Translated from *Uspekhi Khimii*, 54, 619-636 (1985) U.D.C. 549.192

Estimation of the Stability of Clusters with the Aid of the Theory of the Electron Density Functional

Yu.A.Borisov

The likely usefulness of the application of simple versions of the theory of the electron density functional to the study of the energy characteristics of cluster compounds is discussed. Three types of cluster compounds are considered: clusters of elements as an intermediate form between a molecule and a solid, organometallic clusters, and organoelemental compounds of the *nido*-cluster type. The question of the variation of the bond energy in homoatomic clusters as a function of their size and steric structure is analysed.
The bibliography includes 104 references.

CONTENTS

I. Introduction 361
II. The electronic structure and energy characteristics of atomic clusters 365
III. Stability of organoelemental clusters 368

I. INTRODUCTION

The concept of the "cluster" has been widely used in recent years in various branches of chemistry. The constituent elements (atoms) of a chemical cluster are separated from one another by distances of the order of the chemical bond length and as a rule they form between one another the maximum possible number of bonds. The structural unit of the cluster is a regular or distorted polyhedron in which there are no classical two-centre chemical bonds characteristic of the usual molecules: the bonds in clusters have a many-centre character.

Since the beginning of 1970 metal clusters have been vigorously investigated by theoretical chemical methods (see the relevant reviews[1,2]). Qunatum-chemical study of these compounds within the framework of different versions of the non-empirical SCF LCAO-MO method presents significant difficulties, because the clusters contain a large number of electrons and non-empirical calculations for such systems are far beyond the scope of modern computer techniques. Semi-empirical methods (of the type of CNDO, INDO, MINDO, etc.), which have proved quite useful in organic chemistry, have proved fairly frequently to be inapplicable to transition metal clusters, because they lead to contradictory results.[3]

Quantum-statistical methods for calculations relating to complex compounds have been developing vigorously in recent years. The statistical method was initiated in the studies of Thomas, Fermi, and Dirac.[4] The Thoms-Fermi-Dirac (TFD) model has been widely used in a wide variety of fields such as nuclear, atomic, and solid state theories, astrophysics, etc.[5] The significant progress in the many-particle statistical theory has been associated with studies on the self-consistent theory of a non-uniform electron gas [the method of the electron density functional (MDF)]. The theorem that the determination of the energy of the ground state in the many-particle Schrödinger equation is equivalent to the determination of the minimum in the energy functional for a varying electron density has been proved.[6] By virtue of the theorems of the *V*- and *N*-representability of the electron density,[6-8] the method of the electron density functional has been theoretically justified.

The quantum-statistical many-particle theory has laid the foundations for a series of methods for the calculation of the electronic structure of molecules. These are in the first place different versions of the Slater-Johnson X_α method, in which a statistical exchange potential is introduced.[9] Furthermore, one should include here the discrete variation method,[10-12] which is a variety of the X_α method in terms of a basis set of atomic functions, and the local spin density (LSP) method.[13,14] The latter is a generalisation of the Hohenberg-Kohn-Sham theory[15] and differs from the Hartree-Fock scheme by taking into account all the many-particle effects at the level of the density functional. Apparently the above methods can be expected to be most successful in the solution of various problems of the theoretical chemistry of organometallic compounds, including cluster compounds. Fundamental advances which have already been made in the theory of complex and organometallic compounds are associated with the introduction of these methods in one or other variety.[9,10,16] Since exchange-correlation effects are taken into account in the LSP method, it is not surprising that the method makes it possible to calculate fairly accurately the atomisation energies of molecules[16,17] and solids.[18]

The aim of the present review is to attempt to demonstrate, in terms of simple versions of the method of the density functional, the scope of these approximations in relation to the study of the energy characteristics of cluster compounds.

In the theoretical investigation of atomic clusters, the elucidation of a number of fundamental problems is of interest. One of these is as follows: how big must the cluster be for its electronic structure to be sufficiently close to that of the corresponding crystal? For metals, this problem has been studied within the framework of various approximate quantum-chemical methods. However, it has been found that different methods yield different results. Thus in the X_α method in terms of the scattered wave approximation (X_αSW) the similarity of a cluster to a bulky metallic specimen has been observed already when the cluster contained between 10 and 20 atoms. On the other hand, calculations based on the LCAO-MO method in terms of various approximations (EHM, CNDO, etc.) lead to the conclusion that for such small clusters the details of the electronic structure have nothing in common with metals. Thus there is as yet no unambiguous answer to the first question and the solution of the relevant problem requires both more accurate calculations, for example, within the framework of the LSP method, and experimental studies of the electronic structures of small clusters.

The second fairly important question is to what extent the bond energy in clusters varies with their size and steric structure. This question is closely related to the thermodynamic stability of clusters and their "phase" transformations for different degrees of dispersion. The knowledge of such

relations will make it possible to regulate the degree of dispersion of the given substances as a function of external conditions, which is important in various branches of chemistry. Within the framework of the one-electron method it is not possible to obtain an answer to this question because calculations of the bond energies require allowance for the correlation energy; this is extremely difficult because of the need to employ complex many-determinant wave functions, requiring an extremely long computer time for their evaluation. However, within the framework of the theory of the density functional, it is possible to answer the second question, which is discussed below in relation to carbon, sulphur, phosphorus, arsenic, and alkali metal clusters.

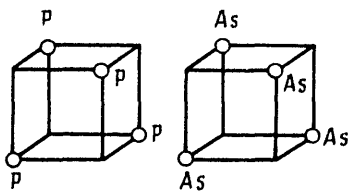


Figure 1. Tetrahedral phosphorus and arsenic clusters.

Atomic clusters can be obtained in molecular beams and also in the form of aggregates in inert matrices.[19] Fig. 1 presents phosphorus and arsenic clusters which can be detected in the gas phase at low temperatures. They have a regular tetrahedral structure. Among non-transition metals, the most unique in the sense of its capacity to produce cluster compounds is boron. Together with polyhedral clusters consisting of boron and hydrogen atoms, there exist boron clusters with beryllium, arsenic, antimony, and transition metals.

Metal clusters are obtained either in molecular beams (before the ionisation chamber of the mass spectrometer) or by condensation from the gas phase on inert supports. The latter method is most promising for the study of the properties of clusters, including their reactivity.

Metal clusters, stabilised on oxide supports, have been vigorously investigated by workers in the field of the surfaces of solids, topochemistry, and catalysis.

Atomic clusters can exist not only in the form of stable formations on the surface of a carrier but they can also be stabilised by various ligands. The simplest of these are solvates, where metallic clusters are stabilised by a ligand environment made up of solvent molecules.

The second large class of cluster compounds consists of organometallic polynuclear complexes having a central metallic nucleus with a distinct cluster structure. A modern review of the problem of the metallic bond in cluster compoounds of this kind has been published recently by Cotton and Chisholm.[20] Fig. 2 presents some examples of characteristic polynuclear cluster compounds of transition metals. According to Cotton and Chisholm,[20] transition metals can be arranged in the following sequence in terms of their ability to form metal–metal bonds in cluster compounds: Mo > Rh > Cr, Re > Tc, Ru, W, Ta, Nb > Fe, Co, Ni, Pd, Os, Ir, Pt.

One of the ways of classifying transition metal cluster compounds is on the basis of the formal oxidation state of the metal. The metal in halides and sulphides is in a high oxidation state, for example, the oxidation state of the metal is +3 in $Re_3Cl_{12}^{3-}$ and $Fe_6S_8(PR_3)_6^{2+}$, +2 in $Mo_6Cl_{14}^{2-}$, etc. There exist various cluster compounds in which the oxidation state of the metal is +1: $(\eta^5\text{-}C_5H_5)_6Ni_6\{HRh[P(OCH_3)_3]_2\}_3$, $[CH_3Rh\text{-}(cyclo\text{-}octa\text{-}1,5\text{-}diene)]_2$, and $H_6Cu_6(PR_3)_6$. A formal oxidation state of zero is observed in a large class of polynuclear metal carbonyls. Simple qualitative theories of the bond in polyhedral boranes[21] are used in calculations for certain classes of polynuclear transition metal clusters.[22] However, these theories are useful only for a formal systematic treatment of clusters and cannot be used to predict any other properties. Such studies can be regarded as a stimulus

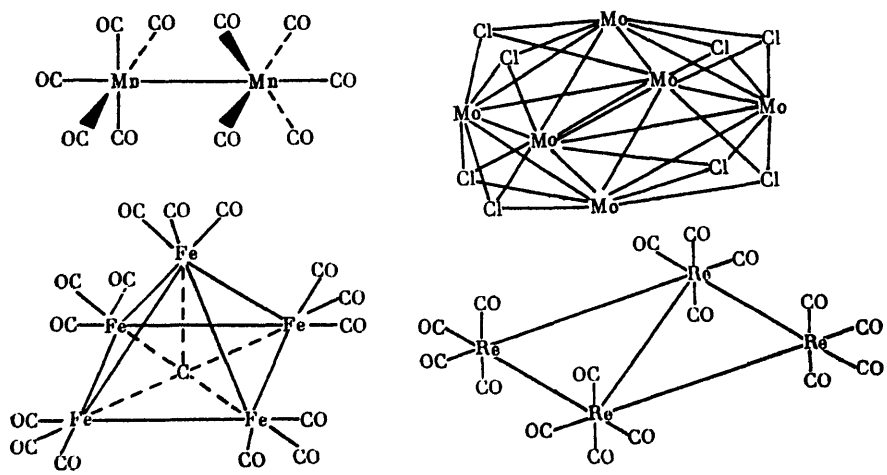


Figure 2. The most characteristic polynuclear cluster compounds.[29]

towards a more vigorous theoretical and experimental investigation of transition metal clusters in order to create a theory of this complex and interesting class of chemical compounds.

