarter century, bases his work on the simplest quantum-chemical method, namely the extended Hückel method.[9]

Thus the chemical bonding in the two-electron diatomic system formed by the hydrogen molecule has been described by the two-electron two-centre bond. The description of polyatomic many-electron systems can now be considered.

III. The chemical bond and organic chemistry. The principle of isolobal analogy

A molecule is a single system bonded by forces of electrostatic interaction and consisting of relatively immobile nuclei and a cloud of rapidly moving electrons. In chemistry, however, the integral picture of chemical bonding is broken down, and replaced by a set of chemical bonds. It can be shown for the case of the methane molecule how the concept of the two-electron two-centre bond, which is strictly applicable to the hydrogen molecule and others, can be transferred to polyatomic molecules.

The carbon atom, like that of all the elements of the second period, has four valence orbitals. These are used to construct four equivalent tetrahedral hybride orbitals (HO),[10,11] each of which contains an electron. In the methane molecule, each of these HO is directed towards its own hydrogen atom. The hybrid orbital of the carbon atom and the atomic orbital of the corresponding hydrogen atom are used to construct localised molecular orbitals (exactly as in the case of the hydrogen molecule). The two atomic orbitals give two molecular orbitals: one bonding and one antibonding. The bonding orbital is occupied by two electrons. The four equivalent two-electron two-centre C—H bonds of methane are described in this way.[12]

The conceptual breakdown of a whole into parts is of course always arbitrary, so that the description of polyatomic molecules by means of two-centre bonds is also arbitrary, but the whole of chemical practice indicates that the concept of the chemical bond is extremely fruitful. The task is essentially to establish the fields of chemistry in which the concept of the two-centre bond reflects the principal features of chemical reality, and those in which it has to be replaced.

The electronic structure of the hydrides of the elements of period II following carbon can now be discussed, beginning with nitrogen. The nitrogen atom, like the carbon atom, has four valence orbitals; these can be used to obtain four tetrahedral orbitals, into which the valence electrons can be put. The nitrogen atom has five valence

electrons, however. If one of these is removed, then one electron remains in each hybrid orbital, so that it is possible, exactly as in the case of the methane molecule, to construct the four two-electron two-centre N–H bonds of the ammonium cation.

But what if the electron is not removed? One of the hybrid orbitals of nitrogen will then contain two electrons (Fig. 3). The bonding and antibonding molecular orbitals constructed from this orbital and the atomic orbital of hydrogen will then have to accommodate three electrons, and one electron enters the antibonding orbital. This is less favourable than remaining in the atomic orbital, and instead of a bond with the hydrogen atom, a lone pair of electrons appears on the nitrogen atom. Nitrogen forms only three N–H bonds. The oxygen atom has two lone pairs, the fluorine atom has three, and the neon atom has four lone pairs, and does not form any bonds.

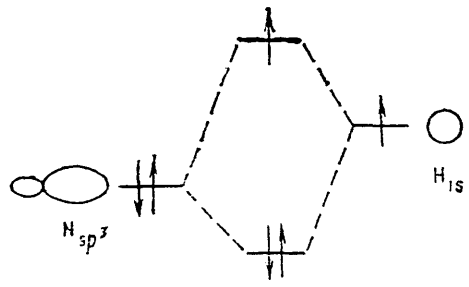


Figure 3. Correlation diagram of a three-electron system.

Thus when spare electrons appear, that is when the number of valence electrons becomes greater than the number of valence orbitals, lone pairs appear.[13] It will be seen that this is not the only way to distribute extra electrons, but it is the simplest and most widespread.

A number of simple groups can now be considered. Firstly, the fluorine atom, which is much more complex than the hydrogen atom. The only similarity between them is that the fluorine atom, like the hydrogen atom, has only one boundary orbital with an unpaired electron—one "working" boundary orbital.† The hydroxyl group also has only one boundary orbital with an unpaired electron, which coincides with one of the valence orbitals of the oxygen atom. Of the remaining three valence orbitals of oxygen, two are occupied by lone pairs and one is involved in the O–H bond. The NH_2 group also has only one orbital with an unpaired electron; of the remaining three valence orbitals of nitrogen, one is occupied by a lone pair, and the other two are involved in the formation of two N–H bonds.

The CH_3 group also has only one symmetrical boundary orbital containing an electron. The other three valence orbitals of the carbon atom are involved in C–H bonds.

† The boundary orbitals are the highest occupied and the lowest unoccupied orbitals.

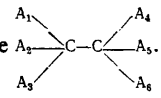
Thus the groups CH_3, NH_2, OH, F, and H have the same number of boundary orbitals containing unpaired electrons. These groups are called isolobal (from "lobe"), and this is represented as follows:

$$CH_3 \overset{0}{\longleftrightarrow} NH_2 \overset{0}{\longleftrightarrow} OH \overset{0}{\longleftrightarrow} F \overset{0}{\longleftrightarrow} H.$$

The well-known principle of isolobal analogy[14–17] can now be used.

According to this principle, isolobal groups can replace one another, so that as soon as methane is known to exist, it means that methyl fluoride may also exist, that the formation of methyl alcohol is probable, that the existence of methylamine is possible, and that ethane should be stable.

The statement that the replacement of a hydrogen atom in methane by a methyl group will give a stable molecule is based only on the fact that three valence orbitals of the carbon atom in the methyl group are involved in bond formation. The fact that they are involved in bonds with hydrogen atoms in particular is not important. Thus the principle of isolobal analogy suggests the existence of

molecules of the type . The formula used the letter A,

to which no definite chemical significance is attached. This can be any group isolobal with hydrogen.

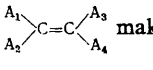
The ethylene molecule, which is made up of two methylene groups CH_2, can now be considered. Two of the sp^2 hybrid orbitals of the C atom of the methylene group are involved in C–H bonds. This leaves two boundary orbitals. The two-electron two-centre bonds of ethylene are constructed from these boundary orbitals: the σ-bond from the sp^2-orbitals and the π-bond from the *p*-orbitals orthogonal to them.[18–20]

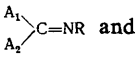
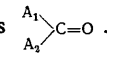
Groups isolobal with the methylene group CH_2 can now be considered.

In the NR group, one of the valence orbitals of the nitrogen atom is involved in the N–R bond, and a second contains a lone pair. This leaves two boundary orbitals, in which the two remaining valence electrons of nitrogen are placed, so that this group is isolobal with the methylene group. The oxygen atom is also isolobal with the methylene group. Thus two of its four valence orbitals are occupied by lone pairs, and the remaining two are boundary orbitals, each containing an unpaired electron. Thus

$$CH_2 \overset{0}{\longleftrightarrow} NR \overset{0}{\longleftrightarrow} O$$

and according to the principle of isolobal analogy the existence of

ethylenes  makes it possible to assume the existence of

imines  and carbonyl compounds .

The acetylene molecule can now be considered. This molecule is made up of two methylidyne groups CH. One *sp*-hybrid orbital of the carbon atom of the CH group is involved in the C–H bond, leaving three orbitals: the symmetrical *sp*-orbital and two antisymmetric *p*-orbitals of the carbon atom perpendicular to it. Each of these boundary orbitals contains one electron. These orbitals are used to construct the three two-electron two-centre bonds of the acetylene molecule: one σ-bond and two π-bonds.[21] A group of any type, size, or structure, so long as it has three boundary orbitals with three electrons, will be isolobal with the CH group. In particular, the nitrogen atom is isolobal with the methylidyne group; one

valence orbital of the nitrogen atom is occupied by a lone pair, and the three remaining orbitals each contain one electron: CH $\leftrightarrow$ N. Thus hydrocyanic acid HCN and in general nitriles RCN exist.

The variety of isolobal groups and the infinite possibilities of their different combinations and superstructures indicates that by making use of the principle of isolobal analogy it is possible to "synthesise" on paper an unlimited number of molecules. And due credit must be given to chemists: very many of these compounds have also been obtained in flasks. Of course, when planning their syntheses, organic chemists did not know that they were using the principle of isolobal analogy.

The demonstration of the principle of isolobal analogy using the simplest examples was intended to emphasise its essential feature, namely the interchangeability of isolobal groups, which in turn is a consequence of the similarity in their ability to form chemical bonds. This ability is determined by the nature of the boundary orbitals.‡ A second, so to speak, technical aspect of the isolobal analogy is the establishment of the isolobal nature of groups. Groups are said to be isolobal if they have the same number of boundary orbitals with similar symmetry properties, similar three-dimensional structures, similar energy values, and the same number of electrons occupying these boundary orbitals.[16,17]

Organic chemistry has done extremely well without the isolobal analogy; more accurately, it has always used it, but only implicitly. the isolobal nature of the characteristic groups of organic chemistry was known to organic chemists, so to speak, historically, and was established empirically with no knowledge of the nature of boundary orbitals, long before the appearance of the concept of orbitals in general. To chemists, the isolobal nature of the above groups is obvious. The fruitfulness of the principle of isolobal analogy is revealed in non-traditional fields at the boundary between organic and inorganic chemistry, and in particular in organometallic chemistry.

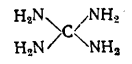
Hoffmann was able not only to express clearly an idea which was in the air but also to select an extremely successful term,[14,15] which spread rapidly. Hoffmann, however, did not simply propose the term and the concept; he used it extensively and demonstrated its value. For most organometallic fragments, which are often very complex, isolobal character is neither obvious nor trivial. Hoffmann had therefore to determine the nature of the boundary orbitals of many organometallic fragments, and this led to the unique library of isolobal groups.[16]

The isolobal analogy makes it possible to understand the structure of complex organometallic compounds and clusters, reveals in so-called monsters usual organic structures in the most remarkable forms, and prompts the choice of completely unexpected directions in the search for new types of compound by analogy with organic chemistry. According to Hoffmann,[16] the isolobal analogy "... brings together different sub-fields of our central science. We are separated, split asunder — organic, inorganic, physical, biological, analytical chemists — by the very largesse of our creation. The variety of molecules we create, and the methods we use to study them, breed jargon and specialisation. Yet underneath the seeming complexity there must be a deep unity ...".