Among the simple rules obeyed by organometallic compounds, we may mention the 18-electron rule, i.e. the rule that clusters with a completely filled outer electron shell have the maximum stability.[23]

Although there are quite a few exceptions to this rule, it is useful in explaining the geometrical structural characteristics of complex organometallic compounds. This applies particularly to transition metal clusters, where simple considerations concerning hybridisation[24] or electron pair repulsion[25] are almost useless.

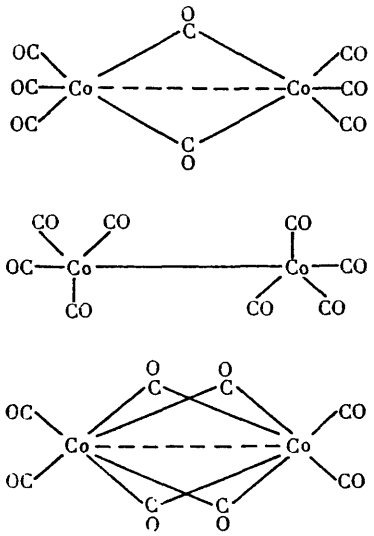


Figure 3. The structures of the dinuclear cobalt carbonyl.[26]

Many unusual structural features of metal carbonyls can be accounted for by a tendency towards the formation of an 18-electron shell. The structure of the polynuclear cobalt carbonyl $Co_2(CO)_8$ (Fig. 3*a*) can be explained from the standpoint of the formation of an 18-electron outer shell configuration. The bridging carbonyl groups form many-centre bonds and formal treatment shows that they each give up one electron to the electron shell of each cobalt atom. The diamagnetism of $Co_2(CO)_8$ indicates the formation of a Co–Co bond. Indeed the Co–Co distance is only 2.5 Å according to X-ray diffraction data.[26] It is of interest to note that in solution a second structure of the above compound (Fig. 3*b*), in which there are no bridging CO groups, coexists with that examined above;[26] this structure also satisfies the 18-electron rule. The hypothetical structure of $Co_2(CO)_8$ illustrated in Fig. 3*c* does not satisfy the 18-electron rule and, as will be shown below, is extremely unstable according to calculations by the method of the electron density functional.

Together with the 18-electron rule, analogies between the structures of cluster organometallic compounds and organopolyhedral molecules have been used in recent years. Hoffmann's principle of isolobality and the skeletal electron counting rules follow from these analogies. Since a careful review has been devoted to these questions,[27] we shall not consider them. The third type of cluster compounds (in our terminology) comprises non-classical organoelemental compounds of the type of polyhedra and *nido*-clusters. A wide variety of non-classical structures having the form of polyhedra (prismane, cubane, congressane) have been observed together with classical structures for molecules made up of carbon and hydrogen atoms only. In 1973 Bochvar and Gal'pern showed with the aid of semiempirical quantum-chemical calculations[28] that even more complex polyhedral carbon clusters can exist: a C_{20} carbododecahedron made up of 12 pentagons and a C_{60} carbo-s-eicosahedron, whose surface is made up of pentagons and hexagons alternating in an unusual manner. In these structures the carbon atoms can be linked by double bonds. Such cluster formations should be regarded as new allotropic modifications of carbon which, in contrast to the familiar graphite, diamond, and carbyne, are monomeric. Complex polyhedra made up solely of carbon and hydrogen atoms or only carbon atoms have not so far been obtained.

Extensive prospects arose in the field of the structural chemistry of polyhedral compounds after the synthesis of carbaboranes whose skeleton is made up of carbon and boron atoms. Table 1[29,30] presents typical boron clusters. A multiplicity of organometallic transition metal complexes based on carbaborane as the ligand have been obtained.[31]

Table 1. Polyhedral boron clusters.

N_a	Borane	Heteroborane	N_e	Polyhedron
4	B_4Cl_4	—	8	tetrahedron
5	$B_5H_5^{2-}$	$B_3C_2H_5$	12	trigonal bipyramid
5	$B_5H_5^{4-}$	—	14	square pyramid
6	$B_6H_6^{2-}$	$B_4C_2H_6$	14	octahedron
6	$B_6H_6^{6-}$	—	18	trigonal prism
7	$B_7H_7^{2-}$	$B_5C_2H_7$	16	pentagonal bipyramid
7	$B_7H_7^{2-}$	—	16	one-cap octahedron
8	$B_8H_8^{2-}$	$B_6C_2H_8$	18	dodecahedron
8	$B_8H_8^{2-}$	—	18	square antiprism
8	$B_8H_8^{2-}$	—	18	two-cap trigonal prism
9	$B_9H_9^{2-}$	$B_7C_2H_9$	20	three-cap trigonal prism
9	$B_9H_9^{2-}$	—	20	one-cap square antiprism
9	$B_2H_9^{4-}$	—	22	one-cap square antiprism
10	$B_{10}H_{10}^{2-}$	$B_8C_2H_{10}$	22	two-cap square antiprism
10	$B_{10}H_{10}^{2-}$	B_9H_9S	22	two-cap square antiprism
12	$B_{12}H_{12}^{2-}$	$B_{10}C_2H_{10}$	26	eicosahedron
12	$B_{12}H_{12}^{2-}$	$B_{11}PH_{12}$	26	eicosahedron
12	$B_{12}H_{12}^{2-}$	—	26	cubo-octahedron

Notation: N_a is the number of atoms in the cluster and N_e the number of skeletal electrons.

Although non-empirical calculations on clusters by the SCF LCAO-MO method are being carried out at the present time,[2] this method for the theoretical study of clusters can hardly be regarded as promising, one reason being that calculations for the cluster compounds of greatest interest from the chemical standpoint are far beyond the limits of the scope of this method.

In the calculation of the stability of the clusters, one must begin with methods in which the electronic correlation energy is taken into account sufficiently completely.[32] Within the framework of the usual non-empirical quantum-chemical methods, this is extremely difficult to achieve because even the calculation for diatomic and triatomic molecules by the configuration interaction method is extremely laborious. In this sense, it appears useful to investigate clusters within the framework of the theory of the electron density functional, which has been employed successfully for the solution of

certain physical problems.[6,14,15,33-40] This theory consists of a quantum-statistical examination of an electron liquid in which atomic nuclei "float". The energy of the ground state of a system consisting of N electrons and M nuclei with the charges z_1, z_2, ..., z_M is represented by the following electron density $\rho(\mathbf{r})$ functional:[6]

$$E[\rho] = -\sum_{\alpha=1}^{M} z_\alpha \int \rho(\mathbf{r}) |\mathbf{r} - \mathbf{R}_\alpha|^{-1} d\tau + \\ + \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2 + \sum_{\alpha<\beta}^{M}\sum^{M} z_\alpha z_\beta |\mathbf{R}_\alpha - \mathbf{R}_\beta|^{-1} + G[\rho], \quad (1)$$

where $\mathbf{r}_i$ is the vector corresponding to the position of the ith electron, $\mathbf{R}_\alpha$ are vectors corresponding to the positions of the atomic nuclei in a three-dimensional cartesian space, and $d\tau_i = dx_i dy_i dz_i$. The functional $G[\rho]$ has not as yet been obtained in an explicit form. However, formally its form is as follows:

$$G[\rho] = \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle - \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2, \quad (2)$$

where $\hat{T}$ is the kinetic energy operator, $\hat{W}$ the interelectron interaction operator, and Ψ a many-electron wave function. The functional $G[\rho]$ includes the kinetic energy $G_t[\rho]$ and the exchange-correlation energy $G_v[\rho]$:

$$G[\rho] = G_t[\rho] + G_v[\rho]. \quad (3)$$

Approximate expressions containing several terms depending on derivatives of the electron density with respect to the coordinates x, y, and z have been found for $G_t[\rho]$ and $G_v[\rho]$ and the individual contributions have been estimated in relation to examples.[38-46] Analysis shows that exchange-correlation energy contributions close to the true values can be obtained for the potential energy with the aid of these expressions. In the case of the kinetic energy, it has been shown that the energy contributions do not decrease sufficiently rapidly as a function of the number of the term of the gradient expansion series, so that the principal inaccuracy of the method of the electron density functional is associated with the approximate form of the kinetic energy.[46] For sufficiently covalent systems, a method for the determination of the kinetic energy from the virial theorem (the virial-statistic approximation) has been recommended.[47-53]

We shall consider the question: what are the advantages of the method of the electron density functional compared with the LCAO-MO method? Firstly, the existence of a direct functional relation between the energy of the system and the electron density makes it possible to construct new and simple models of the chemical bond, which has been demonstrated in a number of studies.[47-53] Secondly, in the theory of the density functional the $3N$-variable problem, where N is the number of electrons, is replaced by a three-variable problem. This is because the exchange-correlation energy is formulated in the form of the electron density functional for the system. The development of the density functional theory has become even more crucial in recent years in connection with the development of methods for the experimental determination of the electron densities of substances.[54] Studies on the calculation of various energy characteristics of crystals from the experimental electron densities or even X-ray reflections are already being carried out.[55,56] The theory of the electron density functional is widely used in the calculations.

In view of the lack of an exact expression for the dependence of the kinetic energy functional on the electron density $G_t[\rho]$, a complete set of methods of the X_α type has been developed in the density functional theory.[9,57-61] In these methods the functional $G_t[\rho]$ is formulated as its quantum-mechanical analogue, so that the kinetic energy of the system is

$$T = \frac{1}{2}\sum_i \int \nabla\varphi_i^* \nabla\varphi_i d\tau, \quad (4)$$

where φ_i are one-particle functions and the summation is carried out over all the occupied spin-orbitals. For spin-polarised systems, the total energy can be formulated in this instance as follows:

$$E[\varphi_{i\alpha}, \varphi_{i\beta}] = -\sum_{\alpha=1}^{M} z_\alpha \int \rho(\mathbf{r}) |\mathbf{r} - \mathbf{R}_\alpha|^{-1} d\tau + \\ + \frac{1}{2}\iint \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} d\tau_1 d\tau_2 + \sum_{\alpha<\beta}^{M}\sum^{M} z_\alpha z_\beta |\mathbf{R}_\alpha - \\ - \mathbf{R}_\beta|^{-1} + \frac{1}{2}\sum_i^{k_\alpha} \int \nabla\varphi_{i\alpha}^* \nabla\varphi_{i\alpha} d\tau + \frac{1}{2}\sum_i^{k_\beta} \int \nabla\varphi_{i\beta}^* \nabla\varphi_{i\beta} d\tau + G_v[\rho_\alpha, \rho_\beta], \quad (5)$$

where ρ_α and ρ_β are the electron densities due to electrons with the spins α and β respectively and

$$\rho_\sigma = \sum_i^{k_\sigma} \varphi_{i\sigma}^* \varphi_{i\sigma}, \quad (6)$$

Where $\varphi_{i\sigma}$ is the spin-orbital wave function for the spin σ and k_σ the number of occupied orbitals for the spin σ. By varying the energy with respect to $\phi_{i\sigma}$, we obtain an equation of the Hartree–Fock type taking into account the exchange-correlation energy determined by the functional $G_v[\rho_\alpha, \rho_\beta]$:

$$\left[-\frac{1}{2}\Delta - \sum_\alpha z_\alpha |\mathbf{r} - \mathbf{R}_\alpha|^{-1} + \int \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} d\tau' + \right. \\ \left. + \frac{\delta G[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma}\right] \varphi_{k\sigma} = \varepsilon_{k\sigma}\varphi_{k\sigma}. \quad (7)$$

The expression for the exchange-correlation potential

$$V_{ex,c}[\rho_\alpha, \rho_\beta] = \frac{\delta G[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma} \quad (8)$$

has a different form in different versions of this method. For example, the following expression is used in the X_α approximation:

$$V_{X_\alpha} = \frac{9\alpha}{2}\left[\frac{3}{4\pi}\rho(\mathbf{r})\right]^{1/3}. \quad (9)$$

The advantages and disadvantages of the potential defined by Eqn. (9) in the X_αSW method, applied to calculations on clusters, chemisorption, and catalysis, have been frequently discussed in the literature.[57-59] Although the known successes of the X_αSW method in calculations on the clusters give rise to some hope, the difficulties due to the arbitrary selection of the atomic sphere radii as well as those in the interpretation of the results engender some scepticism.[62] Other versions of methods of the X_α type, which are the discrete variation method[10-12] and the LSP method,[13,14,16] are free from the disadvantages of the X_αSW method. An appreciable advantage of these procedures is the possibility of using any system of basis functions, including atomic functions, which brings these methods closer to the SCF LCAO-MO procedure.

Certain examples of the employment of simple versions of the theory of the electron density functional for the calculation of the energy characteristics of clusters are presented below and the question of the variation of the bond energy in homoatomic clusters as a function of their size and steric structure is examined.

II. THE ELECTRONIC STRUCTURE AND ENERGY CHARACTERISTICS OF ATOMIC CLUSTERS

In their review Kuz'minskii and Bagatur'yants[2] give a good selection of theoretical studies on the calculation of the electronic structures of metal clusters (mainly the semiempirical EHM, CNDO, etc. methods). The following groups have been examined:

(a) alkali metals (Li_2, Li_3, Li_4, Li_5, Li_6, Li_7, Li_8, Li_9, Li_{10}, Li_{13}, Na_2, Na_3, Na_4, Na_8, K_2, K_3);

(b) alkaline earth metals (Be_2, Be_4, Mg_2, Ca_2, Sr_2, Ba_2);

(c) aluminium group metals (Al_2, Al_5, Al_9, Al_{13}, Al_{19}, Al_{25}, Al_{43}, Al_{59}, Ga_2, In_2, Tl_2);

(d) heavy elements (Sn_2, Pb_2, Bi_2);

(e) noble metals and Group IIB metals (Cu_2, Cu_3, Cu_4, Cu_5, Cu_6, Cu_8, Cu_9, Cu_{10}, Cu_{13}, Cu_{16}, Cu_{19}, Cu_{31}, Cu_{39}, Cu_{43}, Ag_2, Ag_6, Ag_7, Ag_8, Ag_{10}, Ag_{13}, Ag_{19}, Ag_{43}, Ag_{55}, Au_2, Au_6^{2+}, Au_9^{3+}, Au_{11}^{3+}, Zn_2, Cd_2, Cd_{28});

(f) transition metals (Ti_2, Ti_3, Ti_4, Ti_5, Ti_6, V_2, Cr_2, Cr_3, Cr_4, Cr_5, Cr_6, Mn_2, Mn_{13}, Fe_2, Fe_3, Fe_4, Fe_5, Fe_6, Fe_9, Fe_{15}, Co_2, Ni_2, Ni_3, Ni_4, Ni_5, Ni_6, Ni_9, Ni_{13}, Ni_{14}, Pd_2, Pd_{12}, Pd_{19}, W_9, Pt_{13}).

Together with the homoatomic clusters, the above review[2] also quotes the results of calculations (mainly by semiempirical methods) on bimetallic heteroatomic clusters and clusters on a support.

A simple non-empirical version of the theory of the density functional, namely the virial-statistical approximation, has been used[63] to investigate the clusters. In this approximation the kinetic energy is determined from the relation between the virial theorem for the equilibrium interatomic distances in the cluster:

$$T[\rho] = -\frac{1}{2}V[\rho]. \qquad (10)$$

The total energy is then defined by the following formula:

$$E[\rho] = \frac{1}{2}V[\rho]. \qquad (11)$$

The sum of the atomic densities

$$\rho(\mathbf{r}) = \sum_{\alpha}\rho_{\alpha}(\mathbf{r}), \qquad (12)$$

where $\rho_\alpha(\mathbf{r})$ are the Hartree–Fock electron densities of the corresponding atoms α in a free state, was selected in this instance as the approximation for electron density for homoatomic systems. In the simple statistical theory (the TFD equation), Eqn.(12) for the electron density in a homoatomic molecule is fairly rigorous, which has been noted in the studies of Firsov[64] and (later) Slater.[65] Slater notes that the practical experience gained in X_α calculations has shown that Eqn.(12) for the density of the homoatomic molecules is a fairly satisfactory approximation. Analysis of non-empirical calculations[66,67] has also shown that the formation of homoatomic molecules from atoms does not entail a significant redistribution of electron density (the H_2 molecule is an exception).