‡ Different boundary orbitals of the same group may be "working" orbitals, depending on the specific chemical situation. This explains the complexity and ambiguity of isolobal relationships, particularly when lone pairs are present together with unpaired electrons in the boundary orbitals.[16]

Chemistry lives and develops by analogies. An analogy, however, is an analogy, and not a law. Hoffmann often pointed this out, and warned that the isolobal analogy suggests possibilities, but does not necessarily guarantee their realisation.[16]

An example is provided by a molecule which is faultless from the viewpoint of the isolobal analogy, but which it has not yet been possible to synthesise:



Thus by using the concept of the two-electron two-centre chemical bond and the isolobal analogy it is possible to construct and describe an unlimited number of saturated and unsaturated molecules. It cannot be said, however, that all organic compounds are described completely by two-centre chemical bonds.

The conceptual breakdown of a molecule into two-centre bonds is fruitful only when it corresponds to chemical reality, that is when it is possible to regard these bonds as more or less independent of one another. In fact, of course, they do influence one another, but these influences should be slight. This condition is usually satisfied for carbon σ-bonds. This is due to the strength of these bonds, and the fact that they are compact and localised in space. π-Bonds are weaker, and more easily polarised. Their three-dimensional structure is such that the interaction of conjugated π-bonds is considerable. In large planar conjugated systems, individual π-bonds are often changed until they are unrecognisable, and in cyclic aromatic systems it is no longer possible to speak of two-centre π-bonds.

The π-electron systems of aromatic molecules are indivisible; they represent a single whole, to which the concept of two-centre bond is inapplicable.

IV. The chemical bonds formed by non-transition elements

The atoms of the elements of period III, like those of period II, each have four valence orbitals, in which their valence electrons are situated. The single but very significant difference between them and the elements of period II is that their valence orbitals are much larger and more diffuse.[22–24] This follows both from the most general physical considerations and from the fact that in the hydrogen atom and one-electron cations the average radius R of an orbital increases with increase in the principal quantum number n according to the law $R \sim n^2/Z$.[22] In many-electron atoms the relationship is naturally more complex, but the general trend is preserved. It is reflected, for example, in Slater's rules, which define the form of the Slater atomic orbitals.[23] The differences in the sizes of the valence orbitals of the atoms of the elements of periods II and III are also reflected in the positions of the radial density maxima[24] and in other characteristics.

As a result of the larger size of the valence orbitals, the simple bonds formed by the atoms of the elements of period III are longer, weaker, and more easily polarised. As a result, the interaction of these bonds with one another, and more particularly with π-bonds and with lone pairs, that is their ability to take part in hyperconjugation, is much greater. These interactions are not too strong, however, and the concept of the two-electron two-centre chemical bond is still applicable to the chemistry of the elements of period III.

Since the features of interest are those relating to the development of the concept of the chemical bond, and not the explanation of the properties of the elements of period III (see for example the review

by Bochvar and co-workers[25]), only two characteristics of these elements will be considered.

The atoms of the elements of period III are larger than those of period II, it is possible to place five or six atoms round them, and they form hypervalent compounds such as sulphur hexafluoride SF_6 and phosphorus pentachloride PCl_5.

The structure of the phosphorus pentachloride molecule[25,26] can be considered.

Three of the chlorine atoms lie in the equatorial plane. Phosphorus is joined to them by ordinary two-electron two-centre bonds lying at an angle of 120° to one another. These bonds are formed by three sp^2-hybrid orbitals of phosphorus. Phosphorus still has one $3p_z$-orbital at right angles to them (Fig. 4), containing its lone pair. Above and below the phosphorus atom there are two axial chlorine atoms. Phosphorus has two electrons with which to form two P—Cl bonds, but does not have two orbitals, one for a bond with the upper chlorine atom and another for a bond with the lower atom, and has only one, which has to interact with the two orbitals of the axial chlorine atoms.

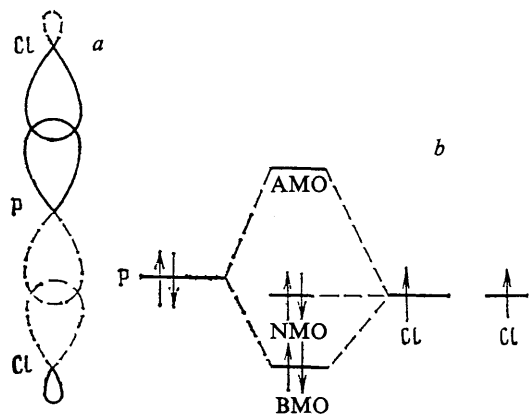


Figure 4. Three-centre bonds in hypervalent compounds: *a*, bonding molecular orbital of the three-centre bond; *b*, energy level diagram.

The three atomic orbitals give three molecular orbitals: one bonding (BMO), one non-bonding (NMO), and one antibonding (AMO). The four electrons are placed in these orbitals. Two enter the three-centre BMO. Three-centre BMO are much more favourable than two-centre BMO,[27] and the two electrons entering the three-centre BMO form the bond between phosphorus and the two axial chlorine atoms. The two remaining electrons enter the NMO; they are not involved in bonding, but do not hinder it.

This situation is characteristic of other hypervalent compounds. In hypervalent compounds a new type of bond appears — the two-electron three-centre chemical bond. The extra electrons not involved in bonding occupy non-bonding molecular orbitals.

The second characteristic of the atoms of the elements of period III is also related to their size. As a result of the greater size of the valence orbitals of the atoms of the elements of period III, these atoms form longer bonds. At these distances, π-overlap is ineffective, and the elements of period III form extremely weak π-bonds.[28–30]

Thus in the nitrogen molecule N_2 the atoms are joined by three strong bonds, one σ-bond and two π-bonds, whereas the P_2 molecule does not exist under ordinary conditions, but is dimerised. It is more favourable for the phosphorus atom to form three strong bonds with three other phosphorus atoms situated at the vertices of a tetrahedron than to form one strong bond and two weak π-bonds in the P_2 molecule.[25]

The silicon atom, like the carbon atom, is tetravalent. One of the electrons of the lone pair, which in the ground state of the Si atom occupies the *s*-orbital, is transferred to the unoccupied *p*-orbital ("is unpaired"), and the energy expended is fully recovered in the formation of two additional strong bonds. The situation is quite different if the additional bonds are π-bonds, whose formation does not compensate the expenditure of energy for the "unpairing" of the lone pair of *s*-electrons.

Thus for carbon,[31] the equilibrium between hydrocyanic acid and its isomer is displaced towards the isomer containing tetravalent carbon HC≡N. The silicon analogue, on the other hand, exists in the form HN=Si with divalent silicon. The silicon π-bonds are so weak that the unpairing of the lone pair of silicon is unfavourable. For the same reason, silicon forms not the analogue of acetylene but its isomer with divalent silicon $H_2C=Si$.

The elements of period III form multiple bonds only when special conditions are fulfilled, for example when there is spatial protection of the multiple bond by bulky substituents.[32,33] The difficulty of synthesising compounds of the elements of period III with multiple bonds is leading to a search for the factors stabilising molecules containing these bonds.[34]

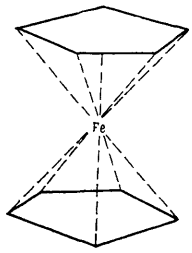
These examples have been considered in order to emphasise that because of the low strength of the π-bonds, the elements of period III do not form large planar conjugated molecules or more particularly aromatic compounds. Thus overall the concept of the two-centre bond plays an even greater role in the chemistry of the elements of period III than in organic chemistry.

V. The chemical bonds formed by transition metals

The situation is radically different for transition metals. Transition metals differ from non-transition elements in that, in addition to *s*- and *p*-valence orbitals, they also have five working *d*-orbitals,[35] that is they have a total of nine valence orbitals. They therefore obey not the octet rule but the effective atomic number (EAN) rule, that is their compounds are stable when the valence level of the transition metal atom contains 18 electrons.§ They can therefore form more bonds, and can have more lone pairs. The octahedral configuration with six bonds is most frequently encountered. The two-centre bonds formed by transition metals with other atoms and in particular with carbon do not differ essentially from the two-electron two-centre bonds formed by non-transition elements.[37] It is not these bonds, but the bonds in transition metal π-complexes, that are specific for transition metals.

§ For a modern substantiation of the Lewis—Sidgwick rule (the EAN rule), see the paper by Mingos and Hawes.[36]

The electronic structure of transition metal π-complexes cannot be described by two-centre bonds. It is possible to take as an example the molecule of ferrocene



In this molecule the iron atom is situated between two parallel cyclopentadienyl rings so that it is next to ten carbon atoms. The iron atom cannot form ten bonds with carbon atoms, however. It has neither the electrons nor the orbitals for this. Since it is not possible to represent the π-complex uniquely using two-centre bonds, and a large number of structures usually have to be considered, the description using resonance theory is too cumbersome, and is used by hardly anyone apart from Pauling himself.[38,39] The opinion has grown that π-complexes have to be described by the molecular orbital method. The MO method, however, considers the molecule as a whole. The results are generally not readily transferable from one molecule to another. Moreover, it is difficult to interpret this description in a manner familiar to chemists.[40]

It is not necessary, however, for transition metal π-complexes, to give up ordinary chemical ideas based on the need for the conceptual breakdown of the whole into parts. It is simply because it is not possible in this case to represent the molecule by two-centre bonds that its conceptual breakdown into larger parts is necessary. In π-complexes the transition metal atom is bonded not to individual atoms of the π-ligand but to its entire π-electron system as a whole.