The bond energies in homonuclear diatomic molecules made up of the atoms of non-transition elements ranging from Li_2 to Bi_2, calculated in terms of the virial-statistical approximation, are compared in Fig. 4 with the experimental values.[68] The atomic electron densities for the ground state in terms of a one-exponential basis set of the Slater type were used in the calculation. In the evaluation of the bond energy no adjustable parameters were employed and account was taken of all the electron shells of the atoms, both valence and skeletal. The distances between the atoms in the diatomic molecules were assumed to be equal to the experimental values.[68] In those cases where the experimental interatomic distances are not available, they were estimated from the formula

$$R(\text{Å}) = 0.3500 + 1.6072\, r_M, \qquad (13)$$

where r_M are the atomic radii of the elements.[69,70]

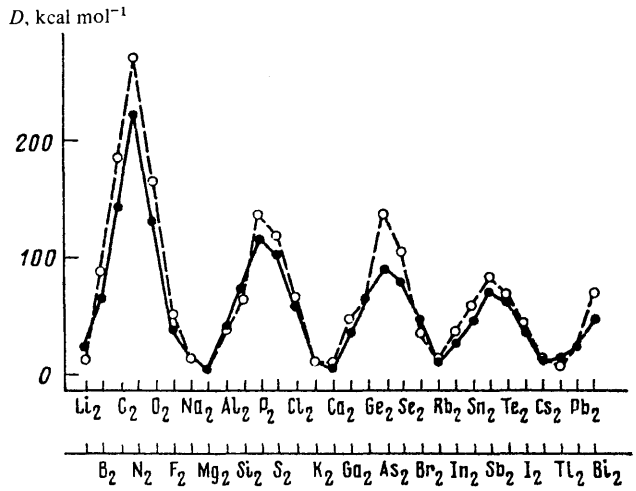


Figure 4. Comparison of the experimental (continuous line) and calculated (dashed line) bond energies in diatomic homonuclear molecules of non-transition elements.[63]

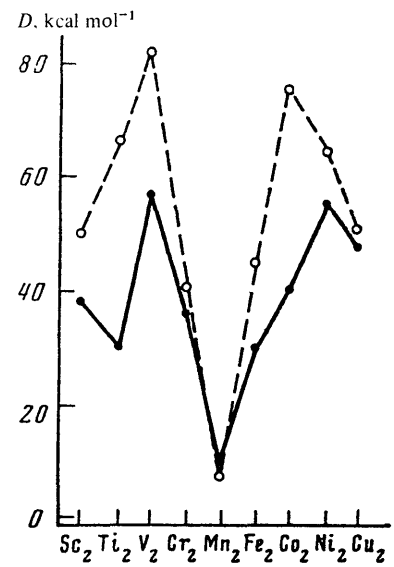


Figure 5. Comparison of the experimental (continuous line) and calculated (dashed line) bond energies in diatomic homonuclear molecules of the elements in the Fourth Period in Mendeleev's Table.[71]

A distinct qualitative agreement between the results of the calculations and the experimental data is observed. It is noteworthy that the non-empirical SCF LCAO-MO method,

which takes into account the electron correlation energy to only an insignificant extent, does not yield even a qualitatively correct picture of the changes in bond energy. In particular, for the fluorine molecule the SCF LCAO-MO calculation does not produce even a positive bond energy. The analogous relations for diatomic gas-phase molecules of the transition metals in the Fourth Period are presented in Fig. 5.[71]

The method described above has been used[63] to calculate the bond energies in the gas-phase sulphur molecules polymerised to different extents. Clusters having the compositions S_4, S_5, S_6, S_7, S_8, S_9, S_{10}, S_{11}, and S_{18} were examined. The geometrical parameters used in the calculations were taken from a theoretical calculation by the method of molecular dynamics.[72] This choice of molecular geometry is dictated by the fact that the experimental studies of S_N structures have been carried out only for a small class of compounds and their results are frequently contradictory. The calculated bond energies, evaluated per sulphur atom, for different molecules and the available experimental data are compared in Table 2. The calculations showed that the S_8 cluster in the form of a ring has the most stable configuration. It is known that orthorhombic crystalline sulphur, in which layers of cyclic S_8 molecules are stacked,[73] is thermodynamically stable. Table 2 also yields the results of calculations on diatomic molecules and tetrahedral clusters of phosphorus and arsenic (Fig. 1);[63] the calculated bond energies per atom have been compared with experimental values.[68] In agreement with the experiment, the calculation shows that the tetrahedral P_4 and As_4 clusters are more stable at low temperatures than the diatomic molecules.

Table 2. Comparison of the calculated and experimental bond energies D of sulphur, phosphorus, and arsenic molecules*.

System	D_{theor}/N, kcal mol^{-1}	D_{exp}/N, kcal mol^{-1}	System	D_{theor}/N, kcal mol^{-1}	D_{exp}/N, kcal mol^{-1}
S_4	66.2	55.94	S_{10}	75.1	—
S_5	71.6	60.43	S_{11}	74.0	—
S_6	72.2	61.60	S_{18}	73.8	—
S_7(Cs)	73.7	61.78	P_2	67.2	58.0
S_7(C_2)	74.8	—	P_4	83.5	71.9
S_8	85.3	62.62	As_2	57.9	45.5
S_9	71.8	—	As_4	73.7	63.3

*Here and henceforth D/N is the bond energy calculated per atom.

Two allotropic forms of carbon, namely graphite and diamond, for which there also exist submodifications involving a change in long-range order, were known previously. In 1978 Korshak et al.[74] discovered carbyne—the third form of carbon, consisting of filamental polymers made up of carbon atoms only. A series of quantum-chemical studies of the character of the bond in carbyne (see, for example, Stankevich and Tomilin[75]) have been carried out. It has been shown that the bonds in carbyne can alternate. Calculations have been made[63] for clusters of three allotropic forms of a carbon—graphite, diamond, and α-carbyne. Fig. 6 presents the calculated dependence of the bond energy per carbon atom on the size of the carbon cluster. The horizontal lines indicate the corresponding bond energy for crystals obtained in terms of the same approximations as those employed in the calculations on the clusters.[76] It is seen from Fig. 6 that the calculated stability series for the three allotropic forms of the carbon crystal agrees qualitatively with experiment: graphite > diamond > carbyne. When carbon clusters containing less than 20 atoms are examined, the stability series is different than for crystals: carbyne > graphite > diamond. When the number of atoms in the cluster is more than 20, a change in the above sequence takes place—curves *1* and *3* intersect (graphite > carbyne > diamond). It is seen from these calculations that, depending on the size of the clusters, the energy relations between different modifications vary. Analysis of the curves for the C_N clusters with $N \leq 50$ and data for crystals gives rise to the hypothesis that, for certain finite dimensions of the clusters, curves *2* and *3*, corresponding to diamond and carbyne, should intersect. On this basis, one may conclude that the carbyne molecule is thermodynamically stable only for a finite chain length. On further increase of its size, it should be converted into a more stable form, for example into a structure with cross-links between the polymer chains.

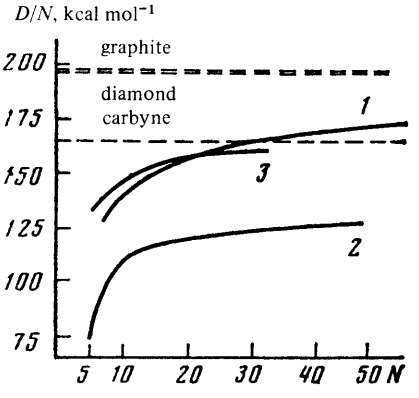


Figure 6. Dependence of the bond energies calculated per atom on the size of carbon clusters: 1) graphite; 2) diamond; 3) carbyne.[63]

Certain hypothetical carbon systems, which are formed as a result of the appearance of regular cross-links between the carbon chain macromolecules, having fourfold screw symmetry axes have been proposed.[77] In one of the hypothetical structures (I) each chain is surrounded by four chains of the same chirality ($I4_132$ symmetry group, identical lengths of all the bonds), while in another structure (II) each chain is surrounded by four chains of opposite chirality ($I\bar{4}m2$ symmetry group, the geometry is described in terms of two parameters: the bond length r_1 between neighbouring atoms in different chains and the bond length r_2 between neighbouring atoms in the same chain with $r_1 < r_2$).

Calculations have been made[78] of the bond energies for six crystalline modifications of carbon: graphite, diamond, α-carbyne, β-carbyne, and the two hypothetical systems (I) and (II). The results of these calculations are presented in Table 3. Evidently the hypothetical modification (I) is much more stable than the carbyne structures (α and β).

The different types of behaviour of the bond energy in carbon clusters as a function of their size for different allotropic forms are caused primarily by the different degrees of unsaturation of the bonds in the clusters. Diamond is a

three-dimensional crystal, graphite is close to a two-dimensional crystal, while carbyne is close to a one-dimensional crystal.

Table 3. The relative energies ΔE of various forms of carbon.[78]

Modification	ΔE, kcal mol^{-1}	Modification	ΔE, kcal mol^{-1}
Graphite	0.0	(II)	32.5
Diamond	1.5	β-Carbyne	33.0
(I)	7.4	α-Carbyne	32.8

The main conclusion which can be reached on the basis of the calculations for the carbon clusters is as follows: the energies of the "phase" transformations of the carbon clusters depend significantly on their dimensions, varying not only in absolute magnitude but also in sign. The question arises of the size of the cluster up to which one can speak of changes in its state of aggregation or a phase transition. Computer experiments performed for systems with a Lennard-Jones interaction potential have shown that phase transitions are observed for clusters consisting of ten particles.[79]

The dependence of the bond energy on the size of the cluster has been studied in greatest detail for alkali metals, particularly lithium. A scheme describing the growth of the lithium crystal has been proposed[80] on the basis of non-empirical calculations. It is noteworthy that the bond energies calculated in the above study[80] per atom for structures most favoured by energy factors increase monotonically for small dimensions of the clusters ($N \leq 5$) and then remain approximately constant at 9–12 kcal mol^{-1} (as N varies from 5 to 13).

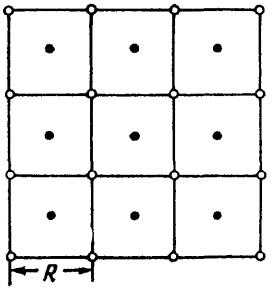


Figure 7. The geometrical structure of lithium clusters.[81]

Within the framework of the method of the gradient expansion of the energy, a study has been made[81] of the variation of the equilibrium distances and bond energies per atom for clusters of the type Li_N with N varying from 9 to 100. These are apparently the largest clusters for which theoretical calculations have been made (disregarding clusters in systems with a simple interaction potential of the Lennard-Jones type). It is noteworthy that, in contrast to the study of Fantucci and Balzarini,[80] Borisov[81] carried out a calculation for a fixed spatial symmetry of the clusters. Fig. 7 illustrates the geometrical structure of lithium clusters for the body-centred cubic lattice used in Borisov's calculations on clusters.[81] The cluster is made up of two types of layers: a layer of type L_1, designated by filled circles and containing 9 lithium atoms, and a layer of type L_2, designated by open circles and containing 16 lithium atoms. The distance between the layers is $R/2$, where R corresponds to the closest Li–Li distance within the limits of one layer. For example, the Li_{50} cluster consits of four layers: $L_1L_2L_1L_2$.

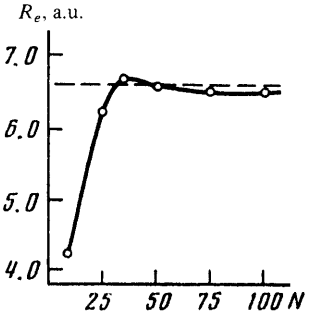


Figure 8. Dependence of the equilibrium Li–Li distance in the Li_N clusters on N.[81]

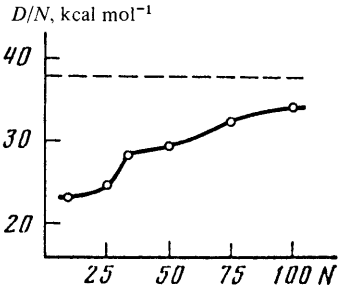


Figure 9. Dependence of the bond energy calculated per atom on the size of the lithium clusters.[81]

The energy of the Li_N clusters was optimised for each cluster with respect to the distance R. Fig. 8 illustrates the calculated dependence of the equilibrium distance R_e (in a.u.) in the Li_N clusters on N for a body-centred cubic structure. The dashed line corresponds to the experimental equilibrium distance R_e for a lithium crystal with a body-centred cubic lattice. Fig. 8 shows that, for low values of N, a marked dependence of R_e on the size of the clusters is observed. For clusters containing 34 lithium atoms, there is virtually no dependence of R_e on N. Fig. 9 presents the dependence of the bond energy per atom on the size of the Li_N clusters. The curve illustrated has a lower slope than the $R_e(N)$ curve and approaches fairly closely the corresponding experimental value for the crystal listed in Table 4.[76] The calculated bond energies have been compared with the available experimental

values.[68] Calculations for the Li_{50} clusters[81] in the body- and face-centred structures have shown that the latter structure is more favourable as regards energy, the difference between the energies amounting to 1.8 kcal mol^{-1}. For comparison, one may note that the corresponding difference for crystals is 0.3 kcal mol^{-1} (Table 4)[76] and the experimental difference is 0.49 kcal mol^{-1}.[82] Consequently the energy of the fcc → bcc "phase" transformation in the lithium clusters decreases with increase in the size of the cluster but does not change sign (in contrast to the transformations in the graphite–diamond–carbyne carbon system).

Table 4. The results of calculations for alkali metal crystals.[76]

Metal	Structure	$-E_{theor}$, a.u.	D_{theor}, kcal mol^{-1}	D_{exp}, kcal mol^{-1}
Li	hex.	7.4120	47.9	—
Li	BCC	7.4114	47.5	37.7
Li	FCC	7.4119	47.8	—
Na	BCC	158.4455	30.4	25.8
Na	FCC	158.4460	30.7	—
K	BCC	581.8500	31.3	21.5
Rb	BCC	2839.9763	22.6	19.6

Notation: E is the total energy of the crystal, hex. a hexagonal lattice, BCC a body-centred cubic lattice, and FCC a face-centred cubic lattice.

III. STABILITY OF ORGANOELEMENTAL CLUSTERS

So far few studies have been published on the calculation of the electronic properties of organometallic polynuclear clusters. Only calculations for individual cluster compounds can be encountered in the literature. The most general question for organometallic clusters is that of the character of the metal–metal bond, which has been discussed in a series of reviews (see, for example, Cotton and Chisholm.[20] The fact that the shortest distances are observed in complexes with bridging ligands has attracted attention in the analysis of the interatomic metal–metal distances in homopolymetallic π-complexes.[83] However, certain calculations have shown that the metal–metal bond is absent precisely in compounds of this type and the cluster is stabilised by interactions via bridges. Thus non-empirical calculations have been performed[84] for two cluster complexes: $Fe_3(CO)_{12}$ and $[C_5H_5Fe(CO)_2]_2$. Fig. 10 illustrates schematically the structures of these clusters. In the $Fe_3(CO)_{12}$ complex (Fig. 10a) and Fe(1) and Fe(2) atoms are joined via two bridging CO groups. Analysis of the occupied molecular orbitals (MO) has shown that there are no MO in which there is a linkage between the *d* orbitals of the Fe atoms. An analogous picture has been observed for the $[C_5H_5Fe(CO)_2]_2$ complex illustrated in Fig. 10b. Thus, despite the short M–M interatomic distances, there is no direct interaction between the metal atoms in the complexes indicated.

Calculations for the dinuclear nickel complex $(\eta^5\text{-}C_5H_5Ni)_2 . C_2H_2$ have confirmed the existence of a single σ-bond between the nickel atoms. Calculations for the $M_2Cl_4(PR_3)_4$ (M = Mo or W) complexes by the X_αSW method have been carried out in a recent study[86] (Fig. 11). They showed that the M–M bond in these complexes is quadruple and that the bonding molecular orbitals are of the σ, π, and δ types. The calculated[86] electronic transition energies have been fully confirmed by experiment (photoelectron spectroscopy). Thus the multiplicities of the M–M bonds in transition metal cluster compounds can vary from zero to four.