The bonding molecular orbital of an ordinary bond is constructed from the atomic orbitals of two atoms. It contains two electrons. This describes the two-electron two-centre chemical bond. The bonding molecular orbital of a generalised bond is constructed from an atomic orbital of the transition metal atom and a molecular π-orbital (MO) with appropriate symmetry from the ligand, which in its entirety acts as the second partner in the bond. This bonding molecular orbital contains two electrons. This describes the two-electron multi-centre generalised chemical bond.[40] Fig. 5 shows generalised chemical bonds (GCB) for the case where the ligand is a ring. The lowest-energy π-orbital of the ring is symmetrical with respect to the metal–ring Z axis. It can interact with a metal hybrid orbital (HO) symmetrical with respect to this axis. A headlight-shaped multi-centre generalised σ-bond is formed.[41] The ring π-orbitals of next lowest energy have one nodal surface, containing the Z axis, and are π-orbitals. They can interact with metal π-orbitals. Two-lobed generalised chemical π-bonds are formed. There are two such bonds.[40]

Generalised chemical bonds are localised metal–ligand (given ligand) bonds, independent of the number and nature of other ligands.[40] It has already been emphasised that the concept of bonds is meaningful only if the interaction of the local bonds into which it is possible to mentally break down the molecule is slight and if these local bonds are more or less independent of one another. A familiar example will show clearly that this condition is fulfilled for generalised chemical bonds.[35]

The example to be considered is benzenetricarbonylchromium. Chromium is joined to the ring by three two-electron multi-centre generalised chemical bonds: one headlamp-shaped σ-bond and two two-lobed π-bonds. The six electrons for these bonds are supplied by the ring. Chromium is joined to each of the carbonyl groups by a two-electron two-centre bond. The six electrons for these bonds are provided by the lone pairs of the carbon atoms of the carbonyl groups. The remaining three valence orbitals of the chromium atom are occupied by lone pairs. The six electrons of the generalised chromium–ring bonds, the six electrons of the bonds formed by chromium with the carbonyl groups, and the six valence electrons of chromium make up a total of eighteen electrons in the valence level of chromium, that is the molecule obeys the EAN rule and is stable. When the chromium atom is replaced by the manganese atom, there will again be 18 electrons if the number of electrons

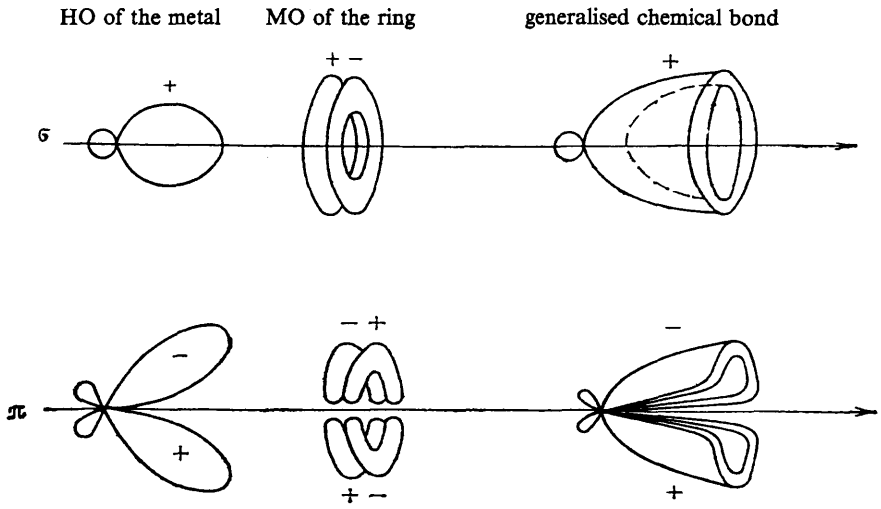
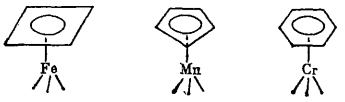


Figure 5. Generalised chemical σ- and π-bonds.

provided by the ring is reduced by one. In $(C_5H_5)Mn(CO)_3$, of the six electrons of the three bonds between the ring and the metal, one is provided by manganese, and five by the cyclopentadienyl ring, replacing the benzene ring. On going to iron, to satisfy the EAN rule, the cyclopentadienyl ring must be replaced by the cyclobutadienyl ring.



In the series of compounds considered, both the metal atom and the ring in the metal–ring bonds change, that is both partners of the generalised chemical bonds change. Nevertheless, the bonds with the carbonyl groups are not sensitive to this, and the arrangement and properties of the carbonyl groups remain almost unchanged in the series being considered.[42–48] Conversely, when the carbonyl groups are replaced by other groups, the changes in the properties of the ring also do not exceed those corresponding to the usual bond influences.[49–51] Thus generalised chemical bonds satisfy the requirement that they should be relatively independent of one another — the principal condition for the fruitful application of the concept of the chemical bond.

Two remarks may be added. Firstly, the similarity between the symmetry of the molecular π-orbital of the ligand and the symmetry of the atomic orbital of the transition metal can be only approximate. Generalised chemical bonds need not be as symmetrical as those between a metal and a ring. For example, the $Fe(CO)_3$ group can combine not only with cyclobutadiene but also with butadiene[52] and even with unsymmetrical heterobutadienes.[53,54] In this case, all that remains of the similarity in the symmetries of the orbitals of the metal and the ligand is the similarity in the distribution of the sign. The ligand π-orbital whose sign remains unchanged in the region between the ligand and the metal interacts with a hybrid σ-orbital of the metal; the ligand π-orbital whose sign changes only once in this region interacts mainly with hybrid π-orbitals of the metal, etc.

The second remark concerns the multiplicity of the metal–ligand bond.

For the atoms of transition metals in the middle of the series, the EAN rule applies rigorously, since they each have nine fully adequate valence orbitals. The ligand in a π-complex also has a whole set of molecular π-orbitals with different symmetry properties. Naturally, with the variety of these two sets of orbitals, it usually happens that there are not one but several pairs of orbitals in which the partners have symmetry suitable for interaction. Thus between a typical transition metal and a π-ligand, several generalised chemical bonds are formed simultaneously, that is the bonds in typical π-complexes are multiple bonds. For a metal of this kind, the bond with a π-ligand is much stronger than an ordinary metal–carbon σ-bond, so that competition between the two types of bond is unlikely.

For the transition metals at the start of the series, donor–acceptor bonds are weakened as a result of the high energy of the unoccupied *d*- and more particularly *p*-orbitals.[55] The formation of several such bonds is also unfavourable because it would lead to breakdown of the electrical neutrality principle, according to which the charges of the atoms in stable complexes should lie in the range from −1 to +1.[56] The most important feature, however, is that the small number of valence electrons in the metal atom excludes synergic stabilisation of the bonds as a result of the superposition of donor–acceptor and dative interactions. All this leads to breakdown of the EAN rule, and at the same time prevents the formation of additional generalised chemical bonds in π-complexes. Thus for example the compound Cp_2TiCl_2 can be described as a derivative of tetravalent titanium, whose four valence orbitals form two bonds with chlorine atoms and two bonds with the rings. The bond formed by titanium with the ring is an ordinary headlamp-shaped generalised chemical σ-bond. The strengths of the ordinary and generalised σ-bonds do not differ greatly from one another. This leads to competition between them.

An example is provided by the tetracyclopentadienyl derivatives of the transition metals at the start of the series. The competition between the ordinary and generalised chemical bonds in these molecules is also indicated by the easy exchange between the rings, joined to the metal in different ways,[57] and by the existence of a whole set of structures: with one h^5- and three h^1-rings (M = Mo [58]); with two h^5- and two h^1-rings (M = Ti,[59] Hf,[60] Nb, Ta [61]); with three h^5- and one h^1-ring (M = Zr [62]); and with four h^5-rings (M = U,[63] Th [64]). The EAN rule is not obeyed in any of these molecules.

Deviations from the EAN rule are also observed for the atoms at the end of the transition metal series. As a result of the rapid decrease in the energy of the *d*-orbitals of the transition metals at the end of the series, the *d*-electrons to a large extent lose the properties of valence electrons and become core electrons.[65] This brings to nought the synergic stabilisation of the donor–acceptor bonds by the dative interactions. At the same time, the increase in the difference in the energies of the *s*- and *p*-orbitals[66] leads to the successive exclusion of the latter from the bonding, leading to the appearance of 16-electron and then 14-electron complexes. The bonds formed by the π-ligands with the metal are no longer multiple bonds, and competition between the ordinary generalised chemical bond with the π-ligand and the ordinary simple two-centre metal–carbon bond again becomes possible.

Moving further down the periodic table does not lead to anything new in the development of the concept of the chemical bond. The non-transition elements of the subsequent periods are very similar to those of period III, and the transition metals of the later periods do not differ fundamentally from those of period IV.

VI. The chemical bond and electron-deficient compounds

The boron atom, like the carbon atom, has four valence orbitals, but only three valence electrons. The molecules of boron chloride BCl_3 and fluoride BF_3 are planar. The B–Hal bonds lying at an angle of 120° to one another are formed by the sp^2-hybrid orbitals of boron. The $2p_z$-orbital of boron remains unoccupied, but the p_z-orbitals of the halogens contain lone pairs of electrons. These pairs partly occupy the unoccupied p_z-orbital of boron, decreasing its unsaturation, and the molecules exist, although the two compounds are the strongest Lewis acids.[67] In boron hydride, the hydrogen atoms have nothing to give to the unoccupied p_z-orbital of boron and nothing with which to soften its unsaturation, and the hydride BH_3 does not exist, but dimerises. The structure of diborane B_2H_6 has been the subject of a discussion extending over several decades. The first workers[68–74] to establish the true structure of diborane included the Soviet scientists Nekrasov and Dyatkina.[70–74] Syrkin has told how Dyatkina's conclusion, based on quantum-chemical calculations, was not believed, because it was considered that the

structure of diborane had been established experimentally,[75,76] by methods including X-ray diffraction.[76] Diborane had been assigned an ethane-like structure. It was true that it was still not clear what held the two boron atoms together, since there were no electrons for a B—B bond (Fig. 6*a*). Many, including Lewis,[77] Sidgwick,[78] and Pauling,[79] tried to find a way out of this difficulty, and considered that the incomprehensible ethane-like structure of diborane had been "explained". Dyatkina was not stopped either by this Areopagus of theoreticians or by "experiment". Being a quantum chemist, she recalculated the diffraction pattern, and showed that the pattern agrees better with the diborane structure which she had proposed than with the ethane-like structure.[74]

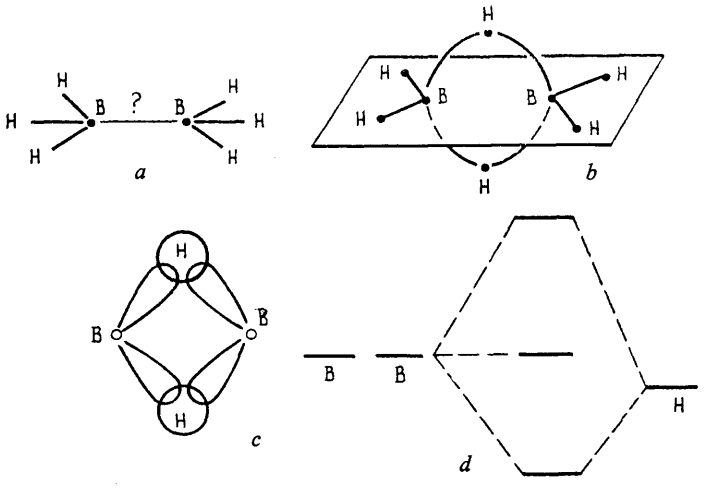


Figure 6. Diborane B_2H_6: *a*, ethane-like structure of diborane; *b*, actual structure of diborane; *c*, B—H—B bridging bonds of diborane; *d*, energy level diagram for the B—H—B bridging bond.