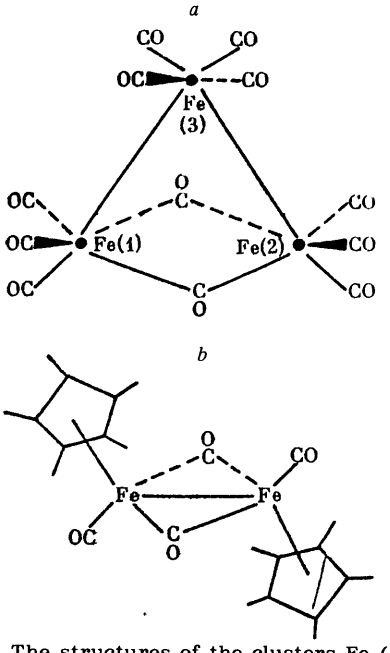


Figure 10. The structures of the clusters $Fe_3(CO)_{12}$ (*a*), $[C_5H_5Fe(CO)_2]_2$ (*b*).[84]

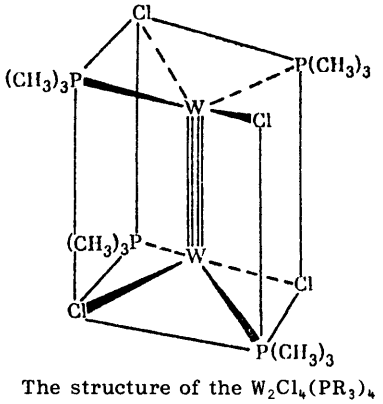


Figure 11. The structure of the $W_2Cl_4(PR_3)_4$ cluster.[86]

The study of the $Co_2(CO)_9$ cluster by various physical methods (infrared spectroscopy and X-ray diffraction)[26] showed that the compound has different structures under different conditions. According to the results of X-ray diffraction analysis,[26] the $Co_2(CO)_8$ solid phase has a structure with two C = O bridge bonds (Fig. 3*a*). In solution form (II) (Fig. 3*b*) coexists with this structure [form (I)], and the ratio of these forms can vary as a function of temperature. Whereas form (I) predominates at low temperatures, at room

temperature the concentration of form (II) is ~50%. Calculations of the atomisation energies for three structures of the dinuclear cobalt carbonyl have been carried out.[71] Structure (III), illustrated in Fig. 3*a* is hypothetical and no evidence for its existence has been obtained. Calculations have shown that stability decreases in the following sequence of structures: (I) > (II) > (III). Structure (III) proved to be least favourable on energy grounds and is hardly likely to exist. As mentioned above, the 18-electron rule also does not hold for this structure. The ease of the interconversion of structures (I) and (II) is indicated by purely chemical investigations. A study of the reaction involving the exchange of CO groups showed that all eight CO groups of the complex can be readily exchanged. Apparently equilibrium is established during the exchange reaction between forms (I) and (II) of the dinuclear cobalt carbonyl.[26]

Table 5. Certain characteristics of transition metal clusters.

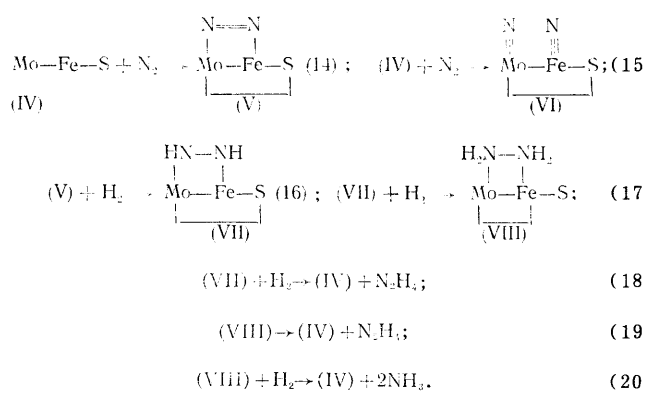
Geometry	N	n_u	n_c	Cluster
Monomer	1	0	9	$Ni(CO)_4$
Dimer	2	1	17	$Fe_2(CO)_9$
Trimer	3	3	24	$Os_3(CO)_{12}$
Tetrahedron	4	6	30	$Rh_4(CO)_{12}$
"Butterfly"	4	5	31	$Re_4(CO)_{16}^{2-}$
Planar square	4	4	32	$Pt_4(O_2CCH_3)_8$
Trigonal bipyramid	5	9	36	$Os_5(CO)_{16}$
Square pyramid	5	8	37	$Fe_5(CO)_{15}C$
Two-cap tetrahedron	6	12	42	$Os_6(CO)_{18}$
Octahedron	6	11	43	$Rh_6(CO)_{15}C$
One-cap square pyramid	6	11	43	$Os_6(CO)_{18}H_2$
Corner-linked bitetrahedron	6	11	43	—
Pentagonal pyramid	6	10	44	—
Trigonal prism	6	9	45	$Rh_6(CO)_{15}C$
One-cap octahedron	7	14	49	$Rh_7(CO)_{16}^{3-}$
One-cap trigonal prism	7	12	51	—
Two-cap octahedron	8	17	56	—
Square antiprism	8	15	57	$Co_8(CO)_{20}C^{2-}$
Two-cap trigonal prism	8	15	57	—
Cube	8	12	60	$Ni_8(PC_6H_5)_6(CO)_8$
Three-cap octahedron	9	18	63	—
Three-cap trigonal prism	9	17	64	—
One-cap square antiprism	9	16	65	—
One-cap cube	9	15	66	—
Two-cap cube	10	19	71	—
Two-cap square antiprism	10	19	71	—
Three-cap trigonal bypyramid	12	28	80	—
Eicosahedron	12	23	85	—
Three-cap hexagonal bipyramid	13	32	85	$Rh_{13}(CO)_{24}H_3^{2-}$
Face-centred cube	14	36	90	—

Notation: N is the number of atoms in the cluster, n_u the number of unoccupied orbitals, and n_c the number of cluster bond orbitals.

Whereas the structure of $Co_2(CO)_8$ most favoured by energy factors has bridge bonds, a direct M–M bond has been observed in the dinuclear manganese and technetium carbonyls. The energies of the M–M bond in the dinuclear $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ clusters have been estimated[87] within the framework of the virial-statistical approximation:[48,49] 52 and 100 kcal mol^{-1} have been obtained for $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ respectively, which exceeds the experimental values by a factor of approximately 2. Such unduly high calculated bond energies are apparently associated with the fact that no account had been taken of the relaxation of the bonds remaining after the rupture of the metallic bond. Thus the calculation and experiments showed that the bond strength increases on passing to heavier elements in the Periodic Table. This is a general phenomenon due to the increase of the degree of overlap of the atomic orbitals of the heavier elements and explains the increased ability of heavy transition metals to produce polynuclear carbonyl complexes.

There are as yet no quantitative theories of the dependence of the ability to form cluster compounds on the nature of the metal. However, qualitative aspects have been discussed[22] and have been justified by EHM calculations. The molecular orbitals of a cluster formed by transition metals can be divided into two classes: the unoccupied antibonding orbitals (UAO) and cluster valence orbitals (CVO). Only the CVO are suitable in terms of energy for combining with ligands and for ensuring the stability of the metallic skeleton of the cluster. Table 5[22] lists certain characteristics of transition metal clusters; it also includes examples of stable clusters corresponding to specified values of N, a specified geometry, and a specified number of valence electron n_k in the cluster valence orbitals. The n_k-electron rules are in fact extensions of the 18-electron rule to mononuclear transition metal complexes ($n_k = 18$ for $N = 1$).

It is known that metal clusters can behave as catalytic centres in various chemical reactions.[29] A simplified mechanism of the binding of nitrogen on the Mo–Fe–S model cluster, to which an important role has been attributed in the biological fixation of nitrogen, has been examined.[71] A scheme for the hydrogenation of nitrogen on the Mo–Fe–S dinuclear cluster, which is similar to that proposed by Likhtenshtein and Shilov for the catalytic hydrogenation of nitrogen in the presence of complex homogeneous catalysts, is presented below:[88]



The atomisation energies of the intermediate forms (V)–(VIII) have been calculated. The bond lengths and angles have been taken from Hardy et al.[89] and the missing interatomic distances have been determined as the sums of the covalent atomic radii.

Table 6 lists the calculated heats Q of individual stages of the reaction. Only a qualitative comparison of the heats Q is possible, because, apart from the roughness of the approximations, no account has been taken in the calculation of effects such as the influence of the protein component of the nitrogenase molecule, the pH of the medium, temperature, etc. It follows from the calculations that stage (15) is very highly endothermic. It is therefore possible to reject immediately the nitride mechanism of nitrogen fixation. In the hydrazine mechanism stage (16) is slowest and results in the formation of diimide coordinated to the catalyst. In order to estimate approximately the activation energies for the individual stages in the hydrogenation of nitrogen, we shall make use of the Brønsted–Semenov relation between the activation energy and the heat of reaction:

$$E_{act} = A_0 + 0.75\,|Q| \qquad (21)$$

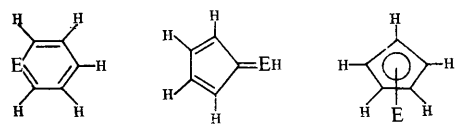
$$E_{act} = A_0 - 0.25\,|Q| \qquad (22)$$

for the endothermic and exothermic reactions respectively. Assuming that stage (14) takes place without an activation energy (this hypothesis does not alter the qualitative conclusions), we shall determine the unknown value of A_0 from Eqn.(22). Assuming further that A_0 does not change on passing from one stage to another (for radical reactions, this approximation holds[90]), the activation energies E_{act} were calculated for all the intermediate stages of the nitrogen hydrogenation reaction (Table 6). Comparison of the activation energies for the individual stages leads to the following probable pathway in the nitrogen hydrogenation reaction: (14) → (16) → (17) → (20). It was found that this pathway leads to the reduction of nitrogen to ammonia. The formation of less reduced forms is energetically unfavourable, in agreement with experiment.

Table 6. The calculated values of Q and E_{act} (kcal mol^{-1}).[71]

Stage	(14)	(15)	(16)	(17)	(18)	(19)	(20)
Q	31.5	−94.1	−50.4	18.9	0.0	−18.9	25.2
E_{act}	0.0	—	45.5	3.5	8.0	12.5	2.0

The mass spectra of π-cyclopentadienyliron carbonyl complexes π-$C_5H_5Fe(CO)_2ER_3$ containing an Fe–E bond, where E is a Group IV element (E = Si, Ge, Sn, or Pb) show intense peaks due to the $C_5H_5E^+$ ions whose intensity is sometimes a maximum.[91–96] They arise as a result of a complex rearrangement from molecular or decarbonylated ions $C_5H_5FeER_3$ (R = alkyl or halogen). This rearrangement takes place with the simultaneous involvement of at least nine bonds and has a very low activation energy. The unusually high intensity of the peaks due to the $C_5H_5E^+$ ions indicates their high stability. It is possible to put forward three possible structures of this ion, namely the elementophenyl (a), the elementofulvenyl (b), or the *nido*-cluster (c):



a *b* *c*

A calculation[97] of the atomisation energies of these structures of the $C_5H_5Ge^+$ ions showed that the structure of the *nido*-cluster has the highest stability. Similar calculations were later performed[98] for all the Group IV elements and it was shown that in all cases the cluster ions are more stable than the isomeric elementophenyl and elementofulvenyl ions and that their stability increases on passing from lead to carbon. The conclusion that the *nido*-cluster has the highest stability agrees with non-empirical calculations for $C_5H_5Si^+$ [99] and semiempirical calculations for the $C_5H_5Si^+$ and $C_5H_5C^+$ ions.[100] It is noteworthy that the predicted[97] stability of the *nido*-cluster of germanium has been confirmed by the synthesis of a compound containing this ion in the form of a *nido*-cluster.[101,102]

Calculations have been performed[103] by the SCF LCAO-MO method in the CNDO/2 approximation for the *nido*-clusters $C_5H_5E^q$, where E are the elements of the First and Second Periods (from H to Ne) and q assumes values of +1, 0, and −1. It was found that the stability of the *nido*-clusters increases with increase of the nuclear charge of the atom E, reaches a maximum, and then again falls towards the end of the Second Period. The $CpBe^-$, CpB, and CpC^+ clusters, in which the eight-electron shell is formally filled, show the highest stability under these conditions. Together with the $Me_5C_5Sn^+$ and $Me_5C_5Ge^+$ *nido*-clusters,[101,102] there exist stable molecules of the semi-sandwich type with an eight-electron shell, namely CpIn and CpTe.[104] On the basis of the results of an investigation,[103] it is possible to put forward the existence of the following *nido*-cluster: CpE^+ (E = C, Si, or Pb), CpE (E = B, Al, or Ga), and CpE^- (E = Be or Mg).

The numerous calculations for clusters of three types ("isolated" homoatomic, polynuclear organometallic, and *nido*-clusters) examined above show that the method of the electron density functional makes it possible to solve many interesting problems involving the energy relations of clusters even in its simple versions. Hitherto these simple versions have been applied to fairly covalent clusters, for which it is possible to neglect the charge transfer between the atoms (or ions). This is because the electron density of the system can be approximated by the sum of the electron densities of the free atoms (or ions).

In the future the method of the electron density functional can develop in two directions when applied to cluster theory: (1) with allowance for charge transfer between the atoms (or ions) by including the corresponding variational parameters in the electron density function, as, for example, has been done by Borisov;[46] (2) with analysis of the experimental electron densities to obtain an approximation to $\rho(\mathbf{r})$ in energy calculations, as has been done for crystals.[55,56] These improvements will naturally lead to certain complications in the calculations but the latter will nevertheless be much simpler than the calculations by the traditional quantum-chemical methods of the type of SCF LCAO-MO. Together with this, one-electron approaches based on the formal treatment of Kohn and Sham,[15] where the electron correlation is taken into account in the form of the electron density functional, show much promise for the calculation of the electronic structures of cluster compounds.

REFERENCES

1. H.H.Dunken and V.Lygin, "Quantum Chemsitry of Adsorption on the Surface of Solids" (Translated into Russian), Izd.Mir, Moscow, 1980, p.208.
2. M.B.Kuz'minskii and A.A.Bagatur'yants, "Itogi Nauki i Tekhniki.Kinetika i Kataliz" (Advances in Science and Engineering. Kinetics and Catalysis), Izd.VINITI, Moscow, 1980, Vol.8, p.99.
3. N.D.Chuvylkin and G.M.Zhidomirov, "Itogi Nauki i Tekhniki. Kinetika i Kataliz" (Advances in Science and Engineering. Kinetics and Catalysis), Izd.VINITI, Moscow, 1980, Vol.8, p.3.
4. N.H.March, W.H.Young, and S.Sampanthar, "The Many-Body Problem in Quantum Mechanics" (Translated into Russian), Izd.Mir, Moscow, 1969, p.19.
5. D.A.Kirzhnits et al., Uspekhi Fiz.Nauk, 1975, 117,3.
6. P.Hohenberg and W.Kohn, Phys.Rev., B 1964, 136, 864.
7. T.L.Gilbert, Phys.Rev., 1975, B12, 2111.
8. V.Yu.Kolmanovich and I.M.Reznik, Dokl.Akad.Nauk SSSR, 1981, 285, 1100.
9. J.C.Slater, "International Series in Pure and Applied Physics", Vol.4, "The Self-consistent Field for Molecules and Solids in Quantum Theory" (Translated into Russian), Izd.Mir, Moscow, 1978, p.35.