The structure of diborane has now been determined with limiting accuracy.[80] In the diborane molecule, four hydrogen atoms are joined to boron atoms by ordinary two-centre bonds. These four bonds lie in the horizontal plane, as in ethylene. The two remaining hydrogen atoms lie symmetrically above and below this plane, joining the boron atoms by two bent B—H—B bonds (Fig. 6*b*). The central part of diborane in the vertical plane is represented in Fig. 6*c*. These bonds are called bridging bonds.

The molecular orbitals of the bridging bond are constructed from the atomic orbitals of a hydrogen atom and two boron atoms. The three atomic orbitals give three molecular orbitals: bonding, non-bonding, and antibonding. The bonding orbital contains two electrons. A two-electron three-centre chemical bond is formed (Fig. 6*d*). Thus diborane contains a total of six two-electron localised bonds: four two-centre B—H bonds and two three-centre B—H—B bridging bonds. Thus 12 electrons are required, and these are provided by the six hydrogen atoms and two boron atoms.

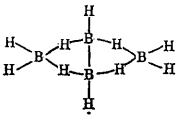
Diborane is a representative of the so-called electron-deficient compounds, that is compounds in which the number of valence electrons is smaller than the number of orbitals. When the number of electrons is greater than the number of atomic orbitals, lone pairs are formed. When the number of electrons ($2n$) is exactly equal to the number of atomic orbitals ($2n$), two-centre bonds are formed. The $2n$ atomic orbitals form $2n$ two-centre molecular orbitals; of these, n are bonding, and n are antibonding. All the valence electrons occupy the n bonding molecular orbitals. If however the number of electrons is smaller, then some of the two-centre bonding molecular orbitals remain unoccupied, but molecules are stable only if all the BMO are occupied. The result is the formation of three-centre bonds. As before, two electrons are involved in the three-centre bond, but it is constructed from three atomic orbitals. Thus when there are insufficient electrons, the extra atomic orbitals can be absorbed by three-centre bonds. If for each extra atomic orbital a three-centre bond is formed instead of a two-centre bond, then all the bonding molecular orbitals will be occupied, and the molecule will be stable.[13,81]

The principle of isolobal analogy suggests that the role of bridge need not necessarily be played by hydrogen, and that the latter can be replaced by any group isolobal with it, for example the methyl group $CH_3 \leftrightarrow H$. In fact, the dimer of trimethylaluminium is constructed in exactly the same way as diborane. It contains two bridging Al—CH_3—Al bonds. The carbon atoms of the remaining methyl groups lie in a plane perpendicular to the plane of the bridges, and are joined to aluminium by ordinary two-centre bonds.[82]

Thus in electron-deficient compounds a new type of bond appears — the two-electron three-centre bridging bond.

Next in order of complexity after diborane come the boron hydrides B_4H_{10} and B_5H_{11}. In the hydride B_4H_{10} [83,84] there are four boron atoms and therefore a deficit of four electrons. It should therefore contain four three-centre bonds to absorb the four extra atomic orbitals, so that the valence electrons will occupy all the BMO.

In fact, in the borane B_4H_{10} the boron atoms are joined by four hydrogen bridges. The remaining six hydrogen atoms are terminal, and are joined to boron by ordinary two-centre bonds. These ten bonds take up 20 electrons. The remaining two electrons join two boron atoms by a two-centre bond.



This description of one of the simplest boron hydrides is already not so simple, but, simple or complicated, it at least adequately reflects the structure of the molecule. Thus the structure is effectively described by more or less independent bonds with a definite location in space: seven two-centre and four three-centre bridging bonds. For the hydride B_5H_{11}, the situation is fundamentally less satisfactory. Before its structure is discussed, however, another type of three-centre bond can be considered (Fig. 7).

In the hypervalent compounds[26] examined above, the three-centre bond is produced because of a deficit of atomic orbitals; the central atom has only one orbital to form bonds with two ligands (Fig. 7*a*). The three-centre bridging bond,[13] formed because of a deficit of electrons, was then described. In this case the orbitals of the outer atoms overlap the orbital of the bridging atom (Fig. 7*b*). In addition to these open three-centre bonds, there exist central three-centre bonds,[13] where the atoms are situated at the vertices of a regular triangle, and their orbitals are directed towards the centre of the triangle. These three atomic orbitals give three MO: one

bonding and two antibonding. The symmetrical BMO contains the two electrons of the central three-centre bond joining three atoms (Fig. 7*c*).

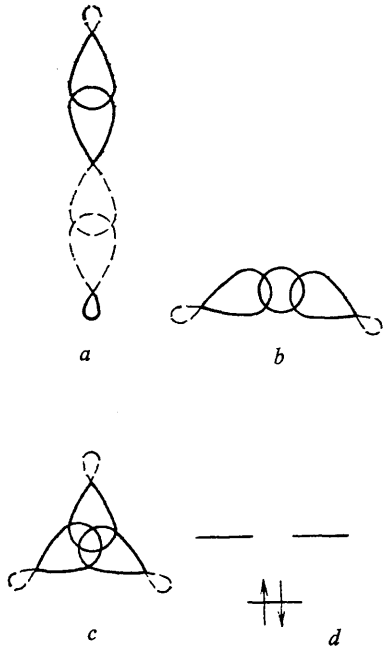
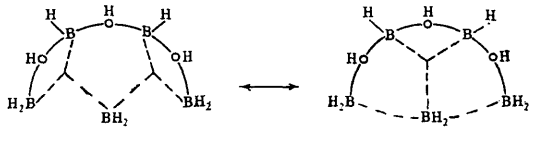


Figure 7. Three-centre bonds: *a*, three-centre bond in hypervalent compounds; *b*, bridging bond in electron-deficient compounds; *c*, central three-centre bond; *d*, energy level diagram of the central three-centre bond.

The boron hydride B_5H_{11},[85,84] in which there is a deficit of five electrons, has two central three-centre bonds and three bridging bonds with hydrogen bridges, that is five three-centre bonds are formed. The remaining eight hydrogen atoms are joined to boron by ordinary two-centre bonds. Another representation of the B_5H_{11} molecule is possible, however. All the localised bonds with hydrogen atoms, both the ordinary two-centre bonds and the three-centre bridging bonds, remain unchanged, but the bonding between the boron atoms can be represented not by two central three-centre bonds but by one central and one open, that is the B_5H_{11} molecule can be described by two different structures.



When a molecule can be described by different structures, it is a clear indication that the representation involving individual more or less isolated bonds does not correspond to chemical reality. The most complex non-conjugated organic molecule can be represented perfectly by a single structure, whereas the description of the simplest aromatic molecule, benzene, whose π-system forms a single whole, requires at least two structures.

The examination of aromatic systems is facilitated considerably by the fact that they are planar molecules whose framework is described by two-centre bonds. The indivisible whole is only their π-electron cloud, which in a first approximation does not interact with the framework[86,87] and can therefore be considered separately. The latent symmetry of π-systems,[88–90] and also the fact that they contain comparatively few electrons (one from each carbon atom), facilitate their examination considerably.

The situation with the boron hydrides is much more complicated. Boron hydrides form three-dimensional molecules, whose framework is usually a polyhedron. The framework of these molecules cannot be described by two-centre bonds. They can be described by a combination of two-centre and open and central three-centre bonds. A whole set of rules on how to do this has been developed[91] (some of these rules have been used implicitly in the description of the simplest hydrides given above). With increase in the size of the polyhedral molecule, the number of structures describing it increases. The description becomes ambiguous. The difficulties arise because the electronic system of the framework of these molecules is in fact a single whole. The attempt to break it down into individual bonds is artificial, and does not correspond to objective reality.

In contrast to the usual dismembering chemical approach, it is necessary to find a single indivisible system which can serve as a model of the electronic system of the boron hydrides, that is which can define their basic properties. The choice of such a model is suggested by the three-dimensional polyhedral structure of the boron hydrides. The greater the number of vertices in the polyhedron, the closer its similarity to the sphere on which its vertices are situated. The similarity between the three-dimensional structures of the boron hydrides and the sphere suggests the existence of an analogy in the basic properties of the wavefunctions of the electrons of these two systems.

Before describing the properties of the wavefunctions of an electron on a conducting sphere, however, the limits of applicability of this model can be considered, by comparing two polyhedra: the icosahedron with 12 vertices and 20 triangular faces, and its double the Archimedean polyhedron or dodecahedron, with 20 vertices and 12 pentagonal faces. The electron clouds of atoms situated at the vertices of the triangular faces of the icosahedron fill the entire face to its centre, so that the entire surface of the icosahedron is covered continuously by the electron cloud. The faces of the dodecahedron are much larger (Fig. 8), and in their central part the density of the electron cloud is negligible. The electrons do not cover the surface of the dodecahedron completely, but are localised along the edges. Thus the model of a sphere over which the electrons move in unhindered fashion is not appropriate for dodecahedral molecules. The model of the sphere is suitable for one-bond surfaces, and corresponds approximately only to polyhedra with triangular faces (Δ-polyhedra), that is Δ-polyhedral clusters.

The term "cluster" is used very broadly in chemistry.[92] It is often applied even to molecules containing simply two or more metal atoms joined to one another. Framework molecules such as cubane, prismane, dodecahedrane, etc. are also described as clusters.

For the present review, however, it is not specific molecules but the development of the concept of the chemical bond that is of interest. From this viewpoint, it is the Δ-polyhedral clusters that are of interest, and all the subsequent discussion will be devoted to them.

VII. The chemical bonding in Δ-polyhedral clusters

The form of the wavefunctions of electrons situated on a conducting sphere can be discussed.[93] The wavefunction of the ground state of an electron on a sphere has the same sign everywhere, and is distributed uniformly over the entire sphere. This totally symmetric state is one, and is conveniently represented as a ball uniformly coloured in a single colour. The next state on the energy scale can be described by a two-colour ball. The red half can be taken as corresponding to the positive sign of the wavefunction, and the blue half to the negative sign. The plane dividing the ball into red and blue halves—the equatorial plane—is the nodal plane of the function. On passing through this plane, the function changes sign, and on the actual plane the value of the function is zero. Thus in this state the wavefunction has one nodal surface.

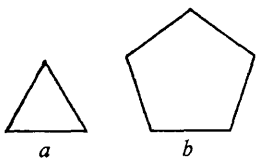


Figure 8. Comparative sizes of the faces of an icosahedron (*a*) and a dodecahedron (*b*) with edges of identical length.

In this case the electron density distribution is not uniform. The density is greatest at a pole, decreases gradually as the equator is approached, becomes equal to zero at the equator, and then increases again, reaching a maximum at the other pole.

The ball can be turned with its red pole upwards, forwards, or to the right. These three arrangements of the two-colour ball correspond to three states of the electron on the sphere with identical energies, that is to degenerate states.

The wavefunctions of the group of states next on the energy scale now have two nodal surfaces. There are five such states. These states are also degenerate. In each successive group of states on the energy scale, the number of nodal surfaces at which the wavefunction changes sign increases.

This is the most important property of the wavefunctions of an electron on a conducting sphere. The nodal properties of the wavefunctions are preserved even if the symmetry of the sphere is destroyed, for example by crumpling it. If bulges or dents appear on the sphere, the strict degeneracy of the wavefunctions is removed. Nevertheless, the ground state, in which the wavefunction has the same sign everywhere, is followed by a group of three wavefunctions with similar energies and one nodal surface, then by a group of five wavefunctions with similar energies and two nodal surfaces, etc.

The examination of the polyhedral boron hydrides can begin with the *closo*-hydrides. The *closo*-hydrides are hydrides in which the boron atoms are situated at the vertices of closed Δ-polyhedra. In these compounds, each boron atom is joined to a hydrogen atom, so that their formula is B_nH_n. The B—H bonds are directed outwards along the radius, and are *exo*-bonds. The *exo*-bonds are strongly localised, and undergo practically no interaction with the rest of the molecule. After the formation of one *exo*-bond, boron still has two electrons and three valence orbitals: one radial, directed towards the centre of the polyhedron, and two tangential, directed one along the parallel, and the other along the meridian. The bonding of the cluster framework involves these so-called framework electrons and orbitals. A boron hydride B_nH_n has a total of $2n$ framework electrons and $3n$ framework orbitals, of which n are radial, and $2n$ tangential. The $3n$ atomic orbitals of boron are used to construct the $3n$ molecular orbitals of the polyhedron. A pictorial representation of the structure of the molecular orbitals obtained from the radial atomic orbitals is provided by the wavefunctions of an electron on a conducting sphere, described above. A pictorial representation of the construction of the molecular orbitals from the tangential orbitals (although the nature of these orbitals is also determined by the form of the wavefunctions of an electron on a conducting sphere) is much more complicated. This will not be considered here, and the results will simply be presented.[94–96]

The most favourable lowest molecular orbital does not have a nodal surface, and the electron density is distributed uniformly over all the boron atoms. It is constructed only from the radial atomic orbitals of boron; the tangential orbitals cannot take part, from symmetry considerations. The $2n$ tangential orbitals of boron form $2n$ molecular orbitals, of which n are bonding, and n antibonding. The bonding molecular orbitals obtained from the tangential orbitals can interact with combinations of the radial orbitals having appropriate symmetry. As a result of this interaction, the bonding molecular orbitals are stabilised, but their number remains unchanged. This gives n bonding molecular orbitals constructed from tangential orbitals with an admixture of radial orbitals, and one totally symmetric bonding molecular orbital, constructed only from radial orbitals, that is a total of $n + 1$ bonding molecular orbitals.

These qualitative conclusions, based on the model approach, have been fully confirmed by MNDO calculations for the boranes.[97]

The $n + 1$ molecular orbitals obtained should contain $(n + 1)$ electron pairs. The boron *closo*-hydrides contain only $2n$ framework electrons, that is there is a deficit of two electrons. Since stability of the molecule requires that all the bonding molecular orbitals be occupied, the boron *closo*-hydrides are stable as the $B_nH_n^{2-}$ dianions.

The two electrons required can also be supplied to the polyhedron in other ways. The CH group also has three boundary orbitals, one σ and two π, that is the composition of the boundary orbitals is the same as that for the BH group, but the CH group has an extra electron. The two electrons required can therefore be obtained if the BH groups at two vertices of the boron hydride are replaced by CH groups. This gives the stable neutral *closo*-carboranes $C_2B_{n-2}H_n$.

The *closo*-boranes and *closo*-carboranes obtained can now be "broken down". This can be done for the case of the icosahedron, the hydride with 12 vertices. It has $12 + 1 = 13$ BMO, so that to be stable, it requires 26 framework electrons, that is this icosahedron will be stable (according to the general rule) either as the $B_{12}H_{12}^{2-}$ dianion (see its prediction,[98] synthesis,[99] and structure[100]) or as the carborane $C_2B_{10}H_{12}$ (see the synthesis of the 1,2-,[101–104] 1,7-,[105] and 1,12-isomers,[106,107] and the structure of the 1,2-,[108] 1,7-,[108] and 1,12-isomers[106]). The removal of BH from one of the vertices gives a molecule with a framework resembling a nest. These structures are called nest-like or *nido*-structures. In the distortion of the structure on going from the *closo*-borane to the *nido*-borane, the

number of bonding molecular orbitals remains unchanged,[109] that is the stability of the *nido*-borane still requires 26 electrons, but there are only 11 BH groups, that is there is a deficit of four electrons.

The electrons required can be obtained in very different ways:[110] the simplest is by replacing four BH groups by CH groups to give the neutral stable *nido*-carborane $C_4B_7H_{11}$. The four electrons can also be obtained by adding four hydrogen atoms to the $B_{11}H_{11}$ nest, to give the boron hydride $B_{11}H_{15}$. These four hydrogen atoms naturally are situated at the edge of the nest, as it were bringing the surface of the *nido*-borane up to spherical. The exact arrangement of these four hydrogen atoms has not been established. Different versions have been discussed: four bridges formed along the edge of the open pentagonal face, or an arrangement in which only some of these hydrogens are bridging, and the others terminal. These terminal B–H bonds are directed along the meridians towards the missing vertex (*endo*-bonds).

The removal of another vertex from the icosahedron gives a structure which is called a spider-web or *arachno*-structure. Surprisingly, this structure as it were preserves the memory of its origin from the icosahedron, and for its stability still requires the same 13 pairs of electrons.[109] Now, however, there remain only 10 vertices, so that there is a deficit of six electrons. Again, these can be obtained in different ways, for example as follows.

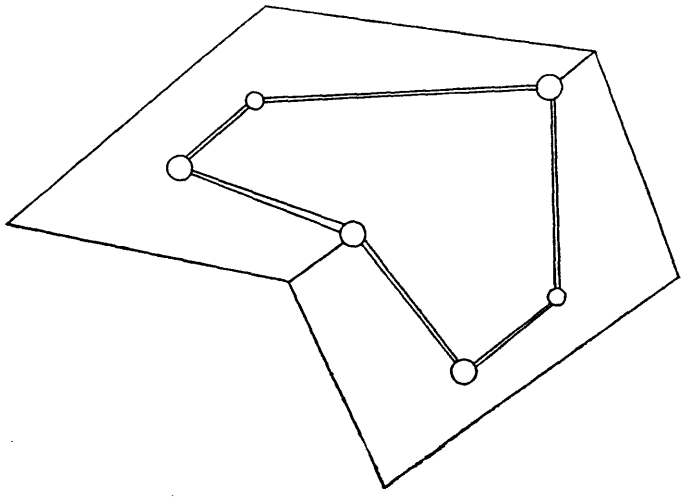


Figure 9. Boundary of the "hole" formed by the removal of two adjacent vertices of an icosahedron.

The edge of the hole produced by the removal of two vertices from the icosahedron forms a hexagon folded in half (Fig. 9). It would be possible to obtain the required six electrons by placing six bridging hydrogen atoms along the edge of this hexagon. They would interfere with one another, however, and the *arachno*-borane $B_{10}H_{16}$ is unstable.[110] Bridging hydrogen atoms are placed only on the two opposite sides of the hexagon farthest from the fold. The atoms in the position of the fold form *endo*-bonds with Lewis bases, which contribute their lone pairs to the cluster.[111] For example, the *arachno*-boranes $B_{10}H_{12}(CH_3CN)_2$,[112,113] $B_{10}H_{12}(NR_3)_2$,[114] and $B_{10}H_{12}(SR_2)_2$ [115] are formed in this way. The procedure involving breakdown of the icosahedron can be continued further. Another form of molecular design, based on the principle of isolobal analogy, that is on the replacement of a BH vertex in the neutral stable carborane $C_2B_{10}H_{12}$ by a group isolobal with it, can be considered. The alkylammonium group is naturally isolobal with the BH-group. The beryllium atom, like the boron atom, has four valence orbitals, but only two valence electrons. Thus to obtain a group isolobal with BH, Be must be joined to a base providing the electrons for the *exo*-bond. The $BeNR_3$ group is isolobal with BH. For the atoms of the group IV elements in the ground state, one valence electron is occupied by a lone pair, and the remaining three boundary orbitals contain two electrons, so that the tin atom, for example, is isolobal with the BH group.

More complex groups isolobal with the BH group can now be considered. The $Fe(CO)_3$ group can be taken first. Iron is a transition metal, so that it has nine valence orbitals. Of the eight valence electrons of the iron atom, six are situated in three valence orbitals, forming its lone pairs. Another three orbitals are involved in the formation of bonds with the carbonyl groups, which provide the electrons for these bonds. This leaves two electrons and three orbitals, one σ and two π. Thus the $Fe(CO)_3$ group, and also the $Ru(CO)_3$ group, are isolobal with the BH group. In the $(C_5H_5)Co$ group, cobalt is joined to the ring by three bonds: one headlamp-shaped σ-bond and two two-lobed π-bonds. The formation of these bonds uses three valence orbitals of cobalt and one of its electrons. Another three valence orbitals are occupied by the three lone pairs of cobalt. This leaves three valence orbitals and two electrons, that is the $(C_5H_5)Co$ group is also isolobal with the BH group. In the case of nickel, a group isolobal with the BH group is obtained when it combines with cyclobutadiene. In addition, the $Pd(C_4Ph_4)$ group is isolobal with the $Ni(C_4H_4)$ group, and hence with the BH group.

The isolobal groups

AlC_2H_5 (Ref.116) $\leftrightarrow$ $BeN(CH_3)_3$ (Ref.117) $\leftrightarrow$ Sn (Ref.118) $\leftrightarrow$

$Fe(CO)_3$ (Ref.119) $\leftrightarrow$ $Ru(CO)_3$ (Ref.120) $\leftrightarrow$ $Co(C_5H_5)$ (Ref.121)

$\leftrightarrow$ $Pd(C_4Ph_4)$ (Ref.122) $\leftrightarrow$ BH

can and do replace the BH group in the icosahedron of the carborane $C_2B_{10}H_{12}$. This gives metallocarboranes,[116–122] including compounds with transition metal atoms.

The ligands can be removed from a transition metal atom situated at a vertex of the icosahedron. This atom provided three valence orbitals and two electrons for the cluster. Six electrons form lone pairs. This leaves three valence orbitals, and if the transition metal is nickel, it leaves $10 - 2 - 6 = 2$ electrons, that is this icosahedron with the stripped nickel atom at a vertex forms a group isolobal with the BH group, so that it can replace this group in another carborane. This gives a structure in which two icosahedra have a nickel atom as a shared vertex (see its synthesis[123] and structure[124]). This iso-electronic cluster also exists for cobalt as the anion,[121] and for iron as the dianion.[125] These are the so-called *commo*-structures.[126]

The fruitfulness of the principle of isolobal analogy is sufficiently clear from the examples given. No more will be given, although it would be possible to describe a large number of other beautiful structures, since in accordance with the principle of isolobal analogy it is possible to replace other vertices and also to extend considerably the list of isolobal groups.

The chief importance of the principle of isolobal analogy is that it enables organometallic chemists to think freely about their field of chemistry. In other words, the principle of isolobal analogy in the chemistry of organometallic compounds fulfils a role analogous to that of the theory of chemical structure in organic chemistry. When the principle of isolobal analogy is used in this way, a considerable simplification of the definition of the isolobal nature of groups is possible. Groups can be described as isolobal if they have the same number of boundary orbitals and the same number of electrons in them. When these two conditions are observed, the requirement of an approximate correspondence in the three-dimensional structure, energy, and symmetry of the boundary orbitals[16] is usually satisfied automatically.

It should however be emphasised that the "isolobal analogy" suggests possibilities, but does not guarantee their existence.[16] The use of "libraries" of isolobal groups[16] may help to estimate more accurately the probability of realising conceived plans.

The naturally developed definition of isolobal groups, according to which the number of boundary orbitals should be the same and they should contain the same number of electrons, was adopted by Hoffmann slightly later,[16] and in his first papers[14,15] he emphasised that isolobal groups are groups with the same number of boundary orbitals, and the presence of the same number of electrons is not required. Although the definition now adopted undoubtedly has a much wider range of application, some advantages of the initial version of the definition of isolobal character are worth noting. In fact, analogous bonding ability and hence the possibility of the mutual replacement of groups are determined mainly by the number and nature of their boundary orbitals. The number of electrons required for bonding, however, can be provided in the most varied ways. Examples include the above-mentioned *commo*-polyhedra $(C_2B_9H_{11})_2Ni$, $[(C_2B_9H_{11})_2Co]^-$, and $[(C_2B_9H_{11})_2Fe]^{2-}$. All three groups $C_2B_9H_{11}M$ (M = Ni, Co, Fe) have the set of boundary orbitals required for the successful replacement of a BH vertex, and the electron deficit is made up by the fact that in the case of Co [121] and Fe [125] these structures are produced as singly- and doubly-charged anions.

The deficit of framework electrons is made up in an interesting way in the diferracarborane $[(C_5H_5)Fe]_2C_2B_6H_8$. In this *closo*-metallocarborane, two BH vertices are replaced by $Fe(C_5H_5)$ groups. The $Fe(C_5H_5)$ group also has the set of boundary orbitals required for the replacement of the BH vertex, but the three boundary orbitals of this group contain only one electron. It would therefore seem that the replacement would lead to a deficit of two framework electrons. In fact, this deficit is made up by the spontaneous ionisation of the iron atoms. This gives a paramagnetic cluster with two iron atoms in the ferricinium state and with the required (22) number of framework electrons.[127]

Another way of making up the deficit of framework electrons is found in the icosahedral rhodium cluster $[Rh_{12}(CO)_{27}Sb]^{3-}$.[128] In this complex, all the vertices of the icosahedron are occupied by rhodium atoms, from three rhodium tricarbonyls and two rhodium dicarbonyls. In the tricarbonyl, three valence orbitals of rhodium are involved in the formation of bonds with the carbonyl groups, which provide the electrons for these bonds. Three valence orbitals of rhodium are occupied by its lone pairs. The remaining three valence electrons of rhodium occupy its remaining three valence orbitals, that is this is a group with three boundary orbitals and three electrons in them. In rhodium dicarbonyl, two of its valence orbitals are involved in the formation of bonds with the carbonyl groups, four orbitals are occupied by lone pairs, and the three boundary orbitals contain only one electron. The rhodium atoms provide $(3 \times 3 + 9 \times 1) = 18$ electrons for the cluster,¶ but a total of 26 are required. From the charge of the cluster (–3), it follows that there is a deficit of five electrons. The cavity of the cluster, however, contains an antimony atom, which provides the five electrons required by the system of framework electrons.

This example introduces another type of bond — the interstitial bond. The interstitial atom is situated inside the cavity in the cluster; its valence orbitals interact with the framework bonding molecular orbitals of the cluster, stabilising them, without changing their number.

The cavities in transition metal clusters are naturally larger than those in boranes, and this method of satisfying the requirement for electrons and stabilising the structure is extremely common.[129] Clusters with interstitial hydrogen, carbon, nitrogen, phosphorus, arsenic, antimony, and sulphur are known.[129] The stabilising influence of the interstitial atom leads to the production of various exotic structures, such as the icosahedron of transition metal atoms given above.

Thus the isolobal analogy produces infinitely varied sets of clusters. The isolobal analogy clearly reveals the unity of the whole of chemistry, leading to the mutual replaceability of groups and atoms from completely different positions in the periodic table. In the attempt to emphasise the unity of chemistry, attention has been drawn primarily not to the differences between clusters but to what they have in common. What they have in common is determined by the similarity between the molecular orbitals of the cluster and the wavefunctions of the electrons of a conducting sphere,[94–96] which leads to the rule of $n + 1$ pairs of framework electrons.[130,131] Nevertheless, however, boranes and transition metal clusters differ significantly. Thus for boranes, polyatomic clusters and in particular icosahedral structures are stable, whereas for transition metal clusters, the octahedral structure is most characteristic. In the build-up of a cluster of transition metals, its polyhedron usually does not expand. Most frequently, the additional atom crowns a triangular face, and a cap consisting of the transition metal with its ligands appears above the face. What then happens to the framework MO? The metal–ligand group which has approached the face of the cluster has three boundary orbitals. The remaining six valence orbitals of the transition metal are involved in bonds with the ligands and are occupied by lone pairs. Of the three boundary orbitals, one is a σ-orbital, and the other two are π-orbitals. These orbitals should interact with the bonding MO of the cluster. Naturally, for this interaction the important feature is not the form of the MO as a whole but its structure at the face which the transition metal atom has approached. Among the BMO of the cluster there will always be some which will not change sign at this face, and some which will change sign once, that is σ- and π-orbitals. These will interact with the boundary orbitals of the approaching group. As a result of this interaction, the BMO of the cluster are stabilised, but their number remains unchanged. This is the so-called capping principle:[132] the number of framework electrons remains unchanged when a cap appears above a face of the polyhedron. Transition metal clusters grow mainly in this way; a cap appears above one face, then another, a third, and a fourth. Caps can appear, however, not only above

¶ The description is idealised. In fact, many of the carbonyl groups are bridging groups, but this does not alter the total electron count.

the original faces of the cluster but also above the newly formed faces. The more the cluster grows, the more frequently a part of the metal lattice can be recognised in its metallic framework.

How large must a cluster be to acquire the properties of the metal? There is as yet no definite answer to this question. The size of the cluster required for this, given by calculations using methods of the SCF-X_α-SW type (about 20 atoms), is much smaller than that given by EHM calculations.[133] In any case, when the number of atoms is sufficiently large, the cluster must be regarded basically as a metal particle.

Hoffmann, who so successfully built a bridge between organic and inorganic chemistry,[16] is now actively engaged in building a bridge between the theoretical approaches of quantum chemistry and the theory of the solid state.[134] This direction of the development of theory will not be considered here, and the review will end with a discussion of gold clusters.

Gold clusters apparently break all the cluster laws, but actually they provide clear confirmation that the electronic system of a cluster is a single entity, whose basic properties are determined by the properties of the wavefunctions of an electron on a conducting sphere.

VIII. The chemical bonding in gold clusters

In all the clusters examined so far in the present review — boranes, carboranes, heteroboranes, metallocarboranes, and transition metal clusters — the atoms of the cluster have formed framework bonds using three orbitals — one radial and two tangential.

This "material" has been used to construct the molecular orbitals of the clusters, which should be similar to the wavefunctions of an electron on a conducting sphere. These two features led to the rule of $n + 1$ electron pairs.

It has been seen how strictly this rule applies. It is possible to change the nature of the vertices in the cluster beyond recognition, it is even possible to remove them completely, yet when there are $n + 1$ electron pairs the framework of the cluster, no matter the number of atoms making it up, takes the form of an n-vertex polyhedron, or a fragment of one in the case where vertices have been removed.

Familiarity with clusters leads to never-ending amazement at the astonishing variety and refinement of the ways in which the rule is followed.

Gold does not obey this rule. What is happening?

Gold is the penultimate element in a transition metal series. At the end of a transition metal series, the energy of the *d*-orbitals is lowered considerably, and the lone pairs of electrons occupying them are gradually transferred to the core and become inactive. At the same time, the gap between the energies of the *s*- and *p*-orbitals increases. The *p*-orbitals become ineffective, and gradually cease to take part in bonding.

The cluster $(AuR)_n$ ($6 \leqslant n \leqslant 12$) can be considered.[135] The Au—R *exo*-bond is formed by an *sp*-hybrid orbital of gold, and is directed outwards along a radius of the cluster. The second *sp*-hybrid orbital of gold is directed along the radius towards the centre of the cluster. This is a radial orbital. The energies of the two unoccupied tangential *p*-orbitals of gold, directed along the parallels and meridians of the sphere, are high on the scale, and these orbitals practically do not function. Thus the gold cluster differs from all the clusters examined so far in the present review in that the tangential system of orbitals plays practically no part in bond formation, and the formation of the cluster involves only the interaction of the radial orbitals. Which of them form the molecular orbitals? The most favourable, that is the totally symmetrical orbital, is constructed only from radial orbitals (all clusters have one). This is followed (remembering the two-colour ball) by three orbitals with similar energies, each of which has one nodal surface. The next MO each have two nodal surfaces; in them, the sign of the function changes too frequently, and the orbitals are unfavourable and anti-bonding. Thus these radial orbitals give only four bonding molecular orbitals: one very favourable totally symmetrical orbital, and three orbitals with similar energies and one nodal surface. This statement is true, irrespective of the number of vertices in the cluster.

Thus because of the low effectiveness of the system of tangential orbitals, the number of BMO in the *closo*-clusters of gold ($6 \leqslant n \leqslant 12$) is four, so that the gold cluster is maintained by eight framework electrons. This is not quite enough for large clusters, but large gold clusters are stabilised by having an interstitial gold atom at the centre. The symmetry of the *s*- and *p*-orbitals of this atom ideally approaches that of the totally symmetrical and three degenerate BMO of the cluster, which are stabilised by the interstitial atom, without changing their number.

The cluster $[Au_{13}(PR_3)_{10}Cl_2]^{3+}$ can be taken as an example. It forms an icosahedron. The 12 gold atoms at the vertices of the icosahedron form *exo*-bonds with the 10 phosphine ligands and two chlorine atoms. The other Au atom is situated at the centre of the icosahedron. Of the 11 valence electrons of the gold atom, 10 are in deep-lying *d*-orbitals and have in fact entered the core, leaving only one electron from each gold atom. Of the total of 13 electrons, two are involved in bonds with the chlorine atoms (the electrons of the remaining *exo*-bonds are provided by the lone pairs of phosphorus), eight occupy the bonding molecular orbitals of the cluster, and three remain unused ($13 - 2 - 8 = 3$) and are removed. This cluster exists as the triply-charged cation.[136]

It is extremely interesting to compare the properties of gold clusters with those of other clusters. The absence of the tangential system of orbitals leads to significant differences between gold clusters and the clusters of other elements, and sometimes even to opposite properties. In particular, in other clusters, reduction leads to opening of the closed *closo*-structure, whereas in gold clusters, on the contrary, the addition of a pair of electrons leads to the conversion of the open toroidal structure of the cluster into a closed spheroidal structure.[135]

IX. Summary

The evolution of the concept of the chemical bond has been examined. The review began with the hydrogen molecule, which occupies a unique position among the millions of all molecules, since it is the only molecule for which the concept of the chemical bond has a completely unambiguous and rigorous significance. It has been shown how the concept of the two-electron chemical bond is transferred to polyatomic molecules, and that, despite the arbitrariness of this concept in polyatomic molecules, it is extremely fruitful, since it reflects the basic features of chemical reality.

The unusually broad range of applicability of the concept of two-centre bonds is due to the clearly-defined spatially directed character of the four hybrid valence orbitals of the atoms of the non-transition elements, as a consequence of which the bonds are relatively independent of one another. This explains the fruitfulness of the concept of individual bonds. If the number of electrons in an atom

is greater than the number required for the formation of two-centre bonds, no dramatic changes are observed; the extra electrons form lone pairs, and the number of bonds formed by the given atom decreases.

The change is more significant when the coordination number of the atom is greater than four, so that there are insufficient valence orbitals for the formation of two-centre bonds with all neighbouring atoms, and it is necessary to introduce the concept of three-centre bonds.

The comparatively large valence orbitals of transition metal atoms enable them to combine not with one but with several atoms of an unsaturated polyatomic ligand simultaneously. The presence of nine valence orbitals in a transition metal atom provides the prerequisite for the formation of a multiple metal–ligand bond (several multi-centre generalised chemical bonds) and hence leads to increased stability of the π-complex.

Thus both hypervalent compounds and transition metal π-complexes can be described in accustomed chemical fashion using three-centre bonds and multi-centre generalised chemical bonds in addition to two-centre bonds.

Thus neither the change from the elements of period II to the non-transition elements of later periods nor the introduction of transition metal atoms into the molecule requires the abandonment of chemistry's reigning ideology, since it is possible to retain the conceptual breakdown of molecules into individual more or less isolated bonds.

The changes in electronic structure resulting not from the replacement of individual atoms but from a change in the overall geometry of the molecule are much more radical. Thus for the atoms involved in the conjugation in planar conjugated systems, it is possible to distinguish valence orbitals having an axis of symmetry perpendicular to the plane of the molecule. The directed character of these orbitals is the same towards all neighbouring atoms. This is the reason for the strong interaction of the conjugated bonds and the delocalisation of the π-electrons in cyclic systems. The mesh of the network formed by the σ-framework of aromatic molecules is too large, so that the π-electron cloud is localised only in the region of the actual framework. Thus in this case there is one-dimensional (reticular) and not two-dimensional delocalisation of the electrons.†

Within the delocalisation region, the π-electrons move practically freely, and any conceptual breakdown of this single system into individual parts contradicts its factual integrity. Thus chemists are dealing every day with molecules to whose π-electron systems the concept of localised bonds is inapplicable.

Two-dimensional delocalisation of electrons takes place not in planar hexagonal network systems but in the closed or almost closed (*nido-*, *arachno-*, and *hypho*-clusters) surfaces of Δ-clusters, whose framework electrons also form a single integral system.

In three-dimensional space, in addition to one-dimensional (linear, reticular) and two-dimensional (Δ-clusters) delocalisation, three-dimensional delocalisation of electrons is also conceivable. It in fact exists in the depth of metals, but the study of this delocalisation belongs to physics. The traditional field of interest of chemistry deals with molecules. In a molecule, the negative cloud of delocalised electrons should be concentrated on a surface bounding a three-dimensional region, so long as positive nuclei are not introduced into this region. From this viewpoint, an example of compounds in which there is three-dimensional delocalisation of electrons is provided by interstitial compounds. These compounds are widely encountered, but they do not differ significantly from Δ-clusters.

It thus appears that all possible basic types of chemical bonding have been dealt with in the present review.

† The terms one-dimensional and two-dimensional are used in the mathematical sense.

References

1. N D Sokolov *Usp. Khim.*, 1988, **57**(2) 177 [English translation in *Russ. Chem. Rev.*, 1988(2)]
2. V A Legasov, A L Buchachenko *Usp. Khim.*, 1986, **55**(12) 1949 [English translation in *Russ. Chem. Rev.*, 1986(12)]
3. N P Gambaryan *Arm. Khim. Zh.*, 1988, **41** 194
4. L Pauling *Perspectives in Organic Chemistry*, Intersci. Publ., New York, 1956
5. B Pullman, A Pullman *Les Theories Electroniques de la Chimie Organique*, Masson, Paris, 1952, 665 pp
6. C A Coulson *Valence* (Translated into Russian), Izd. Mir, Moscow, 1965, 426 pp
7. G Herzberg *Molecular Spectra and Molecular Structure, Vol. I, Spectra of Diatomic Molecules* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1949, 403 pp
8. C A Coulson *Valence*, Clarendon Press, Oxford, 1953, 338 pp
9. R Hoffmann *J. Chem. Phys.*, 1963, **39** 1397
10. L Pauling *J. Am. Chem. Soc.*, 1931, **53** 1367
11. J C Slater *Phys. Rev.*, 1931, **37** 481
12. J N Murrell, S F A Kettle, J M Tedder *Valence Theory* (Translated into Russian), Izd. Mir, Moscow, 1968, 520 pp
13. W H Eberhardt, B L Crawford, W N Lipscomb *J. Chem. Phys.*, 1954, **22** 989
14. M Elian, M M L Chen, D M P Mingos, R Hoffmann *Inorg. Chem.*, 1976, **15** 1148
15. J W Lauher, M Elian, R H Summerville, R Hoffmann *J. Am. Chem. Soc.*, 1976, **98** 3219
16. R Hoffmann *Angew. Chem. Int. Ed. Engl.*, 1982, **21** 711
17. F G A Stone *Angew. Chem. Int. Ed. Engl.*, 1984, **23** 89
18. E Hückel *Z. Phys.*, 1930, **60** 423
19. W G Penney *Proc. R. Soc. London, A*, 1934, **144** 166
20. W G Penney *Proc. R. Soc. London, A*, 1934, **46** 223
21. H B Gray *Electrons and Chemical Bonding* (Translated into Russian), Izd. Mir, Moscow, 1967, 234 pp
22. R Daudel *The Fundamentals of Theoretical Chemistry*, Pergamon Press, Oxford, 1969, 211 pp
23. J C Slater *Phys. Rev.*, 1930, **36** 57
24. J C Slater *Quantum Theory of Atomic Structure*, McGraw-Hill, New York–Toronto–London, 1960, Vol. 1, 502 pp
25. D A Bochvar, N P Gambaryan, L M Epshtein *Usp. Khim.*, 1976, **45**(6) 1316 [English translation in *Russ. Chem. Rev.*, 1976(6)]
26. R E Rundle *Rec. Chem. Progr.*, 1962, **23** 195
27. A Streitwieser *Molecular Orbital Theory for Organic Chemists* (Translated into Russian), Izd. Mir, Moscow, 1965, 435 pp
28. K S Pitzer *J. Am. Chem. Soc.*, 1948, **70** 2140
29. R S Mulliken *J. Am. Chem. Soc.*, 1950, **72** 4493
30. M W Schmidt, P N Truong, M S Gordon *J. Am. Chem. Soc.*, 1987, **109** 5217
31. J N Murrell, H W Kroto *J. Chem. Soc. Chem. Commun.*, 1977, 619
32. Th C Klebach, R Lourens, F Bickelhaupt *J. Am. Chem. Soc.*, 1978, **100** 4886
33.
34.
35.
36.
37.
38.
39.
40.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64

33. T A Van Der Knaap, Th C Klebach, F Visser, et al. *Tetrahedron*, 1984, **40** 765
34. M S Gordon *J. Am. Chem. Soc.*, 1982, **104** 4352
35. D A Bochvar, N P Gambaryan *Arm. Khim. Zh.*, 1984, **37** 624
36. D M P Mingos, J C Hawes *Structure and Bonding*, Springer-Verlag, Berlin, etc.,1985, Vol. 63, p. 1
37. S P Gubin, G B Shul'pin *Khimiya Kompleksov so Svyazyami Metall–Uglerod* (The Chemistry of Complexes with a Metal–Carbon Bond), Izd. Nauka, Novosibirsk, 1984, 282 pp
38. L Pauling *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, New York, 1960, 644 pp
39. L Pauling *The Achievements and Future Development of Bio-organic Chemistry in Molecular Biology* (Translated into Russian), Izd. Nauka, Moscow, 1978, p. 3
40. D A Bochvar, N P Gambaryan *Metody Elemento-organicheskoi Khimii. Tipy Metallo-organicheskikh Soedinenii Perekhodnykh Metallov* (Methods of Organoelemental Chemistry. Types of Organometallic Compound of Transition Metals), Vol. 1, Izd. Nauka, Moscow, 1975, p. 9
41. D A Bochvar, N P Gambaryan, E M Brainina, et al. *Dokl. Akad. Nauk SSSR*, 1968, **183** 1324
42. B Rees, P Coppens *Acta Crystallogr., Sect. B*, 1973, **29** 2516
43. N S Chiu, L Schäfer *J. Organomet. Chem.*, 1975, **101** 331
44. D M Adams, R E Christopher, D C Stevens *Inorg. Chem.*, 1975, **14** 1562
45. P J Fitzpatrick, Y le Page, J Sedman, et al. *Inorg. Chem.*, 1981, **20** 2852
46. D M Adams, A Squire *J. Organomet. Chem.*, 1973, **63** 381
47. M I Davis, C S Speed *J. Organomet. Chem.*, 1970, **21** 401
48. D C Andrews, G Davidson *J. Organomet. Chem.*, 1972, **36** 349
49. M L H Green *Organometallic Compounds, Vol. 2, The Transition Metals* (Translated into Russian), Izd. Mir, Moscow, 1972, 456 pp
50. T V Nikitina *Metody Elemento-organicheskoi Khimii. Tipy Metallo-organicheskikh Soedinenii Perekhodnykh Metallov* (Methods of Organoelemental Chemistry. Types of Organometallic Compound of Transition Metals), Vol. 2, Izd. Nauka, Moscow, 1975, p. 585
51. J D Fitzpatrick, L Watts, G F Emerson, et al. *J. Am. Chem. Soc.*, 1965, **87** 3254
52. E O Fischer, H Werner *Metall-π-Komplexe* (Translated into Russian), Izd. Mir, Moscow, 1968, 264 pp
53. K Stark, J E Lancaster, H D Murdoch, E Weiss *Z. Naturforsch., B*, 1964, **19** 284
54. L V Rybin, A A Pogrebnyak, M I Rybinskaya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1596
55. C S G Phillips, R J P Williams *Inorganic Chemistry*, Oxford Univ. Press, Oxford, 1966, Vol. 2, 570 pp
56. L Pauling *J. Chem. Soc.*, 1948, 1461
57. E M Brainina, N P Gambaryan, B V Lokshin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 187
58. E O Fischer, Y Hristidu *Chem. Ber.*, 1962, **95** 253
59. J L Calderon, F A Cotton, B G Deboer, et al. *J. Am. Chem. Soc.*, 1970, **92** 3801
60. V I Kulishov, E M Brainina, N G Bokii, Yu T Struchkov *J. Organomet. Chem.*, 1972, **36** 333
61. E O Fischer, A Treiber *Chem. Ber.*, 1961, **94** 2193
62. V I Kulishov, E M Brainina, N G Bokii, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2626
63. E O Fischer, Y Hristidu *Z. Naturforsch., B*, 1962, **17** 275
64. E O Fischer, A Treiber *Z. Naturforsch., B*, 1962, **17** 276
65. J C Slater *Phys. Rev.*, 1955, **98** 1039
66. C E Moore *Atomic Energy Levels*, US Department of Commerce, Washington, 1949, Vol. 1; 1952, Vol. 2
67. F A Cotton, G Wilkinson *Advanced Inorganic Chemistry* (Translated into Russian), Vol. 2, Izd. Mir, Moscow, 1969, 494 pp
68. W Dilthey *Angew. Chem.*, 1921, **34** 596
69. A F Core *Chem. Ind. (London)*, 1927, **5** 642
70. B V Nekrasov *Zh. Obshch. Khim.*, 1940, **10** 1021
71. B V Nekrasov *Zh. Obshch. Khim.*, 1940, **10** 1156
72. Ya K Syrkin, M E Dyatkina *Zh. Fiz. Khim.*, 1941, **15** 459
73. Ya K Syrkin, M E Dyatkina *Acta Physicochim. USSR*, 1941, **14** 547
74. M E Dyatkina, Ya K Syrkin *Dokl. Akad. Nauk SSSR*, 1942, **35** 200
75. S H Bauer *J. Am. Chem. Soc.*, 1937, **59** 1096
76. H Mark, E Pohland *Z. Kristallogr.*, 1925, **62** 103
77. G N Lewis *J. Chem. Phys.* 1933, **1** 17
78. N V Sidgwick *The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927, 230 pp
79. L Pauling *The Nature of the Chemical Bond* (Translated into Russian), GONTI Khim. Lit., Leningrad, 1947, 440 pp
80. K W Hedberg, V Schomaker *J. Am. Chem. Soc.*, 1951, **73** 1482
81. W N Lipscomb *J. Phys. Chem.*, 1957, **61** 23
82. P H Lewis, R E Rundle *J. Phys. Chem.*, 1953, **21** 986
83. C E Nordman, W N Lipscomb *J. Phys. Chem.*, 1953, **21** 1856
84. E B Moore, R E Dickerson, W N Lipscomb *J. Phys. Chem.*, 1957, **27** 209
85. L R Lavine, W N Lipscomb *J. Phys. Chem.*, 1954, **22** 614
86. P G Lykos, R G Parr *J. Phys. Chem.*, 1956, **24** 1166
87. P G Lykos, R G Parr *J. Phys. Chem.*, 1956, **25** 1301
88. C A Coulson, G S Rushbrooke *Proc. Camb. Phil. Soc.*, 1940, **36** 193
89. C A Coulson, H C Longuet-Higgins *Proc. R. Soc. London, A*, 1947, **192** 16
90. T P Zivkovic *Int. J. Quantum Chem.*, 1987, **32** 313
91. R E Dickerson, W N Lipscomb *J. Chem. Phys.*, 1957, **27** 212
92. S P Gubin *Khimiya Klasterov* (The Chemistry of Clusters), Izd. Nauka, Moscow, 1987, 263 pp
93. D K Hoffman, K Ruedenberg, J G Verkade *Structure and Bonding, B, etc.*, Springer-Verlag, 1977, Vol. 33, p. 57
94. A J Stone *Polyhedron* 1984, **3** 1299
95. A J Stone *Inorg. Chem.*, 1981, **20** 563
96. A J Stone *Mol. Phys.*, 1980, **41** 1339
97. P Brint, J P Cronin, E Seward, et al. *J. Chem. Soc., Dalton Trans.*, 1983, 975
98. H C Longuet-Higgins, M de V Roberts *Proc. R. Soc. London, A*, 1955, **230** 110
99. A R Pitochelli, M F Hawthorne *J. Am. Chem. Soc.*, 1960, **82** 3228
100. J A Wunderlich, W N Lipscomb *J. Am. Chem. Soc.*, 1960, **82** 4427
101. M M Fein, J Bobinski, N Mayes, et al. *Inorg. Chem.*, 1963, **2** 1111
102. T L Heying, J W Ager, S L Clark, et al. *Inorg. Chem.*, 1963, **2** 1089
103. L I Zakharkin, V I Stanko, V A Brattsev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 2069
104. L I Zakharkin, V I Stanko, V A Brattsev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 2238
105. D Grafstein, J Dvorak *Inorg. Chem.*, 1963, **2** 1128

106. S Papetti, T L Heying *J. Am. Chem. Soc.*, 1964, **86** 2295
107. J F Sieckhaus, N S Semenuk, T A Knowles, et al. *Inorg. Chem.*, 1969, **8** 2452
108. H Schroeder, G D Vickers *Inorg. Chem.*, 1963, **2** 1317
109. A J Stone, M J Alderton *Inorg. Chem.*, 1982, **21** 2297
110. R E Williams *Adv. Inorg. Chem. Radiochem.*, 1976, **18** 67
111. R J Pace, J Williams, R L Williams *J. Chem. Soc.*, 1961, 2196
112. J V D M Reddy, W N Lipscomb *J. Am. Chem. Soc.*, 1959, **81** 754
113. J V D M Reddy, W N Lipscomb *J. Chem. Phys.*, 1959, **31** 610
114. M F Hawthorne, A R Pitochelli *J. Am. Chem. Soc.*, 1959, **81** 5519
115. D E Sands, A Zalkin *Acta Crystallogr.*, 1962, **15** 410
116. B M Mikhailov, T V Potapova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1152
117. G Popp, M F Hawthorne *J. Am. Chem. Soc.*, 1968, **90** 6553
118. R L Voorhees, R W Rudolph *J. Am. Chem. Soc.*, 1969, **91** 2173
119. M P Garcia, M Green, F G A Stone, et al. *J. Chem. Soc., Dalton Trans.*, 1985, 2343
120. A R Siedle *J. Organomet. Chem.*, 1975, **90** 249
121. M F Hawthorne, T D Andrews *J. Chem. Soc., Chem. Commun.*, 1965, 443
122. P A Wegner, M F Hawthorne *J. Chem. Soc., Chem. Commun.*, 1966, 861
123. L F Warren, M F Hawthorne *J. Am. Chem. Soc.*, 1967, **89** 470
124. D St Clair, A Zalkin, D H Templeton *J. Am. Chem. Soc.*, 1970, **92** 1173
125. M F Hawthorne, D C Young, P A Wegner *J. Am. Chem. Soc.*, 1965, **87** 1818
126. M F Hawthorne, D C Young, T D Andrews, et al. *J. Am. Chem. Soc.*, 1968, **90** 879
127. E K Nishimura *J. Chem. Soc., Chem. Commun.*, 1978, 858
128. J L Vidal, J M Troup *J. Organomet. Chem.*, 1981, **213** 351
129. J N Nicholls *Polyhedron*, 1984, **3** 1307
130. K Wade *J. Chem. Soc., Chem. Commun.*, 1971, 792
131. K Wade *Adv. Inorg. Chem. Radiochem.*, 1976, **18** 1
132. D M P Mingos, M I Forsyth *J. Chem. Soc., Dalton Trans.*, 1977, 610
133. E L Muetterties *Chem. Eng. News, Special Report*, 1982, (31) 28
134. R Hoffmann, S D Wijeyesekera, S Sung *Pure Appl. Chem.*, 1986, **58** 481
135. D M P Mingos *Polyhedron* 1984, **3** 1289
136. C E Briant, B R C Theobald, J W White, et al. *J. Chem. Soc., Chem. Commun.*, 1981, 201