10. D.E.Ellis and G.S.Painter, Phys.Rev., 1970, B2, 2887.
11. E.J.Baerends, D.E.Ellis, and P.Ros, Chem.Phys. 1973, 2, 41.
12. G.L.Gutsev and A.A.Levin, Zhur.Strukt.Khim., 1978, 19, 976.
13. O.Gunnarsson and B.I.Lundqvist, Phys.Rev., 1976, B13, 4274.
14. A.K.Rajagopal, Adv.Chem.Phys., 1980, 41, 59.
15. W.Kohn and L.J.Sham, Phys.Rev., A, 1965, 140, 1133.
16. O.Gunnarsson, J.Harris, and R.O.Jones, Int.J. Quant.Chem., Symp., 1977, 10, 71.
17. O.Gunnarsson, J.Harris, and R.O.Jones, J.Chem. Phys., 1977, 67, 3970.
18. V.L.Moruzzi, J.F.Janak, and A.R.Williams, "Calculated Electronic Properties of Metals", Pertamon Press, New York 1978.
19. E.L.Muetterties, Chem.Eng.News, 1982, 60, 28.
20. F.A.Cotton and M.H.Chisholm, Chem.Eng.News, 1982, 60, 40.
21. K.Wade, Chem.Comm., 1971, 792.
22. J.P.Lauher, J.Amer.Chem.Soc., 1978, 100, 5305.
23. D.A.Bochvar and N.P.Gambaryan, in "Metody Elementoorganicheskoi Khimii, Tipy Metalloorganicheskikh Soedinenii Perekhodnykh Metallov" (Methods of Organoelemental Chemistry. Types of Ortanometallic Compounds of Transition Metals), Izd.Nauka, Moscow, 1975, p.9.
24. C.A.Coulson, "Valency" (Translated into Russian), Izd.Mir, Moscow, 1965, p.211.
25. R.Gillespie, "Molecular Geometry" (Translated into Russian), Izd.Mir, Moscow, 1975, p.11.
26. R.A.Sokolik, in "Metody Elementoorganicheskoi Khimii, Tipy Metalloorganicheskikh Soedinenii Perekhodnykh Metallov" (Methods of Organoelemental Chemistry. Types of Organometallic Compounds of Transition Metals), Izd.Nauka, Moscow, 1975, p.19.
27. V.I.Minkin and R.M.Minyaev, Uspekhi Khim., 1982, 51, 586 (Russ.Chem.Rev.).
28. D.A.Bochvar and E.G.Gal'pern, Dokl.Akad.Nauk SSSR, 1973, 209, 610.
29. E.L.Muetterties, T.N.Rhodin, E.Band, C.F.Brucker, and W.R.Pretzer, Chem.Rev., 1979, 79, 91.
30. R.N.Grimes, "Carboranes" (Translated into Russian), Izd.Mir, Moscow, 1974.
31. L.I.Zakharkin and V.N.Kalinin, Uspekhi Khim., 1974, 43(7), 1207 [Russ.Chem.Rev., 1974(7)].
32. N.G.Rambidi, N.F.Stepanov, and A.I.Dement'ev, "Itogi Nauki. Stroenie Molekul i Khimicheskaya Svyaz'" (Advances is Science. Molecular Structure and the Chemical Bond), Izd.VINITI, Moscow, 1979, Vol.7, p.111.
33. H.Hodges, Canad.J.Phys., 1973, 51, 1428.
34. Y.Tal and F.W.Bader, Int.J.Quant.Chem., 1978, 12, 153.
35. D.A.Kirzhnits, Trudy FI Akad.Nauk SSSR, 1961, 16, 3.
36. M.B.Partenskii, Uspekhi Fiz.Nauk, 1979, 128, 69.
37. A.S.Bamzai and B.H.Deb, Rev.Mod.Phys., 1981, 53, 95.
38. D.A.Kirzhnits, Zhur.Eksper.Teor.Fiz., 1957, 32, 115.
39. N.D.Lang, Solid State Physics, 1973, 28, 225.
40. A.K.Rajagopal and S.P.Singhal, Phys.Rev., 1977, B16, 601.
41. Yu.A.Borisov, Zhur.Strukt.Khim., 1978, 19, 3.
42. Yu.A.Borisov, Zhur.Strukt.Khim., 1978, 19, 726.
43. Yu.A.Borisov and V.V.Surikov, Zhur.Strukt.Khim., 1981, 22, 164.
44. Yu.A.Borisov and V.V.Surikov, Zhur.Strukt.Khim., 1981, 22, 166.
45. Yu.A.Borisov, Zhur.Strukt.Khim., 1983, 24, 141.
46. Yu.A.Borisov, Chem.Phys.Letters, 1982, 93, 197.
47. Yu.A.Borisov, Dokl.Akad.Nauk SSSR, 1975, 224, 1330.
48. Yu.A.Borisov, Zhur.Strukt.Khim., 1976, 17, 974.
49. Yu.A.Borisov, Zhur.Strukt.Khim., 1976, 17, 979.
50. Yu.A.Borisov, Zhur.Strukt.Khim., 1977, 18, 29.
51. Yu.A.Borisov, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 16.
52. D.A.Bochvar and Yu.A.Borisov, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1166.
53. Yu.A.Borisov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1917.
54. V.G.Tsirel'son and R.P.Ozerov, Zhur.Strukt.Khim., 1978, 19, 558.
55. A.A.Varnek, V.G.Tsirel'son, and R.P.Ozerov, Dokl. Akad.Nauk SSSR, 1981, 257, 382.
56. J.Bentley, J.Chem.Phys., 1979, 70, 159.
57. K.H.Johnson and R.P.Messmer, Int.J.Quant.Chem., 1976, S10, 147.
58. K.H.Johnson and R.P.Messmer, J.Vacuum Sci. Technol., 1974, 11, 236.
59. K.H.Johnson, Colloq.Int.CNRS, 1977, (255), 27.
60. G.V.Gadiyak et al., Zhur.Strukt.Khim., 1982, 23, 125.
61. G.M.Zhidomirov et al., in "Metody Kvantovoi Khimii" (Methods of Quantum Chemistry), Chernogolovka, 1979, p.81.
62. P.Rennert, Acta.Phys.Hung., 1974, 37, 219.
63. Yu.A.Borisov and N.I.Raevskii, Zhur.Strukt.Khim., 1982, 23, 10.
64. O.B.Firsov, Zhur.Eksper.Teor.Fiz., 1957, 32, 1464.
65. J.C.Slater, Int.J.Quant.Chem., 1975, S9, 7.
66. S.Bratoz, R.Daudel, M.Roux, and M.Allaven, Rev. Mod.Phys., 1960, 32, 412.
67. R.F.Bader, W.H.Henneker, and P.E.Cade, J.Chem. Phys., 1967, 46, 3341.
68. Handbook, "Molekulyarnye Postoyannye Neorganicheskikh Soedinenii" (Molecular Constants of Inorganic Compounds), Izd.Khimiya, Leningrad, 1979, p.10.
69. A.G.Ryabukhin, Zhur.Fiz.Khim., 1979, 53, 2356 [Russ.J.Phys.Chem., 1979(9)].
70. J.C.Slater, J.Chem.Phys., 1964, 41, 3199.
71. Yu.A.Borisov and N.I.Raevskii, Zhur.Strukt.Khim., 1983, 24, 97.
72. J.Kao and N.L.Allinger, Inorg.Chem., 1977, 16, 35.
73. F.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1979, p.218.
74. V.V.Korshak, A.M.Sladkov et al., Vestnik Akad.Nauk SSSR, 1978, 1, 70.
75. I.V.Stankevich and O.B.Tomilin, Zhur.Strukt.Khim., 1977, 18, 772.
76. Yu.A.Borisov and N.I.Raevskii, Zhur.Strukt.Khim., (in the press).
77. M.V.Nikerov et al., Akad.Nauk SSSR, Ser.Khim., 1981, 1177.
78. D.A.Bochvar et al., "I Vsesoyuznaya Konferentsiya po Kvantovoi Khimii Tverdogo Tela. Tezisy Dokladov" (The 1st All-Union Conference on the Quantum Chemistry of Solids. Abstracts of Reports), Izd. Leningrad.Gos.Univ., Leningrad, 1982, p.12.
79. V.N.Bogomolov, Uspekhi Fiz.Nauk, 1978, 124, 171.

80. P.Fantucci and P.Balzarini, J.Mol.Catal., **1978**, 337.
81. Yu.A.Borisov, Chem.Phys.Letters, 1976, **44**, 17.
82. "Spravochnik Khimika" (The Chemist's Handbook), Izd.Khimiya, Moscow, 1971, Vol.1, p.774.
83. B.P.Biryukov and Yu.T.Struchkov, Uspekhi Khim., 1970, **39**, 1672 [Russ.Chem.Rev., 1970(9)].
84. M.Benard, Inorg.Chem., 1979, **18**, 2785.
85. M.Benard, J.Amer.Chem.Soc., 1978, **100**, 7740.
86. F.A.Cotton, J.L.Hubbard, D.L.Lichtenberger, and I.Shim, J.Amer.Chem.Soc., 1982, **104**, 679.
87. Yu.A.Borisov, "Koordinatsionnaya Khimiya" (Coordination Chemistry), 1984, Vol.10, No.5, p.588.
88. G.I.Likhtenshtein and A.E.Shilov, Zhur.Fiz.Khim., 1970, **44**, 849 [Russ.J.Phys.Chem., 1970(4)].
89. R.W.F.Hardy, R.C.Burns, and G.W.Parshall, in "Inorganic Biochemistry" (Translated into Russian), Izd.Mir, Moscow 1978, Vol.2, p.157.
90. N.N.Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems of Chemical Kinetics and Reactivity), Izd.Akad.Nauk SSSR, Moscow, 1958, p.41.
91. G.Innorta, A.Foffani, and S.Torroni, Inorg.Chim. Acta., 1976, **19**, 263.
92. W.Malisch and M.Kuhn, Chem.Ber., 1974, B.**107**, 979.
93. J.Lewis, A.R.Manning, J.R.Miller, and J.M.Wilson, Chem.Soc., A, 1966, 1663.
94. M.Höfler, J.Scheuren, and D.Spilker, J.Organomet. Chem., 1975, **102**, 205.
95. D.S.Field and N.J.Newlands, J.Organomet.Chem., 1971, **27**, 213.
96. Yu.S.Nekrasov, D.V.Zagorevskii, V.F.Sizoi, and F.S.Denisov, J.Organomet.Chem., 1975, **97**, 253.
97. Yu.S.Nekrasov et al., Izv.Akad.Nauk SSSR, Ser. Khim., 1979, 1420.
98. Yu.S.Nekrasov et al., J.Organomet.Chem., 1981, **205**, 157.
99. K.Kogh-Jespersen, J.Chandrasekhar, and J.von Rague Schleyer, J.Org.Chem., 1980, **45**, 1608.
100. Yu.A.Borisov, Yu.S.Nekrasov, and V.F.Sizoi, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 494.
101. P.Jutzi, F.Kohl, and C.Krüger, Angew.Chem.Int.Ed., 1979, **18**, 59.
102. P.Jutzi, F.Kohl, P.Hoffman, C.Krüger, and Tsay Yi-Mung, Chem.Ber., 1980, **B113**, 757.
103. N.I.Raevskii, Yu.S.Nekrasov, V.F.Sizoi, and Yu.A.Borisov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2828.
104. A.N.Nesmeyanov and R.A.Sokolik, in "Metody Elementoorganicheskoi Khimii: Bor, Alyuminii, Gallii, Indii, Tallii" (Methods of organoelemental Chemistry: Boron, Aluminium, Gallium, Indium, and Thallium), Izd.Nauka, Moscow, 1964, p.401.

Nesmeyanov Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow