Russian Chemical Reviews **66** (4) 281 – 300 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 546.12 + 546.2 + 546.85:541.51 + 541.27

Principles of the electronic structure of complexes of non-transition elements

G P Kostikova, D V Korol'kov, Yu P Kostikov

Contents

I.	Introduction	281
II.	Empirical concepts	282
III.	Semiempirical calculations of molecular orbitals	282
IV.	Non-empirical MO calculations and X-ray spectra of complexes	283
V.	X-Ray photoelectron spectra of compounds of non-transition elements	286
VI.	Principles of electronic structures of complexes of non-transition elements	296
VII.	Conclusion	297

Abstract. The results of quantum-chemical calculations of electronic structures of complexes of non-transition elements are surveyed. Their X-ray emission and X-ray photoelectron spectra are analysed. General principles of the electronic structure of these complexes are established. It is shown that the effective participation of partially or completely occupied valence np^m orbitals of the central atom A of AL_k complexes in the formation of delocalised MOs, the negligibly small contribution of vacant A*nd* orbitals to the bonds with ligands, the valence inertness or rather low contribution of occupied Ans^2 orbitals (except for $2s^2$ AO) to the valence MOs, and the initiation of multiple bonds (in the electronic structure of complexes) due to covalent or hypervalent π-interactions involving only 2*p* (but not 3*p*, 4*p*, *etc*.) atomic orbitals are the most significant factors influencing the electronic structure of non-transition element compounds. The concept of *d* orbitals and hypervalent bonds is critisised. The bibliography includes 130 references.

I. Introduction

The essence of the problem of the electronic structure of non-transition element compounds is quite simple. The main task is to find out what valence orbitals of central atoms (A) in the complexes AL_k ($k \geqslant 1$) of non-transition elements participate in the formation of bonds with ligands (L) described by delocalised molecular orbitals (MO).

In ionic compounds of alkali and alkaline earth metals, the leading part is played by the ns^1 and ns^2 orbitals; in other complexes of these metals, the contributions of the *np* orbitals should also be taken into account (especially in complexes formed by A^{II}). The physicochemical nature of the majority of compounds of Group I and II metal is too specific, and its analysis is beyond the scope of our review.

The electronic structures of complexes of Group III and IV non-transition elements can be described fairly adequately in terms of the A*ns* and A*np* orbitals and usually correspond to the traditional concept of sp^m-hybridisation of the basis AOs, especially in the case of boron and carbon complexes. The electronic structures of complexes of aluminium, silicon and their analogues with coordination numbers above 4 are more complicated.

The problem of describing the electronic structures of complexes of Group V – VIII non-transition elements is even more complicated, because the ground states of atoms of these elements contain one or more electron pairs localised in the valence *ns* and *np* AOs (in this case, the total number of valence electrons in an atom is greater than the number of valence orbitals, which is equal to four). At this point, the problem branches. The structures of the valence shells of the simpler molecules such as HF, HCl, H_2O, H_2S, NH_3 or PH_3, in which the chemical bonds are mostly formed by unpaired A*np*-electrons, are relatively simple; problems arise in determining the contributions of the occupied Ans^2 orbitals to the valence MOs and in solving the problem of hybridisation of the basis *ns* and *np* orbitals of the central atom.

The problem of describing an electronic structure is the most complicated in the case of higher compounds of Group V – VIII non-transition elements. The term 'higher compounds' is used in relation to molecular systems in which the oxidation state of a non-transition element A exceeds the number of unpaired *np*-electrons in the ground state of the atom, while the number of the unpaired A*np*-electrons alone is insufficient to ensure that all the A – L bonds in the complex AL_k are two-electron two-centre interactions. The term 'higher compounds' cannot be regarded as appropriate, and its use can be justified only in striving for short presentation. According to this terminology, not only compounds of elements in the maximum oxidation states (Cl^{7+}, S^{6+}, *etc*.) are referred to as higher compounds, but also those in which the A atom is in a lower oxidation state (for example, complexes of formally trivalent chlorine ClO_2^{1-} or tetravalent sulfur, SO_3^{2-}).

Undoubtedly, the key role in the formation of bonds with ligands in the higher complexes of non-transition elements belongs to the valence np^m orbitals of the central atom. Therefore, the main point in studying the electronic structures of these compounds is to elucidate the degree to which the vacant *nd* orbitals and ns^2 orbitals occupied in the ground state of the central atom participate in the delocalised valence MO.

The problem of the description of electronic structures of complexes of non-transition elements has a long-standing history. Three stages, not separated from one another (in time or in the essence of the problems solved), can be distinguished, namely, empirical, semiempirical and non-empirical periods. The name of

G P Kostikova, D V Korol'kov, Yu P Kostikov St. Petersburg State University, Universitetskii prosp. 2, 198904 St. Petersburg, Peterhof, Russian Federation. Fax (7-812) 428 69 39.
Tel. (7-812) 428 67 33 (G P Kostikova)

Received 15 April, 1996
Uspekhi Khimii **66** (4) 307 – 327 (1997); translated by Z P Bobkova

the last stage is conventional; this stage combines theoretical *ab initio* calculations of the electronic structures of non-transition element complexes carried out by the SCF and MO LCAO methods, by the methods of scattered waves and by X_α-discrete variation; experimental studies of these complexes by X-ray emission and X-ray photoelectron spectroscopy; coordinated studies of electronic structures using both X-ray spectroscopy and the MO theory and general theoretical approaches to the problem.

II. Empirical concepts

In our review, attention is concentrated on the electronic structures of higher compounds of Group V – VIII non-transition elements. A considerable part is occupied by the discussion of the nature of, and the reasons for the differences between, the electronic structures of complexes formed by elements of the Second Period and by elements of the Third and higher Periods.

To describe the electronic structures of higher compounds of Group V – VIII non-transition elements of the Third and subsequent Periods, two alternative concepts were developed as early as the 1950s. According to one of them (the concept of *d* orbitals), it is assumed that both the ns^2 and np^m orbitals of the central atom A occupied in the ground state and its vacant *nd* orbitals are involved in the binding with ligands.[1,2] The bonds between the atom A and the ligand were described by multi-centre MOs formed according to the requirements of group theory with efficient participation of the *ns*, *np* and *nd* orbitals of atom A (strictly specified for each type of molecular symmetry) and the corresponding group orbitals of the ligands. This concept was based on the idea of $sp^m d^n$ hybridisation of valence orbitals of the central atom and made it possible to pass from the canonical delocalised MOs to equivalent localised MOs, *i.e.* to describe the electronic structure of an AL_k complex by a certain set of two-electron two-centre covalent A – L σ- and π-bonds. A fairly important role has been allocated to the allowance for the symmetry of the complex. The vacant *nd* orbitals of the central atom able to participate in the σ- or π-interactions with the ligand orbitals were strictly specified in conformity with the symmetry point group. The concept of *d* orbitals (sometimes referred to as the theory of complete hybridisation) has been presented clearly and systematically in monographs.[3,4]

The second concept is the concept of hypervalent bonds. It is based on the idea of three-centre four-electron interactions proposed by Pimentel and Rundle[5–7] and assumes that the bonds of atom A with ligands are mostly formed through the valence np^m orbitals of the central atom. The ns^2-electrons are used only in some cases, whereas the vacant *nd* orbitals remain valence-inactive and do not participate in the A – L bonds. The electronic structure of an AL_k complex is described as a set of two-electron two-centre covalent A – L bonds involving the unpaired electrons of the A atom and three-centre four-electron (hypervalent) $L_{(1)} - A - L_{(2)}$ bonds involving the paired np^2-electrons or, more rarely, the ns^2-electrons of the A atom.[8,9] In the case of complexes with central atoms in the highest oxidation states (SF_6, PF_5, *etc.*), the Ans^2 orbitals are assumed to participate necessarily in the valence MOs. The concept of hypervalent bonds (or the theory of three-electron bonds), the history of its development and its numerous consequences have been considered in monographs.[3,4,10]

In the 1950s and 1960s, the concept of *d* orbitals occupied a leading position in the theory of electronic structure of compounds AL_k of non-transition elements. This can be explained retrospectively as follows. In those years, theoretical studies were mainly concerned with complexes of transition metals. Their electronic structures have been modelled using the crystal field theory, the ligand field theory and the MO theory including various versions of calculation procedures. The theory of the electronic structures of compounds of non-transition elements has remained the Cinderella of quantum chemistry and has been 'fascinated' by the successes in the rapidly progressing theory of electronic structure of transition metal complexes. Researchers believed that the electronic structure of AL_k cannot present anything conceptually new, interesting or significant compared to that of complexes ML_k of transition metals M; the electronic structures of the latter have usually been described using all the valence AOs [*ns*, $(n-1)d$, *np*] with allowance for the symmetry requirements. Therefore, views on the electronic structures of AL_k have largely resulted from the groundless transfer of the general ideas of the theory of the electronic structure of ML_k to coordination compounds of non-transition elements and from the wide use of the statement that the principles of the electronic structure of two types of complexes — AL_k and ML_k — are close and even identical. Moreover, the concept of *d* orbitals has been supported by many experimenters, who have searched and seemingly 'found' evidence supporting participation of the A*nd* orbitals in the electronic structures of AL_k and in the A – L bonds.

However, at that time, some arguments in favour of the concept of hypervalent bonds were found. Syrkin and Linnet[11–13] noted that *d* AO make fairly low contributions to the electronic structures of non-transition element complexes. They stressed that the characteristics of those vacant *d* orbitals of non-transition element atoms that should be included in the basis set of atom A cannot be theoretically estimated with a sufficient ac-curacy. Furthermore, since the A*nd* orbitals in AL_k can be delocalised near the ligands, the problem of *d* AOs is generally less significant than it had seemed initially. The requirement that the number of hybrid orbitals of the central atom in an AL_k complex should coincide with the number of two-centre bonds and the *a priori* judgment of the multiplicity of the A – L bonds cast special doubt upon the concept of *d* orbitals. Therefore, the setback of these ideas observed in the last few years is surprising.[14]

In the 1960s, it was believed that the problem in question could be solved by systematic quantum-chemical calculation of the electronic structures of non-transition element complexes. Both concepts are 'one bone and one flesh' in MO theory. Within the framework of these concepts, the electronic structures of AL_k complexes can be described using both delocalised MOs and localised two- and three-centre MOs. Therefore, since the middle 1960s, quantum-chemical calculations have been used systematically to model the electronic structures of various AL_k complexes in various approximations of the MO theory.

III. Semiempirical calculations of molecular orbitals

The greatest number of calculations for AL_k complexes have been carried out by semiempirical MO LCAO methods. Owing to computational difficulties only few *ab initio* calculations for complex multi-electron and multi-centre AL_k compounds, based on the Hartree – Fock – Roothaan (SCF MO LCAO) method with fairly complete and balanced atomic basis sets, were performed at that time.

The MO LCAO calculations have provided extensive information; these results have been presented fully and comprehensively and in a clear and systematic form in the review by Dyatkina and Klimenko.[15 †]

The review begins with comments on the calculations of spatial and energy characteristics of vacant *nd* orbitals of isolated atoms and atoms in a ligand field. These calculations did not give an answer to the direct question, whether the *nd* AOs can participate in bonds, but indicated that the spatial characteristics of *d* orbitals (unlike those of *s* and *p* AOs) can vary over wide limits, from very diffuse to contracted orbitals, depending on the valence state of the atom. The calculations for excited states of atoms also have not clarified the situation, although they have provided useful information on the energies of excitation from the

† We advise those who are interested in the problem of vacant AO, to read this brilliant review, which was published in 1973 and marks the completion of a stage in the development of the quantum-chemical views about electronic structure of non-transition element compounds.

ground states of atoms to their valence states in which the *nd* orbitals are occupied by electrons and on the orbital energies of these electrons.[16]

Based on the results of semiempirical MO LCAO calculations for various AL_k complexes, the authors of the review made some conclusions that seemed the most reliable and significant at that time. These conclusions can be outlined as follows.

The populations of *d* AOs are substantial but not more than 0.5–1 electron. According to the theory of localised bonds, the populations of *d* orbitals are postulated to be large integer values, and thus the contributions of these orbitals are overestimated twice or even more. The contributions of *d* orbitals are greater in compounds with high valences of the central atom (such as SO_2, SO_4^{2-}, SF_6) and increase with an increase in its formal valence. In addition, the contributions of *d* AOs increase with the decrease in the degree of ionicity of bonds (in oxygen compounds they are greater than in fluorine compounds, the number of ligands being the same). No considerable donor-acceptor $Lp_\pi \rightarrow Ad_\pi$ interactions can be detected even in those cases where these interactions are allowed from the symmetry viewpoint. The allowance for *d* orbitals influences the calculated properties of molecules in different ways. For example, it should be noted that the calculation of dipole moments and inversion barriers requires that *d* orbitals be necessarily included in the basis set of AOs even for elements of the Second Period (although in this case, the contributions of *d* AOs are lower than those for atoms of the Third Period elements). However, the MO energies are less sensitive to the expansion of the basis set due to *d* AOs. Therefore, it would be hasty to judge the role of *d* AOs based only on the analysis of one or several molecular properties, the more so as an increase in the influence of *d* AO on a particular characteristic is not always proportional to the increase in the electron population of *d* AO. It is necessary to analyse a variety of properties that respond in different ways to the inclusion of *d* orbitals in the atomic basis set. The results of calculations do not identify any correlations between the contributions of *d* AOs to the MOs and electronic characteristics of the atom and, hence, they do not make it possible to discuss the variation of the *nd* AO populations as a function of the position of the non-transition element in the Periodic Table.

In addition to the MO LCAO semiempirical calculations, the maximum overlap method has also been used to study the role of *d* orbitals and the extent to which they participate in the hybrid orbitals of tetrahedral oxo-anions. The tetrahedral hybrid orbitals

$$\varphi = \alpha\chi_s + \beta\chi_p + \gamma\chi_d,$$

were calculated with allowance for the contributions of both d_σ and g_p components. The $s^l p^m d^n$ electronic configurations of the central atoms were estimated from the relations $l:m:n = \alpha^2:\beta^2:\gamma^2$. The results of the calculations showed that the relative *d*-contribution to the electron population of atom A varies over wide limits (from 0.02 for BrO_4^- to 0.3 and 0.4 for ClO_4^- and AsO_4^{3-}), but it is always several times smaller than the *d*-contribution to the electron population of central atoms M in analogous tetrahedral oxo-anions formed by transition metals (for example, VO_4^{3-}, CrO_4^{2-}, MnO_4^-).

In other studies,[18–21] the problem of vacant *d* orbitals of non-transition element atoms has been discussed in terms of the results of semiempirical calculations of valence electron density distribution in two- and multi-atomic fluorides, chlorides, oxides and complexes of the $AX_{k-n}Y_n$ type with coordination numbers of 3, 4 and 6. The calculations were carried out by the MO method in the zero differential overlap (ZDO) approximation. It was found that *d* orbitals play an insignificant role in the formation of chemical bonds between central atoms and ligands. In particular, it was shown that the fact that the energies of dissociation of the Si, P, S and Cl monofluorides are larger than those of the C, N, O and F monofluorides is not associated with the role of *d* orbitals of the atoms of Third Period non-transition elements but is due to the specificity of their *s* and *p* AO, *i.e.* to specific spatial and energy characteristics of A3*s* and A3*p* orbitals.

The statistical theory of Thomas–Fermi atoms[22] has also been invoked to the solution of the problem of vacant 3*d* orbitals of the atoms of non-transition elements of the Third Period. It was shown that these atoms, unlike those of elements of the Second Period, have no states occupied by electrons and characterised by the orbital quantum number $l = 2$; the states with $l = 2$ can be occupied only in the case of cations. The electron populations of the states with $l = 2$ is determined by the degree of ionisation of the atom; both lower and upper limits to the degree of ionisation exist. Depending on its effective positive charge, the same central atom can have, or not have, occupied 3*d* states. A particular degree of ionisation of the atom is necessary but insufficient for the 3*d* AO to be occupied, because the extent of this occupation is also determined by the nature of the donor of valence electrons. Thus the population of the 3*d* AO of chlorine in ClF_2^+ is close to zero (0.05 a.u.), despite the considerable degree of formal ionisation of the chlorine atom ($q_{Cl} = +1.18$ a.u.), which is favourable for the population of its 3*d* AO. Apparently, this is due to the low electron-donating ability of fluorine atoms ($q_F = +0.09$ a.u.).

In recent years, semiempirical calculations have been seldom used to solve the problem of vacant *d* orbitals; sometimes, the results of these calculations are compared with the photoelectron spectroscopy data for the corresponding complexes.[23,24] The results of the latter indicate that *d* orbitals contribute significantly to the valence electron structures of higher sulfur fluorides, silicon oxo-complexes, *etc.*

Nevertheless, the conclusion that the problem of *d* orbitals cannot be solved adequately within the framework of the semiempirical approach is beyond any doubt.[15] The semiempirical MO LCAO calculations exaggerate the role of *d* orbitals and give a wrong picture of the electron density distribution; they are of little use for the description of the qualitative variation of *d*-contributions in various series of molecules, do not prove in any way the real participation of the A*nd* AOs in the A–L bonds and give so great a scatter of the calculated values of *d*-populations that attempts to extract unambiguous information from them are hopeless. These calculations confuse rather than clarify the problem of outer *d* orbitals.

In the early 70s, it seemed that the final solution of the *nd* AO problem would become possible as a result of systematic non-empirical calculations for a great number of complexes; generalisation of experimental values for a broad range of molecular properties; thorough analysis of the regularities in the variation of these properties and establishing correlations between the molecular properties and calculated characteristics of the contributions of *d* orbitals to the valence molecular orbitals in the electronic structures of complexes. However, the first studies along these lines have already shown that counting on the non-empirical approach to the estimation of the role of *d* AOs in the valence electronic structures of complexes of non-transition elements also has no prospects.

IV. Non-empirical MO calculations and X-ray spectra of complexes

The need to determine reliably the populations of the outer (vacant) atomic orbitals in an explicit form and their contributions to various molecular properties imposes stringent requirements upon the MO method used for the calculations. The non-empirical SCF MO LCAO method and X_α-methods meet these requirements best of all. However, even fairly legitimate calculations carried out for AL_k complexes in terms of these methods have not resulted in the solution of the *nd* AO problem.

The following approach is normally used to solve the *nd*-AO problem in terms of *ab initio* and X_α-methods. The participation of A*nd* orbitals in $\sigma(d_\sigma\text{-}s,p_\sigma)$ or $\pi(d_\pi\text{-}p_\pi)$ bonds with ligands is set depending on whether or not the inclusion of the nd_σ and nd_π orbitals into the atomic basis set results in the calculated energies of single-electron MO approaching the corresponding experimental values and/or in a decrease in the total energy of the molecular

system. The electron population of the A*nd* orbitals in the complex is estimated from the same viewpoint.

Unfortunately, no unambiguous conclusions have been drawn from the results of calculations for complexes of non-transition elements accumulated over the past two decades.

The results of some of the *ab initio* SCF MO LCAO and SCF SW X_α-calculations attest to an appreciable electron population of the A*nd* orbitals in the complexes studied,[15,25–29] whereas according to other calculations, this population is equal to zero.[30–32] In addition, the results published for the same compounds are sometimes at variance with one another. For example, the population of the atomic A*nd* orbitals in SF_6 has been found[29] to be 1.2 e$^-$, whereas according to another study,[32] the electron structure of SF_6 is hypervalent and is described without participation of the 3*d* orbitals of the central atom. X_α-calculations for SF_6 has led Condliy and Johnson[31] to the conclusion that the S3*d* orbitals remain virtually unoccupied.

In a typical case, the inclusion of *nd* AOs into the atomic basis set leads to a slight decrease in the energy of those MOs which can contain *nd* AOs [for example, $e_g(\sigma)$ and $t_{2g}(\pi)$ MO in an octahedral complex]. However, this decrease in the MO energies does not occur for all *nd* exponents, and, besides, the energies of the rest of the single-electron MOs can increase when the *nd* AOs are taken into account. Therefore, despite the fact that allowance for the A*nd* orbitals is believed to result (according to the variational principle) in a decrease in the total energy of the molecule, this is due to the change in the energies of the Coulomb and exchange interelectron interactions rather than to stabilisation of single-electron energy levels.[33] This paradoxical result is reproduced in the *ab initio* and SCF SW X_α-calculations for SF_6, SeF_6, TeF_6 and PF_5 complexes and for the isoelectronic series PO_4^{3-}, SO_4^{2-}, ClO_4^-.

The results of SCF DV X_α-calculations[34–38] of the electron structures of many halides and halo-anions of non-transition elements AL_4^{p-} ($p = 0-3$) including SF_6, SF_5Cl, SF_5O^-, *etc*. in the basis of numerical Hartree–Fock functions indicate that the chemical bonds and many properties of AL_k^{p-} complexes (reactivity, geometrical structure, stability and its dependence on the charge for series of isoelectronic complexes) are due to the formation of multi-centre MOs. The latter consist of all the valence *s* and *p* orbitals of the central atom and the ligands, which are transformed in terms of the corresponding irreducible representations for the symmetry groups of the complexes under study.[34–38] Most of the calculations do not confirm the participation of the vacant A*nd* orbitals in the bonds with ligands. In particular, when the electronic structure of SF_6 has been calculated in the *s*,*p* basis, good agreement between the calculated single-electron energy levels and the experimental ionisation potentials has been observed.[34,37] The addition of the S3*d* orbitals to the Hartree–Fock basis did not change the order of the levels and did not result in significant improvement of the calculated single-electron MO energies with respect to the experimental values for the *d* exponent varied over a fairly broad range. However, it should be noted that in the case of TeF_6, good agreement between the calculated and experimental MO ionisation potentials is observed when the calculation is carried out with the *s*, *p*, *d* basis set of the central atom;[37] thus, a more adequate description of the sequence of MO energies in TeF_6 is achieved when the atomic basis is supplemented by the Te5*d* orbitals. Based on the results obtained by DVM X_α-calculations of the molecular orbitals of the SF_5O^- anion, isoelectronic to SF_6, the increase in the multiplicity of the S–O bond has been explained by the fact that all the valence AOs of oxygen participate in binding with the AOs of sulfur to a greater degree than those of fluorine, without assuming the occurrence of the $S3d_\pi-O2p_\pi$ interactions.[38] Perhaps, the higher multiplicity of the bonds in the SO_4^{2-} tetraoxo-anion is also not associated with the $S3d_\pi-O2p_\pi$ interaction.

In the non-empirical calculations, the agreement between the calculated and experimental geometric parameters of a complex (type of the polyhedron, bond lengths, bond angles) are often used as a criterion for elucidating the role of *nd* AOs. In this case, one must take care whether the addition of *nd* functions of the central atom to the atomic basis set improves the geometry (*i.e*. the agreement with experiment). Again, some *ab initio* results imply that A*nd* orbitals exert only insignificant influence on the optimum geometrical parameters of sulfur halides and show their low electron population.[39] Conversely, some other calculations attest that *d* functions need to be taken into account in order to describe adequately the geometric structures of molecules of this type and, in these cases, the populations of A*nd* orbitals are found to be high.[40–43] However, in this case, too, some interesting peculiarities have been found. Firstly, the large population of *nd* AOs has a substantial influence on the energies of Coulomb and steric repulsions and does not lead to enhancement of the $d_\pi-p_\pi$ interaction. Moreover, in addition to the *d*-contribution, the second-order Jahn-Teller effect, caused by the presence of low-lying excited states with appropriate symmetries, can also be a crucial factor influencing the geometric (and electronic) structures.[41] Secondly, the addition of *d* functions results in almost identical effects for complexes of elements of the Third Period (SF_4, SOF_2, SO_2F_2)[42] and of the Second Period (NO_2^+, NO_2^-, NO_3^-, NO, *etc*.).[43] In both cases the addition of 3*d* orbitals to the basis set improves the geometry and reduces the total energy of the molecule, which correlates well with the population of *d* AOs. The higher the formal valence of the central atom, S or N, the larger the effect of stabilisation due to *d* AOs. Similarly, non-empirical calculations for homonuclear polyhedral molecules P_4, As_4, P_8 and As_8 using a pseudopotential and a two-exponent basis set indicate that the expansion of the basis set due to vacant *nd* AOs makes it possible to explain the fact that the P_4 and As_4 clusters are more stable than the $2P_2$ and $2As_2$ systems, respectively.[44] It was noted[44] that the crucial factor determining the higher stability of P_4 with respect to $2P_2$ is the increase in the electron population of *d* AOs from 0.06 to 0.10. However, very close values have been found[45] not only for the As_2 and As_4 clusters but also for N_2 and N_4, although the hypothetical N_4 molecule is known to possess much higher energy than $2N_2$.

Here we encounter a quite typical situation, which has been analysed in detail in the review by Bochvar *et al*.[46] Up to now, while we discussed the problem of *d* orbitals, we proceeded from the assumption of real atomic *d* orbitals in the sense in which the valence *s* and *p* orbitals in a molecule are real. Then we assumed that non-zero electron populations of *d* AOs can serve as an actual criterion and a measure for their participation in the A–L bonds. Note in this connection that Coulson[47] has suggested that two cases should be distinguished: (1) the contribution of *d* AOs is large (about 0.5–1 electron or more), then one can speak of their real participation in bonds; (2) the contribution of *d* AOs is small, then they act as polarising functions, and the discussion of their populations makes no particular sense. The second case represents a different aspect of the problem of *d* orbitals, based on the fact that the radial parts of *d* functions obtained in MO calculations by minimising the total energy of the molecule (with allowance for the variation of the AO exponents) differ markedly from the radial parts of *d* orbitals of isolated atoms (they are more contracted) and approach the radial parts of the corresponding valence *s* and *p* AOs; for example, $3d \rightarrow 3s, 3p$.[48,49] This strong contraction is observed in all cases and is independent of the *d*-population and of the effective charge on the atom in a molecule. These altered *d* orbitals are no longer related directly to vacant valence orbitals of the atom. Now they have a different meaning: they should be regarded as certain corrections in *ab initio* calculations that take into account polarisation of valence *s* and *p* AOs upon the formation of bonds and make the total molecular wave function more precise. Mulliken has suggested that the populations of these outer $d_{\sigma,\pi}$ AOs should be regarded as the populations of those valence σ,π AOs, which they polarise.[50]

If we assume that the role of *d* orbitals reduces to corrections for calculations, then we should find out what the relative significance of these corrections is in the calculations of the electronic structures of compounds of Second and Third Period

elements. The inclusion of 3*d* functions into the central atom basis sets in the calculations for compounds of elements of the Second Period is always accompanied [15] by their strong compaction ($3d \rightarrow 2s, 2p$), non-zero electron populations, and by a decrease in the total energy of the molecular system.[15,46] Thus, in the case of *ab initio* calculations for compounds of elements of the Second Period, the atoms of which have no valence *d* orbitals at all, the 3*d* functions also act as effective corrections. Using numerous nitrogen and phosphorus compounds as examples, Bochvar *et al.*[46] demonstrated convincingly that the role of *d*-type corrections in the calculations for compounds of Second and Third Period elements is approximately the same; in these two cases, *d*-populations are close and the effects of *d* AOs on various molecular properties are quite comparable in magnitude. For quantum-chemical reasons, the participation of *d* orbitals in the electronic structures of compounds of Second Period elements has never been considered to be necessary; therefore, the second ('correction') aspect of the allowance for *d* orbitals seems to be more and more preferable. It can be assumed that in *ab initio* calculations for compounds of Third Period elements, the role of *d*-type orbitals is to counterbalance the defects caused by an inadequate *sp* basis set.[51]

Expansion of a basis set increases the number of variational parameters; consequently, the test function becomes more flexible and, hence, the total energy of a molecular system always decreases (owing to the variational principle). Basis set expansion is typical of quantum-chemical calculations. The expansion of the basis set in terms of the Roothaan method makes it possible to obtain (within the specified accuracy) the wave functions corresponding to the Hartree – Fock limit. However, the total energy of a molecular system is less sensitive to the basis set expansion than other electronic characteristics and, therefore, it cannot be a reliable criterion for establishing the Hartree – Fock limit in calculations by the Roothaan method (the virial theorem and the Gelman – Feynman theorem are used as additional criteria).[52] In addition, the stability of a molecular system cannot be fully explained in the Hartree – Fock terms; for this purpose, the correlation energy and core effects should also be taken into account.[53,54]

It is clear from the above that it is impossible to determine correctly the populations of *d* AOs and, hence, to solve the problem of vacant *d* orbitals in terms of merely quantum-chemical Hartree – Fock – Roothaan (HFR) calculations (even the most accurate) with a multi-exponential expanded and balanced basis set, without allowance for configuration interactions (CI) (which is typical of most of *ab initio* calculations). Apparently, only in terms of the multi-configuration approximation for a self-consistent field (MC SCF), will an adequate estimation of *d*-contributions to various properties of the systems under consideration be possible. (All the above is also true for the little-studied problem of occupied Ans^2 orbitals.) Within the scope of the MO LCAO method, the problem of outer *d* AOs is additionally complicated because, as noted above, the term *d* AO is used with two meanings, and there is no clear criterion to distinguish between the 'real *d* AOs' and 'polarising *d* functions'.[15] It should also be borne in mind that the question of outer *d* AOs arises only in the MO LCAO approximation, which is most extensively used now but is not the only one existing.

Since the early 70s, ultrasoft X-ray spectroscopy has been used actively in studies dealing with the problem of vacant *d* orbitals. X-Ray emission spectra provide vital information on the electronic structures of complexes; relative energies of all valence MOs and the contributions of the majority of atomic orbitals to them can be found in this way. According to the dipole selection rules, those MOs that contain contributions of the 3*s* and 3*d* orbitals of atoms of the element under investigation ($3s$–$2p$ and $3d$–$2p$ transitions) can be manifested in the *L*-spectra of elements of the Third Period (Cl, S, P, Si, *etc.*).[55–57] The complete sets of X-ray fluorescence spectra for a large number of chlorine and sulfur compounds have been studied most extensively in this respect.[58–63] In the opinions of the researchers cited, these spectra unambiguously indicate that 3*d* orbitals of chlorine and sulfur atoms do contribute to chemical bonds. These and other similar data on ultrasoft X-ray spectroscopy covering a wide range of non-transition element compounds are believed to be indisputable experimental evidence for effective participation of A3*d*-electrons in chemical bonds.

However, another viewpoint also exists. Analysis of X-ray emission *L*-spectra of sulfur and chlorine compounds [64] permits one to distinguish several reasons for the complicated and inconsistent structure of emission Cl*L*- and S*L*-spectra. One of them is decomposition of a substance during recording of the spectrum with both the primary excitation of the spectra by electrons and the secondary excitation by photons. Experimental (emission Cl*L*-spectra of ClO_4^-) and theoretical (SCF SW X_α-calculations of ClO_4^-) data confirm that a large fraction of the intensity of the low-energy band in the X-ray emission *L*-spectrum is due to products of decomposition of ClO_4^-.[65] It should also be taken into account that under the conditions of recording X-ray emission spectra, interaction of a compound studied with the copper anode surface is possible. Finally, one more reason lies in the fact that in the assignment of spectral bands, the superimposition of short-wave radiation with higher-order reflection on the recorded spectrum (for instance, the sixth order reflection of $L_{\alpha_{1,2}}$- and L_{β_1}-lines of copper) is not monitored (and, hence, is not taken into account).

The theory of X-ray emission spectra is largely based on the single-electron orbital model. The X-ray lines in a multi-electron system are assumed to be due to a transition between two states having particular electron configurations and described by the Hartree – Fock method. In the one-particle approximation (in the approximation of 'frozen' orbitals) in which the relaxation effects are ignored, the Hartree – Fock orbitals of the ground state of the molecular system under study are used in calculations of excited states. The results of SCF *ab initio* calculations of the fine structures of X-ray emission spectra for SO_2, CS_2, SCO and Cl_2 molecules have been reported,[66] and it has been found that the orbital model has only limited utility for the interpretation of the spectra due to the presence of significant correlation effects. In the CK_β-spectra of CS_2 and SCO, high-intensity transitions from the lower antibonding molecular orbitals (which are vacant in the ground state) have been detected. To explain the presence of short-wave satellites, the X-ray re-emission mechanism (inelastic non-shifted scattering) has been invoked. Previously, high-intensity short-wave satellites have been found in *K*- and *L*-spectra of boron, carbon and sulfur and interpreted as re-emission transitions from excited levels.[61,67–69]

Thus, the data of ultrasoft X-ray spectroscopy cannot be regarded as indisputable evidence for the participation of *d* orbitals of the central atoms in the chemical bonds in complexes of non-transition elements, since experimental results often disagree with one another and their traditional interpretation is incorrect and unambiguous. It is significant that stricter investigations carried out more recently have a different character. The energies and intensities of the X-ray *L*-emission of the central atom for PO_4^{3-} and ClO_4^- have been measured experimentally and calculated theoretically by the SCF SW X_α method.[70] The inclusion of A3*d* orbitals in the basis set improves the agreement between the calculated and measured intensities of lines and energies of X-ray spectral transitions (the transition energies were calculated using the transition state approximation) but has almost no influence on the orbital energies of the PO_4^{3-} and ClO_4^- ground states. This implies that A3*d* orbitals participate only slightly in their electronic structures. A study of the electronic structure of $POCl_3$ carried out by X-ray and X-ray photoelectron spectroscopy and by SCF MO LCAO, MINDO/3 and SCF SW X_α *ab initio* calculations [71] has shown that the contribution of *d* orbitals of the phosphorus and chlorine atoms to the occupied valence molecular orbitals of $POCl_3$ is relatively small.

The results of studies on the effect of the chemical shifts of the emission X-ray lines for compounds of non-transition elements do not lead to unambiguous conclusions on the role of *d* orbitals either. The chemical shifts of the emission K_{α_1}- and K_{β_1}-lines of xenon in the X-ray spectra of XeF_2, XeF_4, Li_4XeO_6, $NaHXeO_4$ and Na_4XeO_6 with respect to similar xenon lines in a hydroquinone clathrate have been measured.[72] These chemical shifts were compared with the Mössbauer isomer shifts of xenon for the same compounds.[129] The results were interpreted in terms of the model of valence electron configuration of a free effective ion. X-Ray transition energies and the electron density on the nucleus in this ion were calculated by the Dirac–Slater method. The question of whether the Xe5*d* orbitals participate in the bonds with ligands remained open; however, the workers[72] pointed to the possibility of this participation in the electronic structures of high-valence oxygen compounds of xenon. Analogous results have been obtained somewhat earlier for a number of iodine compounds.[73, 74]

Based on the most general statements of the MO theory and the perturbation theory, Shustorovich has justified theoretically the fact that A*nd* orbitals do not make a significant contribution to the valence MOs of complexes of non-transition elements.[33, 75, 76] An indispensable condition for effective electron interaction between the valence orbitals of the central atom and the ligands is proximity of their orbital energies. In the second order of perturbation theory (for non-degenerate levels), the energy of stabilisation for a bonding MO

$$\varphi = C_A\chi_A + C_L\chi_L ,$$

(where C is a variational parameter) is determined by the formula

$$\Delta E_{AL} \sim \frac{\beta_{AL}^2}{|\alpha_A - \alpha_L|} , \qquad (1)$$

where α_A and α_L are the Coulomb integrals characterising 'self-consistent' energies of χ_A and χ_L orbitals (in those approximations of the MO theory in which an effective single-electron Hamiltonian is used), β_{AL} is the resonance integral determining the energy of interaction between the χ_A and χ_L AOs and proportional to the overlap integral S_{AL}. In the atoms of Group IV–VIII non-transition elements, the energies of *nd* orbitals are 10–15 eV higher and the energies of *ns* orbitals are 10–20 eV lower than those of *np* orbitals. This indicates that the contributions of *ns*, *np* and *nd* orbitals of atom A to the bonds with ligands are necessarily inequivalent. In typical cases, the energies of the valence orbitals of ligands are somewhat lower than the energies of the A*np* orbitals. Therefore, the vacant A*nd* orbitals prove to be too high-lying for them to interact efficiently with the occupied valence orbitals of ligands. For the same reason, the occupied Ans^2 orbitals are not always able to participate in the bonds with ligands: their energy is often too low compared to those of the valence orbitals of the ligands. Generally, the high *ns*–*np* and *np*–*nd* separation energies for atom A attest to a crucial role of the A*np* orbitals in the formation of the electronic structure of AL_k complexes and to much smaller contributions of the Ans^2 and, especially, A*nd* orbitals to the valence MOs. Characteristic properties of coordination compounds of non-transition elements can be calculated without using the *nd* orbitals of the central atom, which act as polarisation corrections for the orbital basis set.[26, 77–80] As a whole, the general theoretical ideas prove unambiguously that the vacant A*nd* orbitals make no significant contribution to the valence MOs in the electronic structures of non-transition element complexes; the role of the occupied Ans^2 orbitals is less clear.

While researchers discuss the problem of *d* orbitals (more precisely, when a large contribution of *d* AOs to the electronic structure of a complex is stated *a priori*), they often refer to the symmetry criteria and stress that for any point group of symmetry of an AL_k complex, there are always some orbitals among the A*nd* AOs that belong to the same irreducible representations as the valence orbitals of the ligands. Therefore, σ or π interaction of the A*nd* orbitals with the ligand orbitals is always possible to one or another extent.

Later, this thesis has been made more precise in the following way:[81] the *d* AOs make a real contribution to the electronic structures of complexes in the case where these orbitals, being included in the basis set, form, in conformity with the symmetry properties, new bonding MOs upon interaction with the AOs of the ligands (for example, *e* orbitals in MX_4 or t_{2g} and e_g in MX_6); otherwise, they should be regarded as polarising corrections. However, firstly, non-empirical calculations show that *d* AOs are by no means always involved in bonds, even when it is possible from the symmetry viewpoint. Secondly, the results of a comparative study of the influence of *d* functions in various calculation versions ‡ imply [82] that *d* orbitals with appropriate symmetry are not more important than the rest of *d* AOs. Besides, in calculating the electronic structure of the excited state of a molecule, the criterion of symmetry is less significant for the selection of *d* AOs than the optimisation of an additional diffuse *d* AO needed to describe MO of the Rydberg type. Finally, what is the most essential, the allowance for *d* AOs is not necessary for the construction of the appropriate number of MOs in the electronic structure of an AL_k complex of a certain symmetry. For example, when only one *ns* and three *np* orbitals of the central atom are available, one can construct, resorting to the AOs of ligands, six equivalent MOs corresponding to the canonical orbitals (a_{1g}, t_{1u}, e_g) of an octahedral complex; having only three *np* orbitals of the central atom at disposal, one can construct four equivalent MOs corresponding to the canonical orbitals (a_1, t_2) of a tetrahedral complex.[33] In the former case, the e_g MO is a non-bonding ligand orbital, while in the latter case, this refers to the a_1 MO.

Thus, since the results of nonempirical calculations of the electronic structures of non-transition element complexes are ambiguous and the interpretation of the ultrasoft X-ray spectroscopy data is by no means irreproachable, it is still an urgent task to describe the general principles of the electronic structures of non-transition element complexes and to answer the basic theoretical question: what valence orbitals of central atoms do participate in the formation of delocalised MOs?

V. X-Ray photoelectron spectra of compounds of non-transition elements

The most significant studies accomplished in recent years reveal the inconsistency of the concept of *d* orbitals. However, the existing theory of the electronic structure of non-transition element complexes is still contradictory in some aspects and lacks inherent unity. Besides, there exists not only the problem of vacant *nd* AOs, but also the problem of occupied ns^2 AOs, and the latter has been quite little investigated until recently. Further development of the theory requires precise experimental studies on the electronic structures of these compounds.

Below we discuss the results of systematic studies of typical complexes of non-transition elements carried out by photo- and X-ray photoelectron spectroscopy, which are now the basic physical methods used to study occupied electron levels in free molecules and crystals.[83–85] In appropriate points of the discussion, we present data from X-ray emission and Mössbauer spectroscopy, Auger electron spectroscopy and spectroscopy of internal conversion electrons. We include only those experimental results that have been obtained repeatably by various authors and virtually agree with one another, *i.e.* results that can be regarded as final. The discussion material covers compounds of Group IVA–VIIIA elements. The discussion is based in many respects on our own studies in which the parameters of the X-ray photoelectron

‡ Using *d* functions of the central atom, appropriate from the symmetry viewpoint; with a basis set of the central atom incorporating *d* functions not corresponding to the criterion of symmetry; taking into account the full set of *d* functions in a balanced basis set.

spectra (XPS) of the valence band and inner levels of the central atoms were interpreted for the first time independently of the results of theoretical calculations on the electronic structures of the corresponding complexes. The analysis of line intensities was performed using photoionisation cross-sections and included systematic comparison of relative intensities. In the analysis of the energy positions of the lines, we used the energies of the valence orbitals and the core levels of the corresponding free atoms. As a result of these studies, X-ray electron criteria have been established that make it possible to estimate the degree of participation of vacant *nd* and occupied ns^2 orbitals of the central atom in the molecular orbitals of the A – L bonds.

1. Vacant A*nd* orbitals

To determine the degree to which *nd* orbitals of the central atom A participate in the valence MOs of non-transition element complexes from the parameters of their X-ray photoelectron spectra, two approaches have been used: analysis of the relative intensities of the XPS valence lines and of the energies of the inner levels of the A atom in these complexes.[85,86]

At present, there are only a few reviews devoted to the analysis of the XPS of non-transition element compounds.[85,87] In the majority of cases, the analysis of XPS and the interpretation of the electronic structure of complexes based on it are carried out resorting to the results of the corresponding non-empirical calculations. Most of these coordinated investigations seem to support the view on the considerable contribution of A*nd* orbitals to the electronic structure of complexes. This relates, first of all, to the most studied series of isoelectronic tetraoxo-anions,[85,87,88] ClO_4^-, SO_4^{2-}, PO_4^{3-} and even to xenon fluorides.[89,90]

However, apparently, the conclusions about the large contributions of *d* AOs based on the analysis of XPS are not quite correct. This is indicated not only by the fact that the results of some SCF calculations are in excellent agreement with XPS even without allowance for *d* AOs.

In fact, the valence XPS of tetrahedral oxo-anions ClO_4^-, SO_4^{2-} and PO_4^{3-} and many other oxo-anions[85,87,91,92] contain identical numbers of bands and are quite similar to one another in the positions of bands and in their relative intensities. A typical example is provided by the X-ray photoelectron spectrum of the ClO_4^-, which is shown in Fig. 1 *a*. In this spectrum, the two upper bands corresponding to the $1t_1$ and $3t_2$ MOs with the same electron population ($6e^-$) are close in energy and have almost identical intensities. This means that these MOs consist of only $2p_\pi$ orbitals of the oxygen atoms, and there is scarcely any significant contribution of the A*nd* orbitals to the $3t_2$ MO (the contribution of A*nd* AOs to the $1t_1$ MO is forbidden from the symmetry viewpoint). Otherwise, the relative intensities of the two bands under consideration would have been markedly dissimilar owing to the different photoionisation cross-section of the *nd* levels of the atom A and the 2*p* levels of the oxygen atoms.

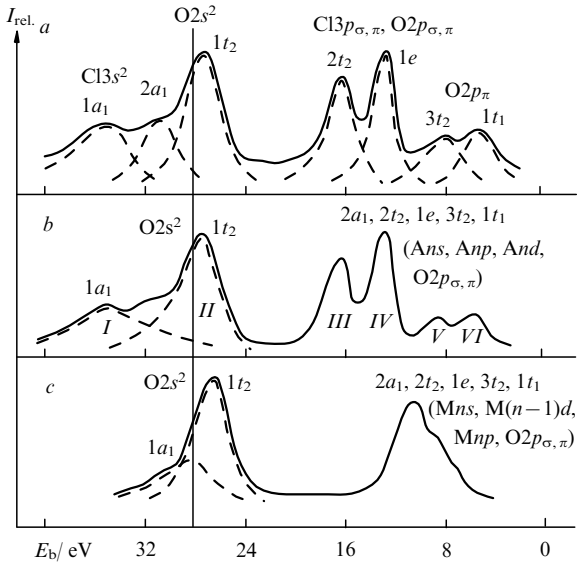


Figure 1. Valence band X-ray photoelectron spectra of tetrahedral tetraoxo-anions ClO_4^- (*a*), AO_4^{n-} (*b*), MO_4^{n-} (*c*).
For numbers *I*–*VI*, see the text.

Analysis of the intensities of the two next bands corresponding to the $1e\,(4e^-)$ and $2t_2\,(6e^-)$ molecular orbitals does not permit one to distinguish unambiguously between the absence or the presence of a contribution from the A*nd* orbitals to these valence MOs, because this contribution is, in principle, allowed from the symmetry viewpoint for both 1*e* and $2t_2$ MOs composed of the Cl3*p* and O2*p* orbitals. However, the high intensity of these bands suggests that the A*nd* orbitals do not make any significant contribution with low ionisation cross-sections to them. In addition, the 1*e* and $2t_2$ MOs lie lower in energy than the $1t_1$ and $3t_2$ molecular orbitals and, therefore, a contribution of the fairly high-lying A*nd* orbitals to the 1*e* and $2t_2$ MOs is even less likely than their contribution to the $1t_1$- and $3t_2$ MO, which contain no A*nd* AOs.

Further evidence for the absence of a contribution of the A*nd* orbitals to the valence MOs of the AO_4^{n-} oxo-anion is the fact that the structure of the upper energy bands in the valence XPS of tetrahedral oxo-complexes of transition metals MO_4^{n-} is absolutely different. The latter are isostructural and isoelectronic with AO_4^{n-}.[85,87,91,92] The electronic structures of the M – L bonds in the oxo-complexes are described with allowance for the valence ns^2 and $(n-1)d$ orbitals of the central atoms M (Fig. 1*b,c*).

Similar conclusions can be drawn from the results of X-ray photoelectron studies of some other complexes of non-transition elements.[93–97] A specific place in this series of studies is occupied by the study of Siegbahn,[97] who carried out a detailed analysis of the intensities of lines in the valence photoelectron spectra of SF_6 recorded with various types of ionising radiation (He-I, He-II) and concluded that the spectral parameters would have been different if the 3*d* orbitals of the sulfur atoms had played a significant role.

Thus, the intensities of XPS valence bands indicate that there is no $And_{\sigma,\pi} \leftarrow Lnp_{\sigma,\pi}$ donor-acceptor interactions involving vacant A*nd* orbitals in the electronic structures of non-transition element complexes. This was shown, for example, in the studies of SO_4^{2-} (without $S3d_\pi \leftarrow O2p_\pi$) or SF_6 (without $S3d_\sigma \leftarrow F2p_\sigma$), although from the viewpoint of the *d* orbital concept, the XPS studies should have revealed the participation of the *nd* orbitals of the central atom in the formation of delocalised valence MOs of the complexes.

Another X-ray electron confirmation of the fact that vacant A*nd* orbitals do not participate in the A – L bonds is the character of dependence of the energies of inner levels of the central atom A on its oxidation state (formal valence) in the complexes.

Based on the results of a systematic study of the X-ray photoelectron spectra of the inner levels of central atoms in many complexes of non-transition elements, it has been shown[86] for the first time that the variation of the energy and of the chemical shift of some inner level of atom A in a series of compounds formed by this element follow a linear dependence on its formal valence. For series including numerous compounds of a non-transition element, starting from the Third Period, for example, NaCl – $NaClO_4$ (Cl2$p_{3/2}$), KBr – $NaBrO_4$ (Br3$d_{5/2}$), KI – KIO_4 (I4$d_{5/2}$), CdS – Na_2SO_4 (S2$p_{3/2}$), CdSe – Na_2SeO_4 (Se3$d_{5/2}$), CdTe – H_6TeO_6 (Te4$d_{5/2}$, Te3$d_{5/2}$), no substantial deviations from linearity for the correlations: 'energy of an inner level of A – the oxidation number of A' have been found (Fig. 2). When the chemical shifts were calculated from the experimental E_b values, the binding energy of the inner level of the central atom in its compound with the lowest oxidation state is taken as the zero point. The results obtained for all the systems studied are alike: the binding energy and the chemical shift of the inner level of atom A increase linearly with increase in its oxidation number. Moreover,

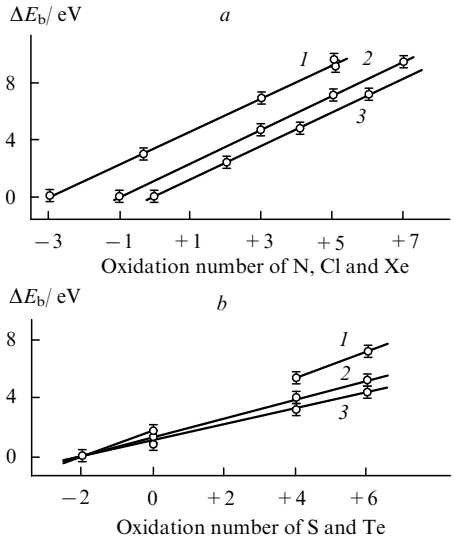


Figure 2. Chemical shifts for inner levels of atoms A as functions of their oxidation numbers.
a: N1$s_{1/2}$ (*1*); Cl2$p_{3/2}$ (*2*); Xe3$d_{5/2}$ (*3*); *b*: S2$p_{3/2}$ (*1*); Te3$d_{5/2}$; Te4$d_{5/2}$ (*3*)

this 'linear effect' does not depend on the type of the inner level of the atom A (for example, Te3$d_{5/2}$ and Te4$d_{5/2}$, Fig. 2).

This linearity was explained [86] as resulting from the low contribution of vacant A*nd* orbitals to the valence MOs of A – L bonds. Indeed, participation of vacant *nd* orbitals of the atom A in bonds with ligands (for example, with the 2*p* AO of oxygen in oxo-complexes) is possible only through a donor-acceptor mechanism with transfer of the valence electron charge from the occupied orbitals of ligands to the vacant *nd* orbitals of the atom A (A*nd* ← L*np*, 0 : 2), and this should have led to a relative increase in the electron charge on the atom A, to the corresponding decrease in the binding energy of its inner level, and to a deviation from the linear dependence described above up to its disappearance. This is why the 'linear effect' implies that the virtual *nd* orbitals of the central atom almost do not participate in the bonds with ligands in compounds of phosphorus, arsenic, antimony, sulfur, selenium, tellurium, chlorine, bromine, and iodine, *i.e.* of typical non-transitional element of the Third Period and subsequent Periods. This conclusion is also strongly supported by the following facts. Firstly, the linear correlation between the binding energy and the chemical shift of the inner energy level of anion A holds for those compounds of a non-transition element, the electronic structures of which are known to contain no contribution of the A*nd* orbitals (Na_2S, CdS, S, see Fig. 2) and is extended in the same form to its compounds with high oxidation states (Na_2SO_3, Na_2SO_4) in which the concept of *d* orbitals suggests effective participation of A*nd* orbitals in the A – L bonds. Secondly, a similar linear dependence is also observed for nitrides and nitrogen oxo-complexes as well as for xenon fluorides (see Fig. 2) [98, 99] in which the absence of any contribution of *nd* orbitals of the central atom to the bonds with ligands is beyond any doubt. Thirdly, in the series of coordination compounds of transition metals in which all the valence orbitals of the central atom including M($n-1$)*d* AOs can participate in M – L bonds, the dependences of the inner level energies of the atom M on its oxidation state are complicated and non-linear; in this case, there is no linear correlation (or any other correlation, up to the 'star sky'), owing to the differences in the relative roles of the covalent M – L, donor-acceptor M ← L and dative M → L bonds in each particular ML_k compound.

2. Occupied Ans^2 orbitals with $n \geqslant 3$

The problem of participation of Ans^2 AOs in A – L bonds in non-transition element complexes can be solved by studying their valence X-ray photoelectron spectra. For this purpose, one should find out whether the band of the quasiatomic Ans^2 level is retained in the spectrum or is missing due to the involvement of the Ans^2 orbitals in valence delocalised MOs of the complex.

Fig. 1 shows the typical valence X-ray photoelectron spectra for tetraoxo-complexes of non-transition elements AO_4^{m-} and transition metals MO_4^{m-} obtained for A = Cl, Br, I, S, Se, Te, As and M = V, Cr, Mn, Mo, W, Re. [87, 91, 92] The traditional interpretation [87, 91] of the valence XPS of an AO_4^{m-} or MO_4^{m-} complex (*i.e.* the assignment of the bands to particular MO of the complex) is based on the results of semiempirical and non-empirical quantum-chemical calculations for the electronic structures of tetrahedral oxo-anions. In the spectrum of AO_4^{m-} (see Fig. 1*b*), high-energy bands *I* and *II* were assigned to the atomic O2s^2 levels (the $1a_1$ and $1t_2$ MO), bands *III* and *IV* were attributed to the $2a_1$, $2t_2$, and $1e$ molecular orbitals of the A – O σ-bonds formed upon interaction of the valence A*ns*, A*np*, A*nd*, and O2*p* orbitals; finally, bands *V* and *VI* were assigned to the non-bonding O2p_π levels (the $3t_2$ and $1e$ MOs, poorly resolved in energy). This assignment provokes serious objections for a number of reasons.[92]

Firstly, the valence spectra of isoelectronic and isostructural (T_d) AO_4^{m-} and MO_4^{m-} tetraoxo-anions are absolutely different, and this is natural, because the valence electronic configurations of the central atoms A and M are different. However, within the region of O2s^2 levels, one should expect (from the viewpoint of the above interpretation) that the forms and energies of the X-ray photoelectron bands would be fairly similar if not completely alike. However, there is no similarity (Tables 1 and 2). The O2*s*-lines in the spectra of MO_4^{m-} are highly symmetrical (the asymmetry index is close to unity) and have virtually identical energies irrespective of the nature of the central atom. This means that in the MO_4^{m-} tetrahedral anions, the O2s^2 levels and the corresponding $1a_1$ and $1t_2$ MOs are very close in energy (the splitting energy Δ = 1 – 2 eV), which is in full agreement with the results of *ab initio* calculations [100] for the electronic structure of MO_4^{m-}. According to these calculations, the O2s^2-electrons are quasiatomic and are not involved in the formation of bonds with the central atom. At the same time, in the spectra of AO_4^{m-}, the two bands with higher

Table 1. Valence bands in the spectra of tetraoxo-anions of nontransition elements/ eV.

AO_4^{m-}	E_b of line *I* (Ans^2, $2a_1$)	E_b of line *II* (O2s^2, $1a_1 + 1t_2$)	Widths of lines *I* and *II* at the basis	*A*±0.05	Levels of A – σ-bonds; O2p_π levels				
					$2t_2$	$1e$	$3t_2$	$1t_1$	line width at the basis
ClO_4^-	36.0	28.6	18.0	0.6	18.3	15.2	10.5	8.6	13.8
SO_4^{2-}	32.0	27.6	14.2	0.6	16.9	13.7	10.3	7.2	14.8
PO_4^{3-}	30.5	27.1	13.4	0.5	16.0	12.0	7.2	9.1	15.9
SeO_4^{2-}	30.8	27.2	12.8	0.7	17.8	12.9	9.1	–	–
AsO_4^{3-}	31.0	27.1	12.0	0.6	16.7	13.1	10.1	10.1	12.0
IO_4^-	29.8	26.5	14.4	0.5	17.6	12.0	8.7	8.7	14.4

Note. *I*, *II* are lines in Fig. 1; *A* the ratio of intensities of lines *I* and *II*.

Table 2. Valence bands in the spectra of transition metal tetraoxo-anions.

MO_4^{m-} complex	$O2s^2$ levels ($1a_1 + 1t_2$)				Levels of M – O σ-bonds; $O2p_\pi$ levels	
	I	II	III	IV	I	II
CrO_4^{2-}	25.3	11.0	3.9	1.16	14.1 – 6.1	8.0
MoO_4^{2-}	25.2	10.8	3.2	1.00	14.4 – 6.0	8.4
WO_4^{2-}	25.2	10.6	3.2	1.00	13.8 – 6.6	7.2
ReO_4^-	25.4	8.0	3.6	1.04	13.4 – 5.8	7.6

Note. The following designations are used: I is the energy of a line /eV; II is the line width at the basis /eV; III is the width at the half-height /eV; IV is the asymmetry index.

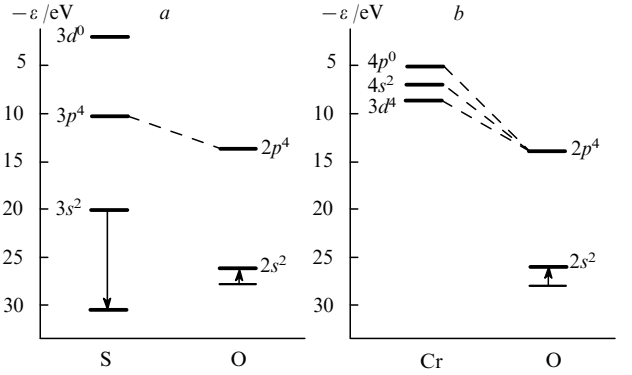


Figure 3. Changes in the energy of quasiatomic orbitals upon the formation of oxo-complexes of a non-transition element (*a*) and a transition metal (*b*).

energies, which are assigned traditionally to the quasiatomic $O2s^2$ levels, have much more complex shapes. In conformity with the generally accepted views, the splitting energies for the $1a_1$ and $1t_2$ MOs calculated from the XPS parameters are relatively large (Δ = 5–6 eV; in the case of ClO_4^-, Δ = 7.4 eV) and this is at variance with the low energy of splitting of the $O2s^2$ levels in MO_4^{m-}.

Secondly, if bands *I* and *II* (see Fig. 1*b*) were actually due to the $O2s^2$ levels in conformity with the generally accepted interpretation, the ratio of their intensities would be 1 : 3, since the ionisation cross-sections for the $1a_1$ ($2e^-$) and $1t_2$ ($6e^-$) $O2s^2$ levels are virtually identical (because their energies are close) and the ratio of their intensities is determined only by their electron populations, *i.e.* it is 1 : 3. However, in all valence XPS of the AO_4^{m-} complexes without exception, the ratio of the intensities of lines *I* and *II* is markedly larger and ranges from 0.5 to 0.7 (instead of the expected 0.33).

Thirdly, the energies of the $O2s^2$ levels in the MO_4^{m-} complexes are close to those of the $O2s^2$ level in the free oxygen atom (the vertical line at 28.5 eV in Fig. 1). If band *I* in the spectrum of AO_4^{m-} is attributed to the $O2s^2$ level, it is impossible to explain its substantial stabilisation, taking into account the negative effective charge on the oxygen atoms in AO_4^{m-} (as well as in MO_4^{m-}). The situation can hardly be saved by referring to the stabilisation by the crystal field of the positively charged cations (K) in the crystal structure of K_mAO_4 (in this case, this stabilisation would be also manifested in K_mMO_4).

The detailed analysis of the intensities and energies of the two bands with the highest energies (*I* and *II*) in valence XPS of AO_4^{m-} shows [92] that the former band corresponds to the quasiatomic ns^2 level of the central atom A, which is not involved in the valence delocalised MOs and hardly participates in the bonds of the atom A with ligands; the latter band, like the corresponding band in the spectra of transition metal tetraoxo-anions, is due to the quasiatomic $2s^2$ levels of the oxygen atoms ($2a_1$ and $1t_2$ MOs). This interpretation (see Fig. 1*a*) eliminates simultaneously all the contradictions mentioned above and makes it possible to understand the characteristic features of the X-ray photoelectron spectra and the essential difference between these spectra of isostructural and isoelectronic tetraoxo-anions of non-transition elements and transition metals.

In fact, since the electronegativity of oxygen is higher than that of the central atom in the AO_4^{m-} complex (as well as in other oxo-complexes of non-transition elements and transition metals), a positive effective charge appears on the central atom and a negative charge appears on oxygen (it is also necessary to take into account the negative charges of the AO_4^{m-} and MO_4^{m-} anions themselves). This results in stabilisation of quasiatomic As^2 orbitals with respect to those in the free atom A and in destabilisation (to a markedly lesser degree) of the quasiatomic $O2s^2$ levels with respect to those in free oxygen atoms (Fig. 3*a*). This is why the highest-energy (~35 eV) band *I* in the valence XPS of AO_4^{m-} cannot belong to the $O2s^2$ levels but represents the quasiatomic ns^2 orbital of the central atom A, which is markedly stabilised (by 7–10 eV) with respect to the ns^2 orbitals of the free atom A. The same energy of stabilisation (up to 10 eV) of both the core and quasiatomic valence orbitals of the central atom A upon the formation of higher complexes has been pointed out by Siegbahn,[83, 84, 97] based on the analysis of the parameters of numerous X-ray photoelectron spectra.

The energy separating bands *I* and *II* in the valence spectrum of AO_4^{m-}, which has earlier been regarded as the energy of splitting of the $1a_1$ and $1t_2$ $O2s^2$ levels, is actually the difference between the energies of the quasiatomic As^2 orbital and the $O2s^2$ levels and can vary over wide limits depending on the individual nature of the atom A (on the energy of the ns^2 orbitals in the free atom A) and on its formal valence.

Now we make an important comment. Whereas in the oxo-complexes of non-transition elements AO_4^{m-}, the quasiatomic ns^2 orbital possesses the greatest binding energy in the valence band, in the case of fluorides AF_k^{m-}, it is the $F2s^2$ levels that are characterised by the greatest binding energy in the valence band. This is due to the fact that the energy of the $2s^2$ orbital of F is much greater (37.8 eV) than that of the $2s^2$ orbital of O (28.5 eV); therefore, the quasiatomic As^2 orbital, which is highly stabilised in the electronic structure of the fluorides AF_k^{m-}, cannot 'outrun' in energy the $F2s^2$ levels, which are somewhat destabilised. Therefore, in the valence XPS of both MF_k^{m-} and AF_k^{m-}, the lines with the highest energies correspond to the $F2s^2$ levels.

The valence ns^2 orbitals of the central atom in the electronic structure of MO_4^{m-} (unlike those in AO_4^{m-}) are incorporated in the valence MOs (their energies being markedly higher than those of the O2*s* states) and thus participate efficiently in the M – L bonds. Therefore, the quasiatomic $2s^2$ levels of oxygen have the greatest binding energies (Fig. 3*b*) in the valence band and, hence, the valence XPS of a MO_4^{m-} complex does not and cannot contain a band similar to band *I* in the spectrum of AO_4^{m-}.

The degree of ionicity of bonds and consequently the effective negative charge on the ligands in MO_4^{m-} are higher than those in isoelectronic AO_4^{m-} complexes, since the electronegativities of atoms M are markedly lower than those of A. Therefore, one can expect that the O2*s*-line in the valence XPS of MO_4^{m-} should be destabilised (with respect to 28.5 eV) to a greater extent than that in the case of AO_4^{m-}. Experimental studies (Fig. 1) have completely confirmed this assumption.

The ratio of intensities of lines *I* and *II* (see Fig. 1*b*) in the valence spectrum (if the former is assigned to the As^2 state) should not be equal to 0.33, but should vary, as is actually observed in experiments, depending on the nature of the central atom A (Cl, Br, I, S, Se, P, or As), on the corresponding changes in the ionisation cross-sections [101] of the valence ns^2 levels of these atoms and on the integral intensity of band *I*, if the ionisation cross-section of the $O2s^2$ level and the integral intensity of band *II* corresponding to it are constant.

The energies of the ns^2 orbitals of the central atoms A in the series $ClO_4^- - BrO_4^- - IO_4^-$, $ClO_4^- - SO_4^{2-} - PO_4^{3-}$, *etc.* depend on the electron populations (effective charges) of atoms A; the latter, in turn, are determined by the chemical individuality of the particular atom A, *i.e.* by the energy of ns^2 AOs in the free atom and by the orbital electronegativity. The energy of an ns^2 AO is also influenced by the total electrostatic charge of the complex, by the difference between the orbital electronegativities of the central atom and the ligands and by some other factors. In addition, according to the interpretation being developed, the energies of the O2s^2 levels vary in the same series. In particular, in the series $ClO_4^- - SO_4^{2-} - PO_4^{3-}$ and $BrO_4^- - SeO_4^{2-} - AsO_4^{3-}$, the energy of stabilisation of the Ans^2 level increases with respect to the ns^2 energy in the free atom A; this corresponds to a decrease in the total charge on atoms A in these series due to the decrease in the *ns* and *np* orbital ionisation potentials of A. The destabilisation of the quasiatomic O2s^2 and O2p^2 levels in relation to their energies in a free oxygen atom increases in the same series; this is due to the increase in the valence electron density on the oxygen atoms in AO_4^{m-}. Similar regularities caused by the same reasons are observed in the series $ClO_4^- - BrO_4^- - IO_4^-$ and in analogous series of tetraoxo-anions of sulfur, selenium, phosphorus, arsenic, *etc.*

This new interpretation of valence XPS of oxo-complexes of non-transition elements is versatile and covers not only AO_4^{m-} tetraoxo-anions but also the rest of known oxo-complexes with different numbers of coordinated oxygen atoms, with another symmetry, *etc.* In this case, additional arguments supporting this interpretation appear.

Firstly, the quasiatomic nature of Ans^2 AOs is confirmed by the fact that the intensity of a particular line in valence XPS of compounds of the same non-transition element is almost the same; this is also true for those compounds in which the Ans^2 orbitals are known not to participate in A – L bonds, for example in the $ClO_4^- - ClO_3^- - ClO_2^- - ClO^- - Cl$ series. If an Ans^2 orbital did participate in A – L bonds, the intensity of the Ans^2-line (normalised with respect to a certain core level) would not remain constant irrespective of the structure of the oxo-complexes, owing to different degrees of mixing of Ans^2 and O2*p* orbitals in the valence MOs.

Secondly, as the number of coordinated oxygen atoms in an oxo-complex decreases, the ratio of the intensities of Ans^2- and O2s^2-lines in its valence spectrum increases proportionately. This type of behaviour is characteristic only of quasiatomic electron levels.

Thirdly, if the line with the highest binding energy in valence X-ray photoelectron spectra of oxo-anions and other complexes of a non-transition element actually corresponds to a quasiatomic Ans^2 state, then the energy of this level, like that of any inner level, should increase linearly following an increase in the oxidation state of the atom A. Besides, the 'sensitivity' of the binding energy of a quasiatomic Ans^2 level to the number of ligands with a higher electronegativity (oxygen atoms in this particular case) coordinated to it should be higher than that of other inner levels of the atom A with the same symmetry. In other words, it should be expected that the rate of increase in the *ns* level binding energy will be higher than those for $(n-1)s$, $(n-2)s$, *etc.* levels in the series of compounds with increasing oxidation state of the central atom, because the *ns* level is the most outer level among those considered. In the valence XPS of chromium, sulfur, selenium, and arsenic compounds with various oxidation states, the binding energies for ns^2 levels of atoms A have been determined. This is illustrated by Fig. 4, which shows, as an example, the dependence of the chemical shift of the Cl3s^2 level on the oxidation state of chlorine. Moreover, this Figure contains analogous relationships for the chemical shifts of the *K*(1*s*) and *L*(2*s*) levels of chlorine based on the data of Siegbahn.[84] It can be seen that the binding energy of the Cl3s^2 level actually increases linearly with an increase in the oxidation number of chlorine atoms, the rate of its growth being much greater than those for the energies of core levels.

The fact that the energies of the valence ns^2 levels of central atoms A behave in the same way as the core 1s^2 and 2s^2 levels (as regards a nearly linear variation of their energies as functions of the formal valence of the atom A) seems very important for the solution of the problem of participation of Ans^2 orbitals in the formation of the electronic structure of a non-transition element complex. According to the generally accepted views, only valence-inactive quasiatomic electron levels behave in this manner.

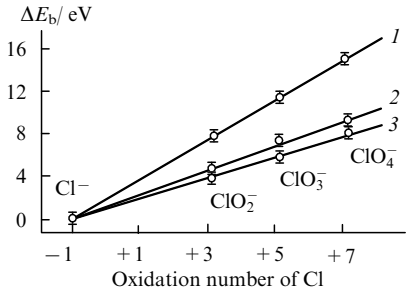


Figure 4. Dependence of the chemical shifts of Clns^2 levels on the oxidation number of the chlorine atom.
(*1*) Cl3*s*, (*2*) Cl1*s*, (*3*) Cl2*s*.

Thus, the analysis of the parameters (energies and line intensities) of valence band X-ray photoelectron spectra of oxo-complexes of non-transition elements of the Third and subsequent Periods (especially, comparison of these parameters with those for oxo-complexes of transition metals) leads to the following conclusion: the occupied ns^2 orbitals of the central atom in AO_k^{m-}, unlike those in MO_k^{m-}, are involved in bonds with ligands to only a small extent. The Ans^2-electrons remain quasiatomic and are markedly stabilised compared to the corresponding electrons in free atoms.

Further X-ray-electron evidence for the valence inactivity of the occupied Ans^2 orbitals is the linear dependence of the inner level energy of the central atom on its formal valence, which has been considered above.[86] In fact, the occupied ns^2 orbitals of the central atom A could participate in two-centre two-electron (covalent) bonds with ligands by the dative mechanism, $As^2 \rightarrow Lnp$ (2 : 0) due to the vacant valence orbitals of the ligands or by forming three-centre four-electron (hypervalent) $L_{(1)}np \leftarrow As^2 \rightarrow L_{(2)}np$ bonds due to the valence orbitals of the ligands with unpaired electrons. In both cases, this would be accompanied by the transfer of electronic charge from the central atom to the ligands, a decrease in the electronic charge on atom A, a corresponding increase in the binding energy of its inner level and by the disturbance of the linearity discussed above. This is due to the fact that, since the penetration ability of the *ns* orbitals in atom A is higher than that of the *np* orbitals, their participation in the bonds with ligands should 'uncover' the nucleus of the atom A to a greater extent and, in conformity with the effect of internal shielding, this should stabilise more efficiently the core levels of the atom A. The linear variation mentioned above of the binding energy of the Xe3$d_{5/2}$ level in the series of xenon fluorides is spectacular in this respect. It is almost obvious that not only the Xe5*d* AOs do not participate in the the electronic structure of xenon fluoride, but the occupied Xe5s^2 orbitals [$\sigma_g(XeF_2$, $D_{\infty h}$ symmetry), $a_{1g}(XeF_4$, D_{4h} symmetry), $a_{1g}(XeF_6$, O_h symmetry)] also remain quasiatomic[89,90] and refer to fully symmetrical irreducible representations; the hypervalent bonds F – Xe – F involve only the valence 5*p* orbitals of the xenon atom.

In general, the 'linear effect' indicates that the vacant A*nd* and occupied Ans^2 orbitals of the central atom A do not make any significant contribution to the A – L bonds and that these bonds are formed via consecutive involvement of valence orbitals of the atom A of only one type, namely, the *np* AOs. The linear increase in the energy of the inner level is due to the variation in the quantitative characteristics of the participation of *np*-electrons in the bonds with ligands following the change in the oxidation state of the central atom A. In the electronic structures of AL_k complexes,

the A*nd* orbitals remain virtual, while the occupied Ans^2 orbitals prove, as a rule, to be valence-inactive and remain quasiatomic.

Thus, taking into account the differences in the shielding effects, in the penetration ability, in single-electron energies, and in the electronegativities of valence *ns*, *np*, and *nd* orbitals of the atom A, one can conclude that if the A*nd* and (or) Ans^2 orbitals did really participate in the A – L bonds, the linear dependence of binding energy (E_b) of the inner level of the atom A on its oxidation state would be necessarily violated. Experimental evidence for the fact that the dependence of E_b of the inner levels always deviates from linearity when Ans^2 orbitals are effectively involved in the valence MOs will be presented below. Analogous facts concerning A*nd* orbitals have not yet been found, but SCF MO LCAO *ab initio* calculations of the electronic structures of the ClO_4^-, SO_4^{2-}, and PO_4^{3-} oxo-anions [26] indicate that when the A3*d* functions are included in the atomic basis set, the effective charge on the central atom A sharply decreases compared to that obtained for a purely *sp* basis set (for example, from +2,4 to +0.8 for Cl in ClO_4^-). Therefore, the electron density on the atom A increases, and this should markedly diminish the binding energy of its inner levels, *i.e.* should result in abnormal values of E_b, deviating from the linear dependence.

The present concept of small contribution of the valence Ans^2 orbitals to the MOs of A – L bonds has also been supported in other experimental and theoretical studies, which are yet few in number. The results of HFR non-empirical calculations [26, 88] show that in the electronic structures of ClO_4^-, SO_4^{2-}, PO_4^{3-} and ClO_3^- oxo-complexes, the A3s^2 orbitals make the major contribution to the lowest valence MO (thus, it is not a pure O2s^2 level) rather than to those MOs, which are located above the O2s^2 energy levels and are responsible for the A – L bonds. In the X-ray emission S*L*-spectra of sulfur compounds, the parameters of the high-intensity long-wavelength band reflecting the transition from the lowest valence MO of the complex imply that this MO is mostly S3s^2 rather than O2s^2. The data of Mössbauer spectroscopy are more difficult to interpret. The results of examination of the Mössbauer spectra (and the chemical shifts therein) of numerous compounds of antimony, tellurium, iodine, xenon do not permit unambiguous conclusions to be made on the participation of valence Ans^2 orbitals in the A – L bonds.[102]

The views about a minor role of valence Ans^2 AO in the bonds with ligands are applicable to many compounds of non-transition elements of the Third and subsequent Periods but certainly, not to all of them.

Let us first consider complexes of non-transition elements of the second halves of the rows, *i.e.* Group V – VII elements: P, S, Cl, Ar (the so called late *p*-elements), and their analogues. Experimental results and general theoretical considerations based on the *ns* and *np* orbital energies and on the energies of (*np* – *ns*)-separation for free atoms A [10] make it possible to draw the following significant conclusion: the valence activity of A3s^2, A4s^2, and, especially, A6s^2 orbitals is low (the inert pair effect [10]). For atoms of Group VII and VI non-transition elements, both the energies of (*np* – *ns*)-separation ($\sim$10 – 15 eV) and the isonisation potentials of *ns* and *np* orbitals are high; this rules out the donor capacity of these atoms and thus predetermines the valence inactivity of their ns^2 orbitals. In the case of the phosphorus atom and its analogues (Group V), the energies of (*np* – *ns*)-separation are no longer large (3 – 7 eV), but the *ns*- and *np*-orbital ionisation potentials are still high. The latter factor proves to be the crucial factor that restricts the participation of the Ans^2 orbitals in bonds with ligands.

The valence 5s^2 orbitals of antimony, tellurium, iodine and xenon atoms participate most likely in bonds with ligands. The (*np* – *ns*)-separation energies in their subgroups are the lowest.[10] First of all, precise studies are needed for the electronic structures of their complexes with large coordination numbers such as $[Sb(OH)_6]^-$, TeF_6, H_6TeO_6, IF_7, H_5IO_6, XeF_6^{2-}, $[H_2XeO_6]^{2-}$, *etc*. Some data on this topic have been already reported. Both the internal conversion electron spectra and XPS of Ag_6TeO_6 attest [103] to the direct participation of the Te5s^2-electrons in the formation of bonds (whereas in TeO_2, the bonds are formed only through the 5*p*-electrons of Te). The valence XPS of Ag_6TeO_6 contains no Te5s^2-line, which is present in the XPS of TeO_2. However, in the interpretation of the valence XPS of complexes of the Ag_6TeO_6 type, there is a risk of taking the absence of the Ans^2-band as direct evidence for the participation of the Ans^2 orbital in the bonds with ligands, whereas this AO can be destabilised (due to changes in the valence electron density distribution or in the internal shielding) and thus, it can be masked by normal valence MOs having close energies, even though it remains a non-valence quasiatomic orbital.

Nevertheless, the actual participation of Ans^2 orbitals in the valence MOs forming the A – L bonds in some complexes seems more likely. In this case, the formation of dative (2 : 0) A$ns^2 \rightarrow$ L bonds or three-centre four-electron $L_{(1)} \leftarrow A ns^2 \rightarrow L_{(2)}$ hypervalent bonds is possible. In any case, the effective participation of valence Ans^2 orbitals in binding with ligands seems to be feasible only when a number of conditions are fulfilled. The main conditions are sufficient electron-donating capacity of the central atom A (which can be increased, for example, by the formation of primary A – L bonds involving the valence A*np*-electrons) and large electron-accepting capacity of the ligands, up to the presence in their valence structures of vacant orbitals with low energies capable of participating in dative two-electron A$ns^2 \rightarrow$ L interactions. It is evident that high oxidation numbers and high coordination numbers of atom A are favourable for the involvement of its Ans^2 orbitals in the valence MOs.

In the case of complexes of early non-transition elements (Na, Mg, Al, Si, and their analogues), the traditional statement that their valence Ans^1 and Ans^2 orbitals are completely (in the majority of cases) involved in covalent bonds with ligands is beyond any doubt. These atoms are characterised by fairly low energies of the (*np* – *ns*)-separation [10] and by relatively low excitation energies of valence states[16]

3. Occupied A2s^2 orbitals

A special position in the theory of the electronic structure of complexes of non-transition elements is occupied by elements of the Second Period. This is due to the specific spatial and energy characteristics of the valence 2*s* and 2*p* orbitals of their atoms. 'The valence behaviour' of the 2s^2 orbitals of atoms of the Second Period elements requires special investigation. To solve the problem of the contribution of the occupied valence 2s^2 orbitals of atoms of these elements to delocalised MOs, the X-ray photoelectron spectra of the inner atomic levels and the valence bands of nitrogen compounds with various formal valences of the nitrogen atom have been studied. Based on the results obtained, conditions of effective participation of the valence 2s^2 orbitals of the central atoms in bonds with ligands have been identified.[104, 105] The energies of the N1*s* and N2*s* levels in nitrogen compounds needed for further discussion are listed in Table 3.

Study of the effects of chemical shift of the inner 1*s* level in X-ray photoelectron spectra of nitrogen compounds demonstrates, first of all, that, in a number of its compounds, the dependence of the binding energy of the N1*s* level on the nitrogen oxidation state is nearly linear (Fig. 5). When the oxidation number of nitrogen increases by unity, the binding energy of the N1*s* level increases by $\sim$1 eV, as has also been noticed in other studies.[106 – 108] The fact that this dependence is linear implies that in these compounds, the valence 2s^2 orbitals of nitrogen atoms barely participate in the bonds with ligands (in the formation of delocalised MOs) and that the N2s^2-electrons remain quasiatomic.[92] The chemical bonds in nitrates, nitrites, cyanides, thiocyanates and nitrides are mainly formed from the valence 2*p*-electrons of the nitrogen atoms, the 2s^2-electrons being inactive.

At the same time, for some lower compounds of nitrogen (NH_4^+, $N_2H_6^{2+}$, NH_3OH^+), the plots for E_{N1s} deviate markedly from linearity (see Fig. 5). These deviations exceed the error in the determination of the N1*s*-energy by a factor of ten. In particular,

Table 3. Energies of inner N1*s* levels and valence N2*s* levels in nitrogen compounds.

Compound	Oxidation number of nitrogen	Energy/ eV	
		N1*s*	N2*s*
$(NH_4)_2SO_4$	−3	401.6	(see [b])
$NH_4H_2PO_4$	−3	401.6	"
NH_4Cl	−3	401.2	"
NH_4F	−3	401.5	"
NH_4^+ (see [a])	−3	401.4	"
NH_3 (coordinated)	−3	399.9	–
$[Rh(NH_3)_6]Cl_3$	−3	398.6	–
NH_3 (solid)[a]	−3	398.3	–
AlN	−3	397.3	22.8
Si_3N_4	−3	397.4	22.8
Si_2N_2O	−3	397.2	22.6
KSCN	−3	397.7	26.3
NaSCN	−3	397.6	26.0
$K_3[Fe(CN)_6]$	−3	397.6	26.0
$N_2H_4\ H_2SO_4$	−2	401.6	(see [b])
$NH_2OH\ HCl$	−1	401.7	"
$[NH_3OH]Cl$	−1	402.1	"
NaN_3			
N_I, N_{III} (terminal)	−1	398.8	29.5
N_{II} (bridging)	+1	403.1	(see [b])
$NaNO_2$	+3	403.2	–
KNO_2	+3	403.2	32.6
NO_2^- (outer-sphere)[a]	+3	403.2	–
NO_2^- (inner-sphere)[a]	+3	403.2	–
KNO_3	+5	403.3	–
$NaNO_3$	+5	407.2	35.4
$LiNO_3$	+5	407.0	35.5
NO_3^- (outer-sphere)[a]	+5	406.6	–
NO_3^- (inner-sphere)[a]	+5	407.3	–

[a] The N1*s*-level energies were taken from Refs 106 and 107 and scaled to the binding energy of the C1*s*-level, equal to 284.5 eV. [b] The N2*s*-level energy was not measured.

the average energy of the N1*s* level in the ammonium cation (401.5 eV) is much greater than that in solid ammonia (398.3 eV) or in other compounds of nitrogen with the same (−3) oxidation number. The energy of the N1*s* level in NH_3 is determined by the effective charge on the nitrogen atom, which appears owing to the non-zero degree of ionicity of the three covalent (1 : 1) N–H bonds involving the unpaired 2*p*-electrons of the nitrogen atom and the 1*s*-electrons of the hydrogen atoms. The formation of an NH_4^+ tetrahedral cation via protonation of an NH_3 molecule is possible only when the fourth N–H bond is formed by a dative mechanism (2 : 0), due to the transfer of electron density from the quasiatomic $2s^2$ orbital of the nitrogen atom to the vacant 1*s* orbital of H^+. Thus, the valence electron density on the nitrogen atom decreases, and its effective charge becomes positive; as a result, the inner N1*s* level (in NH_4^+) is stabilised. This fact can be detected experimentally: on passing from solid ammonia (398.3 eV) to the ammonium cation (401.5 eV), the binding energy of the N1*s* level increases by 3.2 eV.

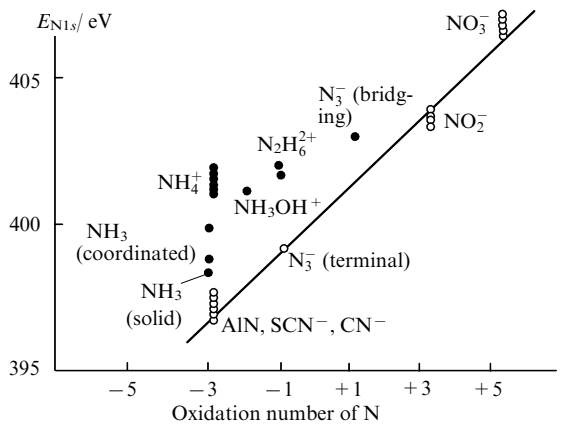


Figure 5. Energy of the N1*s* level as a function of the oxidation number of the nitrogen atom.

It is this participation of the $2s^2$-electrons of nitrogen in the formation of the N–H bonds in NH_4^+ that accounts for the fact that the E_{N1s} value for the NH_4^+ ion is abnormally high, taking into account the clear-cut decrease in the binding energy of the N1*s* level following the decrease in the oxidation number of nitrogen (from nitrates and nitrites to NH_3, nitrides, cyanides and thiocyanates), and does not fit the linear dependence. It is obvious that the same fact leads to the abnormally large chemical shifts and to the deviations from the linear dependence of the N1*s* binding energy on the oxidation state of nitrogen in the case of hydrazinium ($N_2H_6^{2+}$) and hydroxylammonium (NH_3OH^+) compounds and for the central bridging nitrogen atom in the azide anion N_3^-. The deviation from linearity can be different in each particular case, since it depends on the type and the number of ligands bound to nitrogen, on the nature of partners of the nitrogen-containing complex in a crystal, *etc*.

Certainly, in solid ammonia, too, some participation of the $2s^2$-electrons of the nitrogen atom in the formation of hydrogen bonds cannot be ruled out completely; therefore, the binding energy of the N1*s* level in solid NH_3 exceeds somewhat the corresponding value for nitrides, thiocyanates and cyanides. The coordination of NH_3 molecules to transition metal atoms M, *i.e.* the formation of dative M ← NH_3 (2 : 0) σ-bonds through the $2s^2$-electrons of nitrogen atoms and vacant orbitals of M atoms in ammine complexes, stabilises the inner N1*s* levels in these complexes with respect to those in free NH_3 molecules (or in the molecules, weakly associated in the solid state). Therefore, the binding energy of the N1*s* level in ammine complexes is greater than that in solid NH_3; it increases as the M ← NH_3 bonds strengthens, approaching the value characteristic of the ammonium cation.

The dissimilar roles of the $N2s^2$-electrons in the structures of $N_2H_4 - N_2H_5^+$, $N_2H_6^+$ and $NH_2OH - [NH_3OH]^+$ can be explained by analogy with the $NH_3 - NH_4^+$ pair.

The deviations from linearity of the dependence of the E_{N1s} binding energy on the oxidation state of the nitrogen atom for some of its compounds not only indicate that the valence $2s^2$ orbitals of nitrogen atoms participate in delocalised MOs. Besides, it can serve as additional evidence for the fact that the linearity itself in the change of the energy of the inner level of the central atom actually shows the absence of a significant contribution of the valence ns^2 AOs of atoms of non-transition elements to the chemical bonds in the corresponding complexes [92] and the participation of only valence *np*-electrons of the central atom in the bonds with ligands. The involvement in the A–L bonds of orbitals with a different symmetry (*ns*) and with a qualitatively different spatial distribution results in sharp deviations from linearity; this is actually observed for the E_{N1s} binding energy in the series of nitrogen-containing compounds.

The second X-ray photoelectron criterion for the participation (or non-participation) of the $2s^2$-electrons of the central atom in the A–L bonds is the presence or the absence of the N2*s*-line in the valence XPS of nitrogen compounds and the appropriate shifting effects. In fact, the XPS of those compounds, the A*ns*-electrons of which knowingly participate in A–L bonds, contain no A*ns*-lines in the valence band (compounds of Na, Mg, *etc*.). Fig. 6 shows the valence band of the X-ray photoelectron spectra of typical nitro-

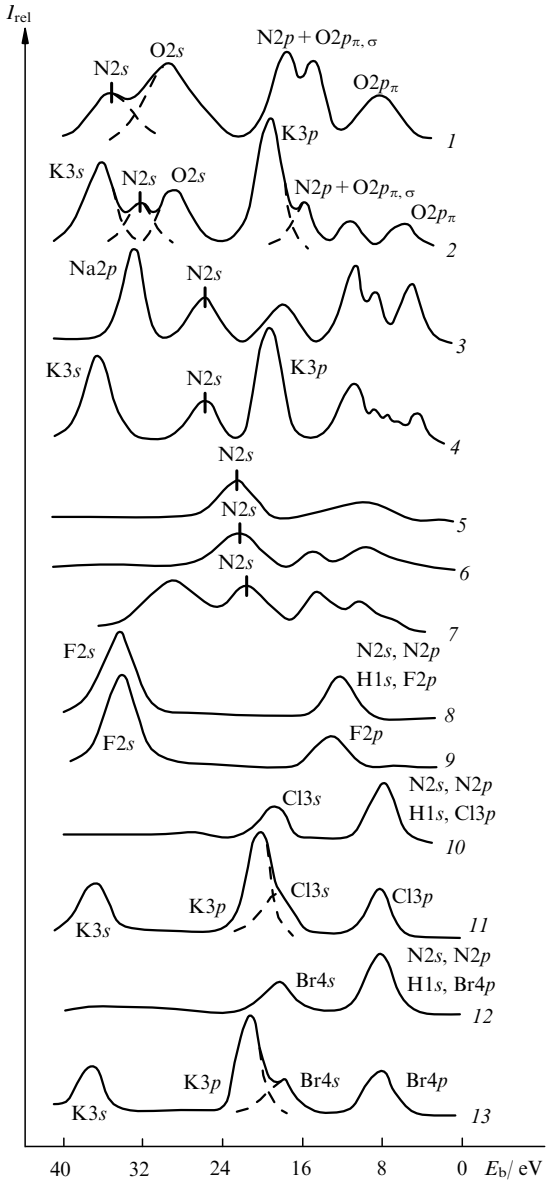


Figure 6. Valence band X-ray photoelectron spectra of nitrogen compounds.
(*1*) $LiNO_3$, (*2*) KNO_2, (*3*) NaSCN, (*4*) $K_3[Fe(CN)_6]$, (*5*) AlN, (*6*) Si_3N_4, (*7*) Si_2N_2O, (*8*) NH_4F, (*9*) LiF, (*10*) NH_4Cl, (*11*) KCl, (*12*) NH_4Br, (*13*) KBr.

gen-containing compounds: nitrates, nitrites, ammonium cations and some others. Of course, the N2*s*-line is present in the spectra of all those compounds of nitrogen in which its valence $2s^2$-electrons do not participate in bonds with ligands and remain quasiatomic (the binding energies of the N1*s* level in these compounds depend linearly on the oxidation state of nitrogen, see Fig. 5). In this case, the line due to the N2*s* level shifts regularly to lower energies as the electronegativity of the atoms bound to nitrogen decreases, *i.e.* from NO_3^-, NO_2^- to Si_3N_4 and AlN. In the NO_3^- anion, the N2*s* level is observed at 35.4 eV, the intensity of this line in the appropriately normalised spectra of particular nitrates ($LiNO_3$, KNO_3, NH_4NO_3) being constant to within the error of determination. For these compounds, the ratio of the integrated intensities of the lines due to the N2*s* and O2s levels also remains constant. In the NO_2^- anion, the N2*s*-level energy diminishes to 32.8 eV, and the ratio of the intensities of N2*s*- and O2*s*-lines increases; this is caused by the increase in the nitrogen-to-oxygen stoichiometric ratio on passing from NO_3^- (1 : 3) to NO_2^- (1 : 2). In the spectra of silicon and aluminium nitrides and silicon oxynitride, the N2*s* level shifts to lower binding energies to an even greater degree approaching the ionisation potential of the 2*s* orbital in the free nitrogen atom.

The main effect that is found in analysis of the valence X-ray photoelectron spectra of nitrogen-containing compounds is that the N2*s*-line is not observed in the spectra of ammonium compounds (see Fig. 6). This fact indicates unambiguously that the $2s^2$-electrons of the nitrogen atom are completely involved in the formation of the N – H bonds in the NH_4^+ cation. The effective participation of the nitrogen 2*s* orbitals in the valence MOs of this cation is supported by one more fact. The valence X-ray photoelectron spectra of NH_4Cl, NH_4Br and KCl, KBr, in which the positions of the Cl3*s*- and Br4*s*-lines remain constant, possess the following significant feature. If the spectra of NH_4Cl and KCl are normalised with respect to the Cl3*s*-line, and the spectra of NH_4Br and KBr are normalised with respect to the Br4*s*-line, it can be seen that the integrated intensities of the most outer bands in the spectra of ammonium compounds are markedly higher (by $\sim 30\% - 40\%$) than those for potassium compounds. This could be possible only in the case where the intensities of the outer bands in the spectra of NH_4Cl and NH_4Br contain some contribution from the molecular orbitals forming the N – H bonds and formed with participation of not only the N2*p*- and H1*s*-electrons with small ionisation cross-sections (91.1 and 2.7 barns, respectively), but also the $N2s^2$-electrons with much larger ionisation cross-sections (1179 barns).[109]

It is evident that the same reasons (the $2s^2$-electrons of the nitrogen atom participate in the bonds in NH_4^+ and do not noticeably contribute to the bonds in NO_3^-, NO_2^-, CN^-, N_2 and NH_3) account for the difference in the forms of KVV-Auger lines of nitrogen (Fig. 7). (It should be borne in mind that here we speak about the coordinated CN^- anion, the electron structure of which differs appreciably from that of the 'free' anion; regarding the N_2 molecule, we speak mainly about the virtually non-bonding $2\sigma_u$ MO consisting mostly of the N2*s* AO.). The valence bands in the KVV-Auger spectra of NO_3^-, NO_2^-, CN^-, N_2 and NH_3 contain two complex lines and are quite similar to one another. However, the spectrum of NH_4^+ contains only one line.[110] Probably, these differences in the KVV-Auger spectra of nitrogen are due to the fact that its $2s^2$ orbitals participate in the bonds with ligands in NH_4^+ and are quasiatomic in NO_3^-, NO_2^-, CN^-, N_2 and NH_3. This analogy in the

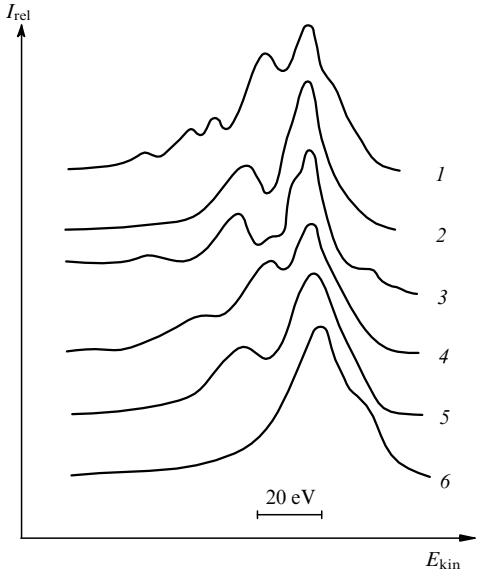


Figure 7. KVV-Auger spectra of nitrogen.
(*1*) NH_3, (*2*) $K_4[Fe(CN)_6]$, (*3*) N_2, (*4*) $NaNO_2$, (*5*) KNO_3, (*6*) NH_4Cl, NH_4Br.

shapes of the valence X-ray photoelectron and Auger spectra of the nitrogen compounds in question is a significant argument in favour of the ideas about the electronic structures of nitrogen-containing complexes developed in this review.

We can see that the X-ray photoelectron spectra of the inner N1*s*-electrons (the linearity in the variation of the E_{N1s} value or disturbance of the linearity) and of the valence electrons (the presence or the absence of the N2*s*-line and shifting effects) and the KVV-Auger spectra (the presence of one or two complex bands) all indicate that the $2s^2$ orbitals of nitrogen either participate efficiently in the valence MOs, or, conversely, remain quasiatomic in the electronic structure of nitrogen compounds. The valence XPS of those compounds for which the linear dependence of the E_{N1s} binding energy on the oxidation state of nitrogen holds, exhibit a line for the N2*s*-electrons, and the KVV-Auger spectra of these compounds contain an additional band. The same spectra of those compounds for which the E_{N1s} values deviate markedly from the linear dependence do not exhibit the spectral bands mentioned above. The valence $2s^2$ orbitals of nitrogen in the former type of compound are scarcely involved in the A – L bonds and remain quasiatomic, whereas those in the latter type of compound contribute considerably to the corresponding delocalised MOs.

Thus, analysis of X-ray photoelectron spectra of complexes of the Second Period elements carried out in relation to nitrogen compounds (containing nitrogen in various oxidation states) shows that the valence $2s^2$ orbitals of these atoms can both participate efficiently in the bonds with ligands and remain quasiatomic. This depends not only on the spatial and energy parameters of the $2s^2$ AO but also on some 'indirect' parameters such as the charge of the complex ($NH_4^+ - CH_4 - BH_4^-$), the $\varepsilon_{2p} - \varepsilon_{2s}$ energy difference of the central atom, *etc*.

However, it is possible that the $2s^2$ AOs always participate in the formation of MOs in the complexes under consideration but the extent of this participation can be very low; therefore, it may not manifest itself in the physical properties of compounds, in particular, in the parameters of the X-ray photoelectron spectra of the valence band and inner levels. The scope of publications devoted to the results of experimental and quantum-chemical studies of the electronic structures of complexes of typical elements is immense. Therefore, it is expedient to identify the criteria for participation or non-participation of the A2s^2 orbitals in the A – L bonds in a general form; it is clear that these criteria will be approximate and will claim only to serve as more or less general rules.

In the majority of compounds of early typical elements (Li, Be, B, C) including diatomic homo- and heteronuclear molecules, the A2s^1 and A2s^2 orbitals, together with the A2p^m orbitals, participate efficiently in typical covalent bonds with ligands, irrespective of the oxidation state of atom A, the nature of ligands L and the geometry of the complex. Both the spatial and energy factors are favourable for this participation. The main maxima of the radial density of A2*s* orbitals are located at a larger distance from the atomic nucleus than the maxima of A2*p* orbitals; the magnitudes of the energy of A2*s* and A2*p* orbitals are relatively small and are close to each other (the separation energies do not exceed 5 – 6 eV); the energies of excitation of valence states are also relatively low.

The electronic structures of compounds of late typical elements (N, O, F) including their diatomic molecules are much more diverse. The spatial factors are again favourable for the A2s^2 orbitals to be involved in the valence MOs of the A – L bonds. However, the energy factor impedes the valence activity of the A2s^2 AOs, since these AOs have very low energies; the fairly large energies of the $2p - 2s$ separation should be taken into account (they amount to 15 – 20 eV, and only for nitrogen, this energy is as low as 6 eV).

In the case of atoms of late typical elements with occupied $2s^2$ orbitals, there exists, as a matter of fact, only one way for these orbitals to participate in bonds with ligands, namely, the formation of dative A – L (2 : 0) bonds. In fact, the formation of hypervalent $L_{(1)} \leftarrow A2s^2 \rightarrow L_{(2)}$ bonds is unlikely, due to the fairly low energies of the A2s^2 orbitals of nitrogen, oxygen and fluorine. Therefore, in this case, the criteria for participation of A2s^2 AOs in the A – L bonds go beyond the spatial and energy characteristics of A2s^2 AOs. For this participation, a number of conditions should be fulfilled, which are determined by the individual nature of the A and L atoms and their state in the molecule (the difference between their electronegativities, the energies of their valence orbitals, the electron populations of their AOs, *etc*.) An important condition for the involvement of A2s^2 AO in the A – L bonds is, as in the case of ns^2 AO with $n \geqslant 3$,[92] the presence of a vacant acceptor orbital with a low energy in the valence structure of the ligand. In this case, the formation of a dative A → L (2 : 0) bond becomes possible even though the donor A2s^2 orbital itself has a low energy. A significant role is played by the electron rearrangements following the formation of the 'primary' A – L bonds involving the valence orbitals of the atom A, which leads to redistribution of the electron density in the complex. A new (with respect to the free atoms) electron density distribution gives rise to a change in the spatial and energy characteristics of the AO. These changes can be taken into account, for example, by varying the AO exponents. For A2*s* AOs, these changes can promote an increase in the overlap with the valence orbitals of L and an approach to them in energy, *i.e*. they enhance the interaction of A2*s* AOs with the ligand orbitals; however, they can also act in the opposite direction. One must bear in mind that relaxation effects (changes in the length and energy) are more pronounced for the A2*s* AOs, which possess high penetration abilities, than for the A2*p* AOs. Therefore, the relaxation effects caused by the formation of the 'primary' A – L bonds can result in inverted lengths of the 2*s* and 2*p* orbitals of the atom A (the 2*s* AO can become less extended than the 2*p* AO) and in increased separation energies of these AOs (*i.e*. substantial stabilisation of the $2s^2$ AO); consequently, the contribution of the A2s^2 AO to the delocalised MOs of the complex would diminish.

Apparently, for A2s^2 orbitals to participate efficiently in the A – L bonds, all (or most) of the above conditions need to be satisfied; each of these conditions can be regarded as necessary but not sufficient. Apparently, this accounts for the fact that in many complexes of late Second Period elements, the A2s^2 orbitals scarcely participate in the bonds and remain quasiatomic.

The A2s^2 orbitals in the electronic structures of the molecules of hydrides FH, OH_2 and NH_3 are quasiatomic and, according to the data of photoelectron spectra,[111] they are stabilised by 2, 4 and 7 eV, respectively, in relation to their energies in the corresponding free atoms. The role of A2s^2 orbitals in the valence structures of the FH_2^+ and OH_3^+ molecular cations is less obvious. The electronic structures of CH_4 and NH_4^+ must be discussed specially; this is necessary to generalise the views about the electronic structures of tetrahedral molecules and ions, CH_4, CF_4, NH_2^+, BH_4^-, BF_4^-, NR_4^+, *etc*.

An important feature of the electronic structure of the NH_4^+ cation lies in the fact that the difference between the energies of its valence molecular orbitals a_1 and t_2 is very small; according to the XPS data, this difference does not exceed 1.5 – 2 eV, whereas the generally accepted estimate of this value is ~10 eV (by analogy with the isoelectronic CH_4 molecule). It follows from the valence XPS of the NH_4^+ cation (see Fig. 6) that both the a_1 and t_2 orbitals are located within the same (outer) band including also F2*p*, Cl3*p* or Br4*p* levels. Whereas the structure of the valence band XPS of NH_4Cl and NH_4Br, in which the Cl3*s* and Br4*s* levels are separated by 8 – 10 eV from the outer line, gives rise to the illusion of a large difference between the energies of the a_1 and t_2 MO in the NH_4^+ cation, the interpretation of the valence spectrum of NH_4F does not involve any ambiguity and, therefore, it is especially representative. In this spectrum nothing is added to the outer (in energy) band (the energy of the F2*s* level closest to it is higher by 25 eV); both ($a_1 + t_2$) valence MOs of the NH_4^+ cation are obviously included in this band, and this leaves no doubt in the fact that their energies are close to each other.

The energies of the a_1 and t_2 MOs of the NH_4^+ cation in the halides lie in the range of 8–12 eV and thus they are markedly higher than the energies of the 2*p* (15 eV) and, especially, the 2*s* AO (20 eV) in the free nitrogen atom. Attention is drawn to the fact that the system of 8 valence electrons is markedly destabilised on passing from NH_3 (MO: $2a_1$ — 11 eV, $1e$ — 16 eV and, especially, N2s^2: $1a_1$ — 28 eV) to NH_4^+. Of course, one should bear in mind that this is a transition from a free molecule to a molecular cation in the crystal, but, nevertheless, the strong destabilisation of the N2s^2-electrons on passing from the quasiatomic state (NH_3) to a delocalised multi-centre MO (NH_4^+) deserves attention.

The minor difference between the energies of the a_1 and t_2 MOs in NH_4^+ is consistent with the relatively small difference (3 eV) between the same MOs in CF_4 and differs appreciably from the corresponding value (9 eV) for the isoelectronic CH_4 molecule.[112] Unlike the 2s^2 orbitals of the central atom in NH_4^+ and CF_4 participating efficiently in the valence MOs, the valence 2s^2-electrons of the C atom in the electronic structure of CH_4 are apparently involved only partly in the bonds with ligands and largely retain their quasiatomic character;[2] this predetermines the higher energy of separation of the a_1 and t_2 MOs in this case. This means that even in the 'classical case' of the CH_4 molecule with sp^3-hybridisation, the problem under consideration is not simple. The C2s^2-electron pair remains significantly unshared (*i.e.* the a_1 MO is non-bonding), and the C–H bonds are formed mainly due to the C2p_σ–H1*s* interactions (owing to the occupation of the bonding t_2 MO); hence, the C–H bonds are orbital-deficient hypervalent bonds (6e$^-$) rather than normal covalent bonds (8e$^-$) described by equivalent MOs in terms of the sp^3-hybridisation of AOs as in CF_4. The above differences between the electron structures of CH_4 and CF_4 are confirmed by the fact that on passing from CH_4 to CF_4, the average (and total) MO bonding energy increases. Undoubtedly, this relation would be the opposite if the electron structures of CF_4 and CH_4 were identical (covalent 8-electron bonds).[10]

Thus, in tetrahedral AL_4 molecules, the difference between the energies of valence a_1 and t_2 MOs is small in the case where the 2s^2-electrons of the central atom participate in A–L bonds; conversely, in the case of 'valence inertness' of the 2s^2 AOs this difference proves to be fairly large. In turn, the effective interaction of the 2s^2 AO of the central atom with the valence orbitals of ligands is largely determined by close energies of the interacting orbitals of A and L (for example, the C2*s* and F2p_σ orbitals in CF_4 are closer to each other than the C2*s* and H1*s* orbitals in CH_4). The relationship between the energies of valence a_1 and t_2 MOs follows a complex dependence on the difference between the orbital electronegativities, on the distribution of valence electron density in AL_4 induced by the formation of the A–L bonds consisting of the 2*p*-electrons of the central atom, on the initial and optimised orbital energies of the A and L atoms depending on the effective charges on them and on some other factors. A small difference between the a_1 and t_2 MO energies may appear in both neutral molecules (CF_4 but not CH_4) and in cations (NH_4^+) and, probably, in anions as well. It can be foreseen that in the BF_4^- tetrahedral anion, the valence a_1 and t_2 MOs are characterised by a low separation energy. Indeed, the valence band XPS of BF_4^- make it possible to reliably determine this difference as being equal to ~2 eV (Fig. 8). To interpret the valence bands in the spectra of $LiBF_4$ and $NaBF_4$, the valence band spectra of LiF and MgF_2 are also presented. The value of 2 eV is also reproduced in the DVM X_α-calculations for the electronic structure of BF_4^-.[113]

In the compounds of late Second Period elements, 2s^2 orbitals of the nitrogen atoms are virtually always involved in the bonds with ligands. In this case, unlike the O and F atoms, the difference between 2*p* and 2*s* orbital energies is relatively small and close to the corresponding values for C and B. The valence activity of the N2s^2 orbitals depends on many factors. It is promoted by low oxidation state of nitrogen, low electronegativities of ligands, and relatively low effective charge on the N atom. These conditions are satisfied, for example, for NH_4^+, $N_2H_5^+$, $N_2H_6^{2+}$ and NH_3OH^+

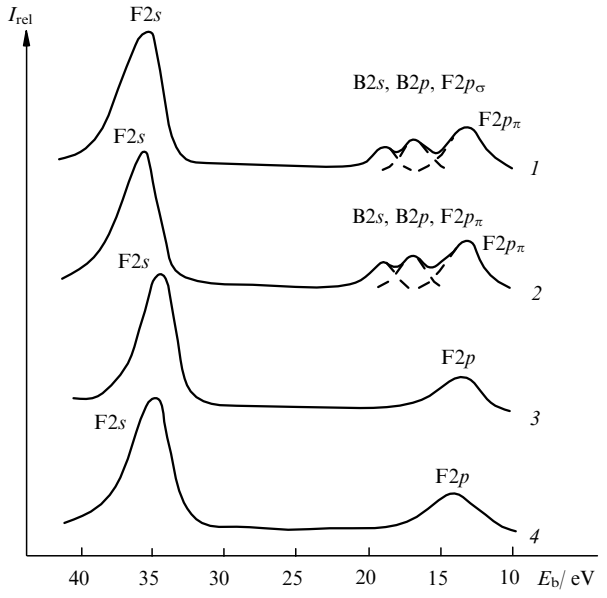


Figure 8. Valence band X-ray photoelectron spectra of the BF_4^- anion (the Na2*p* and Mg2*p* levels are omitted for the sake of simplicity; the Li1*s* level lies beyond the energy range presented).
(*1*) $LiBF_4$, (*2*) $NaBF_4$, (*3*) LiF, (*4*) MgF_2.

cations and their substituted derivatives like NR_4^+ as well as for N_3^- and HN_3. When some of the above conditions are not fulfilled, (for example, for NO_3^-, NO_2^-, *etc.*), the N2*s* orbitals remain quasiatomic and markedly stabilised with respect to those in the free nitrogen atom, if they are bound to ligands with a high electronegativity. This stabilisation, observed when the unpaired N2*p*-electrons are involved in the bonds with highly electronegative ligands, results from the decrease in the internal shielding of the N2s^2 orbitals, which possess a higher penetration ability than N2*p* AOs.

In some cases, this simple picture becomes more complicated. For example, this is the case with NH_3 and NO_2^+. In the former case, the valence inactivity of the N2s^2 orbital is dictated by the lack of vacancies in the valence structures of the ligands (H atoms), while in the latter case, the degree of participation of the N2s^2 orbital in the valence MOs is identical to the behaviour of the C2*s*AO in the isoelectronic CO_2 molecule, which is also linear.

The very low energy of the F2s^2 orbital and the extremely large difference between the 2*p*- and 2*s*-energies virtually preclude the involvement of the F2s^2 AO in the bonds with ligands. These energy limitations diminish somewhat in the case of oxygen atoms and, therefore, participation of the O2s^2 orbital in bonds with ligands seems to be seldom possible. The only well-studied example illustrating this possibility is the $[Ru_2OCl_{10}]^{4-}$ and $[Os_2OCl_{10}]^{4-}$ complexes incorporating linear triatomic M⇇O⇉M groups that include (σ + π) two-centre double bonds and a tetravalent oxygen atom. This unusual electronic structure can easily be understood by taking into account the relaxation effects and the energetic modification of the valence AOs in these complexes following the formation of the 'primary' σ-bonds of the central oxygen atom with both ligands (here, a unique role is played by the two metal atoms). The formation of σ-bonds (as well as the specific environment of the M atoms in $[M_2OCl_{10}]^{4-}$) causes stabilisation of the vacant orbitals of the acceptor atoms (M) and, simultaneously, destabilisation of the two electron pairs in the valence orbitals of the donor (O); this predetermines the subsequent formation of two dative O → M π-bonds. On the whole, all the four valence orbitals of the oxygen atom including the 2s^2 AO are involved completely in the delocalised MOs of the complex. It is possible that the 2s^2 AO of oxygen is partially admixed with the 2p_σ AO in the electronic

structures of oxo-complexes with multiple bonds like [Ti ⥹ O] and [O ⩲ U ⥹ O].

Quantum-chemical calculations for compounds of non-transition elements show[114] that as the A–L interatomic distance increases, the contribution of the $2s^2$ AO to the MOs of the A–L bonds diminishes (probably, due to the fact that on moving away from the nucleus, the 2*s*-electron density decreases faster than the 2*p*-electron density). This has several consequences. For example, in free diatomic molecules and ions, CO, CN^-, NO^+ and some others, the A2s^2 AOs are often incorporated in valence MOs; when these diatomic groups are coordinated to M atoms in transition metal complexes, the multiplicity of the two-centre bonds decreases, because the electron density moves from valence d_π AO of the M atom to the antibonding π^* MO of the diatomic group; the interatomic distance in this group thus increases, and the contribution of the A2s^2 AO to the valence MOs probably diminishes. The same effects account for the change in the A2s^2-contribution and the energy inversion of the 1π and $3(5)\sigma$ MOs in diatomic species on passing from N_2, CO, CN^- and NO^+ with short interatomic distances to O_2, F_2 and some other molecules with longer bond lengths.

To solve the problem of valence $2s^2$ AOs in AL_k complexes, one should take into account that the geometry of these molecules with bond angles of 104.5° need not be associated with a tetrahedral distribution of the electron density. The results of calculations carried out for H_2O not including the $2s^2$ orbital of the oxygen atom lead to a geometry similar to the experimental one, namely, the minimum total energy is achieved for a bond angle of 101–102°, without any sp^3-hybridisation but simply due to interelectron repulsion.

To complete this section, we shall pay attention to the diversity of the electronic structures of compounds of typical elements, which defies simple systematisation (from the viewpoint of participation of the A2s^2 orbitals in the bonds with ligands). All the factors involved must be taken into account: the geometry of the complex, the number of atoms in it, the spatial and energy characteristics of A2*s* and A2*p* orbitals, the differences in the electronic characteristics of atoms A and L, *etc*. A representative example is the isoelectronic ($16e^-$) series of linear triatomic molecules and molecular ions: $CO_2-FCN-NO_2^+-OCN^--ONC^--CN_2^--N_3^--N_2O$. To interpret the differences between the electronic structures of these species one should take into account not only the above parameters but also some specific features characterising the properties of atoms in these systems (whether it is a central atom with a greater role of $2s^2$ orbitals or a ligand with a smaller role of $2s^2$ AOs), the total charge of the complex and some others.

The effective participation of A2*s* AOs in the valence MOs in compounds of the Second Period elements accounts for many characteristic features of these compounds and determines the pronounced difference between the typical elements and the rest of non-transition elements, main manifestations of the Periodic Law in the chemistry of Group A elements and the biogenic character of C, N, O, *etc*.

VI. Principles of electronic structures of complexes of non-transition elements

Numerous results of experimental and quantum-chemical studies on complexes of non-transition elements make it possible to formulate the general principles of their electronic structure. Theoretical generalisations will always be revised, refined and improved. Therefore, we note specially that it is the X-ray photoelectron spectra (XPS) of compounds of non-transition elements that act as the paramount physical basis of our review. The studies of the intensities, energies and chemical shifts of lines in the inner-level and valence band XPS for a great number of complexes of non-transition elements with acido-ligands made it possible to observe regular repetition of consistent effects. Based on these effects, X-ray-electron criteria for the degree of participation and the role of the valence orbitals of central atoms in the formation of the bonds with ligands were established. By analysing all the available XPS in the context of these criteria, the results of the analysis being necessarily consistent with quantum-chemical results and with the data obtained by other types of high-energy spectroscopy, the main principles of electronic structure of non-transition element complexes have been elucidated.[104,105]

The vacant *nd* orbitals of the central atom A scarcely participate in the A–L bonds in the compounds under consideration, including those containing elements in the highest oxidation states, and remain virtual. Apparently, the A*nd* orbitals can contribute to the structures of the electronically excited states of complexes. It cannot be ruled out that in rare cases the A*nd* orbitals also do contribute to the ground states of complexes; this occurs when the ground state contains a considerable proportion of excited configurations.

In the electronic structures of the majority of complexes of atoms of all early (Group I–IV) non-transition elements of the Second and subsequent Periods, the A*ns* orbitals occupied by one or two electrons ($n \geqslant 2$) are involved in the valence MOs and participate in the formation of the A–L covalent bonds, together with the A*np* orbitals. The electronic structures of these complexes can be described in terms of multicentre delocalised (canonical) MOs or by two-centre localised (equivalent) MOs that reflect the valence electron density distribution near the two-centre bond using the concept of hybridisation of the basis AOs. The usual views on AO hybridisation can be preserved only for coordination numbers of A atoms of no more than 4 and only for the sp^m type of hybridisation; and even in this case, this should be done with a certain caution (*cf*. CH_4 and CF_4).

The occupied Ans^2 orbitals ($n \geqslant 3$) of the atoms of late (Group V–VIII) non-transition elements of the Third and subsequent Periods make a fairly small contribution to the valence MOs of most of the complexes. In the case of ligands with high electronegativities, the valence Ans^2 orbitals remain quasiatomic and markedly stabilised (with respect to those in the corresponding free atoms A). The contributions of Ans^2 orbitals to delocalised MOs are appreciable in some complexes with large coordination numbers (for instance, Te5s^2 in Ag_6TeO_6).

The A–L bonds in most complexes of late non-transition elements of the Third and subsequent Periods, unlike those in the analogous compounds of transition metals, are formed with participation of only valence *np* orbitals of central atoms (in contrast to the traditional views stating that the *ns*, *np* and *nd* AOs participate in bonds irrespective of their electron populations in the free non-excited atoms A). Here, the concept of hybridisation of the basis AOs is irrelevant. It is expedient to describe the electronic structures of these acido-complexes in terms of MOs containing no contribution of the A*nd* and Ans^2 orbitals and consisting of only the Anp^m (and, in some rare circumstances, Ans^2) orbitals and in terms of covalent and hypervalent A–L bonds. To describe these complexes within the framework of the general MO LCAO theory, the hypervalent structure is the best approximation. Generally, the chemistry of phosphorus, sulfur, chlorine, argon and their analogs can be regarded as the chemistry of compounds, the electronic structures of which are built mainly from valence np^m orbitals of the central atom and hardly contain any contribution of the Ans^2 and A*nd* orbitals to the valence delocalised MOs.

In the complexes of late elements of the Second Period (N, O, F), the main and sometimes the only contribution to the MOs is made by the valence A2p^m orbitals. In some complexes, the occupied A2s^2 orbitals prove to be valence inactive and remain quasiatomic, while in some other complexes, they participate efficiently in the formation of delocalised MOs. The involvement of the $2s^2$-electrons of central atoms (and sometimes, the ns^2-electrons with $n \geqslant 3$) in the bonds with ligands is possible only when a number of conditions are satisfied; the most important condition is the presence of a low-energy vacant orbital (*i.e*. a strong acceptor AO) in the valence structure of the ligand. The

two-centre A – L bonds consisting of the A2p^m-electrons are formed both by the covalent (1 : 1) and the dative (2 : 0) mechanisms, and those consisting of the A2s^2-electrons are formed, as a rule, by the dative mechanism.

In the electronic structures of complexes of the Second Period elements, covalent and hypervalent π-bonds are often formed, due to the A2p_π-electrons.[115–117] The simultaneous participation of A2*s* AO (together with A2*p* AO) in the A – L σ-bonds leads to the formation of high-multiplicity homo- and hetero-atomic two-centre bonds (N≡N, [C≡N$^-$], C≡O, *etc.*). For $n \geqslant 3$, the possibility of the formation of covalent and, especially, hypervalent π-bonds upon the interaction of Anp_π orbitals is sharply decreased; therefore, the electronic structures of complexes of non-transition elements of the Third and later Periods seldom contain multiple two-centre bonds.[3,45]

In conclusion, let us discuss the theoretical substantiation of the principles formulated above. The primary attention will be focused on two factors, *viz.* the energy and spatial factors.[104]

The theoretical justification of the valence inactivity of vacant *nd* and occupied ns^2 orbitals ($n \geqslant 3$) of the central atoms in the electronic structure of complexes of non-transition elements of the Third and subsequent Periods is based on the fact that the energy difference between these AOs, on the one hand, and the valence orbitals of the ligands, on the other hand, is great. The energies of the vacant *nd* orbitals are too high and those of the occupied ns^2 orbitals are too low compared to the energies of the valence orbitals of the acido-ligands, which have higher electronegativities than atom A (the energies of A*np* orbitals are close to the energies of σ,π orbitals of the ligands). The large difference between the orbital energies is reinforced by the fact that the A*nd* orbitals are fairly diffuse and the Ans^2 AOs are strongly contracted; this also hampers their effective interaction with ligand orbitals (the length of the A*np* AO is the optimum in this respect). Hence, the participation of vacant A*nd* and occupied Ans^2 orbitals in the MOs of bonds with typical ligands is hampered by both the energy and spatial factors.

The theoretical substantiation of the participation of the occupied valence A2s^2 orbitals of the Second Period atoms in the molecular orbitals of complexes with acido-ligands is mainly based on the fact that their A2*s* AOs are more extended in space than the A2*p* AOs (the main maxima of the radial density of the A2*s* AOs are located farther from the nucleus than those of the A2*p* orbitals). For the rest of the valence AOs with $n \geqslant 3$, the situation is known to be the opposite, and this accounts for the fact that A2s^2 AOs participate in A – L bonds far more efficiently than any other *ns* AO. Thus, in this case, the crucial role belongs to the spatial factor, which ensures a high value of the numerator (via the overlap integral) in the expression for the energy of stabilisation of a bonding MO [see formula (1)]. It is owing to their specific spatial characteristics that the 2*s* AOs of atoms A, unlike *ns* AOs with $n \geqslant 3$, often participate efficiently in the formation of delocalised MOs. The crucial role of the spatial factor,[104] which ensures that the magnitudes of the overlap integral for the interaction of the 2*s* orbitals of atom A with the valence orbitals of ligands are larger than those for all the other *ns* orbitals, is stressed by the fact that the contribution of the occupied A2s^2 orbitals to the valence MOs diminishes with increase in the A – L interatomic distances,[114] and also by the fact that the energy factor exerts a restraining influence on the participation of occupied A2s^2 AO in the A – L bonds (in fact, the 2*s* AO energies are much smaller than the energies of valence orbitals of the ligands; therefore, the denominator in the equation mentioned above is always large). However, the energies of A2*s* (generally, A*ns*) orbitals may come closer to those of the valence orbitals of ligands, as a result of redistribution of the valence electron density in the complex, caused by the formation of 'primary' A – L bonds from the valence A2*p* (or A*np*) orbitals, *i.e.* due to electron rearrangements controlled by the differences in the atomic characteristics of A and L. However, the same electron rearrangements can also cause the opposite effect, namely, a decrease in the spatial dimensions of *ns* AOs and in their energies, *i.e.* their energy discrepancy with the valence orbitals of ligands can thus be aggravated.

VII. Conclusion

To avoid unfavourable criticism of theorists engaged in the theory of electronic structures of complexes of non-transition elements or of those going to work in this field in the future, we should like to emphasise that our review deals with the main principles of the electronic structures of complexes of non-transition elements.

Certainly, the quantum nature of electrons gives rise to the tendency for their delocalisation. Therefore within the framework of the MO LCAO formalism, which is a part of the wave mechanics of atoms and molecules, it is always possible and even likely that non-zero contributions to the electron density in the electronic structure of a molecular system are made by those states which remain vacant in free unexcited atoms. This refers, in particular, to the A*nd* orbitals in non-transition element complexes. However, while describing the electronic structure of these systems, one must not lose the sense of proportion required in any situation (the speculations on the problem of *d* orbitals in many papers, reviews and monographs in which too much attention is paid to details, while the main meaning is lost, suffer from the lack of this sense). The more so, because views on the atomic *s*, *p* and *d* orbitals in a molecule are not rigorous. The angular momentum of electrons is not conserved in molecules, and the classification of states as *s*-, *p*-, and *d*-types loses its meaning. Only near the atomic nucleus, is there a region where the influence of the molecular environment is fairly minor compared to the nuclear field, so that the concept of *s*, *p* and *d* orbitals is roughly retained. Therefore, by the participation of A*nd* orbitals in the A – L bonds, we mean the presence of occupied single-electron states that have the form of *d* orbitals near the nucleus of the central atom A and are modified away from the nucleus, in conformity with the influence of the molecular environment.[118]

It is precisely and solely in this sense that we proclaim the general idea on the valence inactivity of A*nd* orbitals in the electronic structure of non-transition element complexes and on the valence activity of Ans^2 orbitals being markedly lower than is usually assumed.

In this review we express our opinion: the role of A*nd* orbitals in the majority of cases is negligibly small. These orbitals are so unfavourable in energy and so diffuse that they are incapable of any substantial interaction with the valence orbitals of the ligands. In *ab initio* calculations, *d* orbitals are important as polarisation functions but their population is much smaller than has been assumed in the sp^md^n-hybridisation model.

Some recent publications devoted to the electronic structures of non-transition element complexes present the results of theoretical studies of several complexes of this type carried out using empirical methods,[119,120] density functional[121] and other high-level quantum-chemical calculations.[122–125] The results of these studies are not inconsistent with the main (conceptual) conclusions made in our review.

However, the foregoing refers to the ground states of complexes. In the excited states, the participation of *d* AO in bonds and their influence on the molecular properties can be markedly higher than those in the ground state. However, up to now, no reliable calculations on the excited states of complexes as applied to the problem of *d* AOs have been reported. It has been shown[126] that the participation of the *d* orbitals of the central atom in MOs can result from the interaction of a non-excited configuration containing no *d*-contribution with electron-excited configurations having fairly occupied *d* orbitals.

In this connection, it seems necessary to consider briefly the X-ray diffraction studies dealing with the electron density distribution in crystals. Precision calculations based on these experi-

ments provide reliable data, convenient for further processing, on the differential and deformation electron densities, the ease of dealing with these results has withstood the test of time better than many complicated constructs and refined approaches. The theoretical interpretation of the results obtained recently along this line point to the substantial electron population of A*nd* orbitals. At present, there are only few results of this type, but they are attracting considerable attention and require a clear and strict explanation.

The direct proof for the population of the Si3*d* orbitals in the SiO_4^{4-} anion is among the first examples of this sort.[127,128] The distribution of the differential ($\Delta\rho$) and total (observed experimentally, ρ^0) electron density in the crystal of γ-Ni_2SiO_4 has been studied quantitatively based on the set of measured structural amplitudes;[127] in this study, a substantial electron population of the Si3*d* orbitals in the tetrahedral SiO_4^{4-} anion and their strong compression were found (the experimental effective charge on the Si atom amounts to +2.5). We believe that if the electron density in the Si3*d* orbitals of γ-Ni_2SiO_4 is actually fairly high, this can apparently be explained in the following way. A large contribution to the real state of SiO_4^{4-} in the γ-Ni_2SiO_4 crystal is made, in addition to the non-excited configuration of the free hypothetical SiO_4^{4-} anion, by its electronically excited configurations, which can contain a considerable proportion of the Si3*d* orbitals. The large contribution of the electronically excited configurations can be due to the 'extreme' environment of the SiO_4^{4-} anion in the crystal of γ-Ni_2SiO_4 consisting of several Ni atoms with high positive charges (+1.3). It is significant that the electronic structure of the SiO_4-group in the SiO_2 crystal rules out the participation of the Si3*d* functions in the valence orbitals. This has been found[129] in a study of photoionisation, X-ray emission (SiK_β, Si$L_{2,3}$, OK_α) and ultraviolet excitation of SiO_2[129] and in SCF SW X_α-calculations of the electronic structure of the SiO_4-group in SiO_2. The environment of the SiO_4-groups in crystalline quartz has nothing in common with that in γ-Ni_2SiO_4; in SiO_2, they can be isolated only as $SiO_{4/2}$, which assumes that the SiO_4-group is surrounded by Si atoms with fairly small charges. There are no indications of any substantial contribution of the Si3*d* orbitals to the electronic structure of Na_2SiO_3. It has been noted [128] that on the cross-sections of deformation densities of $AlPO_4$ and $CaSO_4$ crystals, some peaks can be observed that correspond to the partly occupied 3*d* orbitals of phosphorus and sulfur atoms in the PO_4^{3-} and SO_4^{2-} anions, isoelectronic with SiO_4^{4-}.

One of the complications in solving the problem of A*nd* orbitals lies in the multielectron character of the wave function of the molecule. Therefore, it is necessary to distinguish between the influence of A*nd* AOs on the properties of a molecular system and manifestation of A*nd* AOs in a direct study of the electron density or in calculations of the electronic structure of a molecule by multiconfiguration methods of quantum chemistry.

Thus, there are grounds to believe that, under certain conditions, appreciable electron population of A*nd* orbitals in non-transition element complexes is quite possible and is largely promoted, among other factors, by a great contribution of electronically excited configurations to the wave function of a complex. It can be assumed that substantial A*nd*-electron populations are typical of many short-lived electronically excited states of the complexes under discussion (the contribution of electronically excited configurations to these states is great by definition) as well as some (apparently, relatively rare) stable states of complexes in which, due to certain reasons, the contribution of electronically excited configurations is large.

So, both empirical concepts — the concept of *d* orbitals and hypervalent bonds — although they seem attractive due to their simplicity and apparent versatility, cannot serve any longer for the strict description of the electronic structures of complexes of non-transition elements; in principle, the latter concept is certainly a better approximation. In both concepts, an important role, although non-equivalent, in the formation of bonds with ligands is attributed to the valence ns^2 orbitals of the central atom A, and this point is their common flaw (recall that even in the concept of hypervalent bonds, which is the best approximation for the description of the electronic structures of the complexes in question, the participation of valence ns^2-electrons of central atom A in binding with ligands is assumed for higher compounds in which the oxidation state of A is maximum). The ideas about hybridisation of valence orbitals of the central atom, including isovalent hybridisation, (not increasing the valence), are applicable only to complexes of elements of the Second Period. In this case, they are fairly effective (with the exception of molecular compounds of fluorine and oxygen), because the energy and spatial characteristics of valence 2*s* and 2*p* orbitals give the best fit to each other.[45,104]

The theory of the electronic structure of non-transition element complexes has not yet been completed. Some of its points require refinement and reasoned modification. There are also blank spots in it, which account for the necessity for the formation and development of conceptually new ideas: for example, in connection with the electronic structure of so-called double bonds: S–O in H_2SO_4, P–O in H_3PO_4, the multiplicity of which is actually much less than two.[45] Of course, the main point is the problem of valence of central atoms and the adjoining problem of the instability of PH_5, SH_4, SH_6, *etc*. The existing views stating that SO_3, H_2SO_4 and SF_6 contain hexavalent sulfur and P_2O_5, H_3PO_4 and PF_5 contain pentavalent phosphorus seem to be no more than a myth, which is simple and convenient for a non-theorist chemist but, in many respects, delays the progress of the theory.

The fact (more precisely, the paramount sign) that in the majority of non-transition element complexes, only *p* AO of the central atom participate in the 'central atom–ligand' orbital interactions accounts for the sharp differences between the electronic structures of complexes of non-transition elements and transition metal complexes. In the electronic structure of the latter, both spatial and energy factors are often favourable for efficient participation of all types of valence orbitals of the M atom [*ns*, (*n*–1)*d*, *np*] in delocalised MOs, in conformity with the symmetry of the complex. This, in turn, explains easily and simply, why transition metal complexes are characterised by more diverse bond multiplicities and also by greater valencies of central atoms M than the corresponding non-transition element complexes, and also why the former are generally more stable.

However, apparently, the electronic structure of transition metal complexes is also far from this ideal scheme; this is indicated by the results of recent investigations on the roles of various valence orbitals in the chemical bonding in ML_k complexes. Based on the calculated[130] wave functions for $Ni(CO)_4$ and $Cr(NO)_4$, the structure of the 'central atom–ligand' bonds has been analysed within the framework of a new method, free from the artifacts of the traditional analysis of electron populations. It was shown that it is the 3*d* orbitals of atoms M (3*d*-Ni, 3*d*-Cr) that make the predominant contribution (apart from the ligand orbitals) to the covalent M–L interactions, whereas the contribution of 4*s* and 4*p* AOs is negligibly small.

Although the above results are not general (only two complexes were studied), the main conclusion can be regarded as the beginning of a concept assuming a crucial role of valence (*n*–1)*d* orbitals of atoms M in M–L bonds and, simultaneously, valence inactivity (more precisely, low valence activity) of their *ns* and, especially, *np* orbitals in the electronic structure of transition metal complexes ML_k. Together with the general conclusion about the crucial role of valence *np* orbitals of central atoms A in A–L bonds in complexes of non-transition elements and about the valence inactivity of their *ns* and, especially, *nd* orbitals, this can lead to a nontrivial and a very simple view on the most general principles governing the electronic structure of the two 'polar' types of complex, AL_k and ML_k, namely: transition metal complexes are mostly formed due to the valence *d*-electrons of central

atoms, whereas complexes of non-transition elements are formed from the valence *p*-electrons of central atoms.

The authors are grateful to I B Bersuker and B S Tsukerblat for benevolent criticism and discussion and to V S Strykanov and M I Raitsina for assistance during the investigation.

References

1. L Pauling *The Nature of the Chemical Bond* (New York: Cornel University Press, 1960)
2. C Coulson *Valence* (Oxford: Oxford University Press, 1961)
3. F Cotton, G Wilkinson, in *Advanced Inorganic Chemistry* (New York: Wiley, 1966)
4. D V Korol'kov, in *Evolyutsiya Idei D I Mendeleeva v Sovremennoi Khimii* (Evolution of D I Mendeleev Ideas in Modern Chemistry) (Eds B P Nikol'skii, L S Lilich) (Leningrad: Nauka, 1984) p. 50
5. G C Pimentel *J. Chem. Phys.* **19** 446 (1951)
6. R E Rundle *Rec. Chem. Progr.* **23** 195 (1962)
7. G C Pimentel, R Spratly *Chemical Bonding Clarified through Quantum Mechanics* (San Francisco: Holden-Day, 1970)
8. J I Musher *Angew. Chem., Int. Ed. Engl.* **8** 54 (1969)
9. V B Koutecky, J I Musher *Theor. Chim. Acta* **33** 227 (1974)
10. D V Korol'kov, in *Theory of Valence in Progress* (Ed. V I Kuznetsov) (Moscow: Mir, 1980) p. 210
11. Ya K Syrkin, in *Sto Let Periodicheskogo Zakona Khimicheskikh Elementov* (The Hundredth Anniversary of the Periodic Law of Chemical Elements) (Moscow: Nauka, 1971) p. 85
12. J W Linnett, in *Sto Let Periodicheskogo Zakona Khimicheskikh Elementov* (The Hundredth Anniversary of the Periodic Law of Chemical Elements) (Moscow: Nauka, 1971) p. 103
13. Ya K Syrkin *Periodicheskaya Sistema i Problema Valentnosti* (The Periodic System and the Problem of Valence) (Moscow: Znanie, 1971)
14. I Mayer, P R Surjan *Acta Chim. Hung.* **117** 85 (1984)
15. M E Dyatkina, N M Klimenko *Zh. Strukt. Khim.* **14** 173 (1973) [a]
16. O P Charkin *Zh. Strukt. Khim.* **14** 389 (1973) [a]
17. Cao Yang *Int. J. Quant. Chem.* **28** 641 (1985)
18. S P Ionov, G V Ionova *Zh. Neorg. Khim.* **14** 1691 (1969) [b]
19. S P Ionov, G V Ionova *Zh. Fiz. Khim.* **43** 2199 (1969) [c]
20. A I Karelin, S P Ionov, G V Ionova *Zh. Strukt. Khim.* **11** (3) 454 (1970) [a]
21. S P Ionov, V S Lyubimov *Zh. Fiz. Khim.* **44** 9 (1970) [c]
22. B A Suvorov, L N Orlova, R V Dzhagatspanyan *Koord. Khim.* **7** 1159 (1981) [d]
23. A A Bhattacharrya, A Bhattacharrya, J J Oleksik, G Turner *Inorg. Chim. Acta* **53** L163 (1981)
24. V V Kirsanov, V A Tskhai *Teor. Eksp. Khim.* **18** 654 (1982) [e]
25. A Strich, A Veillard *J. Am. Chem. Soc.* **95** 5574 (1973)
26. H Johansen *Theor. Chim. Acta* **32** 273 (1974)
27. L Noodleman, K A R Mitchel *Inorg. Chem.* **17** 2709 (1978)
28. U Gellius, B Rocs, P Siegbahn *Chem. Phys. Lett.* **4** 471 (1970)
29. U Gellius, B Rocs, P Siegbahn *Chem. Phys. Lett.* **23** 59 (1971)
30. D E Onopko, S A Titov *Teor. Eksp. Khim.* **14** 677 (1978) [e]
31. J W Condliy, K H Johnson *Chem. Phys. Lett.* **10** 616 (1971)
32. A I Boldyrev, V G Zakrzhevskii, O P Charkin *Zh. Strukt. Khim.* **23** (6) 30 (1982) [a]
33. E M Shustorovich *Khimicheskaya Svyaz' v Koordinatsionnykh Soedineniyakh* (The Chemical Bond in Coordination Compounds) (Moscow: Znanie, 1975)
34. G L Gutsev, A A Levin *Chem. Phys. Lett.* **57** 235 (1978)
35. A P Klyagina, A A Levin, G L Gutsev *Chem. Phys. Lett.* **77** 365 (1981)
36. G L Gutsev, A P Klyagina *Zh. Neorg. Khim.* **27** 2173 (1982) [b]
37. G L Gutsev, A P Klyagina, A A Levin *Chem. Phys.* **75** 243 (1983)
38. A P Klyagina, G L Gutsev, A A Levin *Zh. Neorg. Khim.* **29** 1142 (1984) [b]
39. H Oberhamer, J E Boggs *J. Am. Chem. Soc.* **102** 7241 (1980)
40. S-P So *J. Chem. Soc., Faraday Trans.* **77** 213 (1981)
41. C A Ernst, A L Allred, M A Ratner, M N Newton, G V Gibbs, J M Moskowitz, S Topiol *Chem. Phys. Lett.* **81** 424 (1981)
42. N C Baird, K F Taylor *Can. J. Chem.* **59** 814 (1981)
43. N C Baird, K F Taylor *Chem. Phys. Lett.* **80** 83 (1980)
44. C Trinquier, J Malrier, J-P Daudey *Chem. Phys. Lett.* **80** 552 (1981)
45. W Kutzelnigg *Angew. Chem., Int. Ed. Engl.* **23** 272 (1984)
46. D A Bochvar, N P Gambaryan, L M Epshtein *Usp. Khim.* **45** 1316 (1976) [*Russ. Chem. Rev.* **45** 660 (1976)]
47. C A Coulson *Nature (London)* **221** 1106 (1969)
48. B Roos, P Siegbahn *Theor. Chim. Acta* **17** 199 (1970)
49. M Keeton, D P Santry *Chem. Phys. Lett.* **7** 105 (1970)
50. R S Mulliken *J. Chem. Phys.* **36** 3428 (1962)
51. S Rothenberg, R H Jong, H T Schaefer *J. Am. Chem. Soc.* **92** 3243 (1970)
52. N P Borisova, in *Metodika Neempiricheskikh Raschetov v Elipsoidal'nom Bazise* (Procedures for *ab initio* Calculations in Terms of an Ellipsoidal Basis) (Leningrad: Izd. Leningradsk. Gos. Univ., 1986) p. 61
53. G P Kostikova, Yu P Kostikov, D V Korol'kov *Dokl. Akad. Nauk SSSR* **287** 671 (1985) [f]
54. G P Kostikova, Yu P Kostikov, D V Korol'kov *Teor. Eksp. Khim.* **22** 572 (1986) [e]
55. L N Mazalov, V D Yumatov, V V Murakhtanov *Rentgenovskie Spektry Molekul* (X-Ray Spectra of Molecules) (Novosibirsk: Nauka, 1977)
56. V I Nefedov *Zh. Strukt. Khim.* **13** 352 (1972) [a]
57. L N Mazalov *Rentgenovskie Spektry i Khimicheskaya Svyaz'* (X-Ray Spectra and the Chemical Bond) (Novosibirsk: Nauka, 1982)
58. A P Sadovskii, L N Mazalov, G N Dolenko *Zh. Strukt. Khim.* **14** 1048 (1973) [a]
59. G N Dolenko, A P Sadovskii, L N Mazalov *Zh. Strukt. Khim.* **15** 418 (1974) [a]
60. A P Sadovskii, G N Dolenko, L N Mazalov *Izv. Akad. Nauk SSSR, Ser. Fiz.* **38** 606 (1974)
61. V I Nefedov, V A Fomichev *Zh. Strukt. Khim.* **9** 126 (1968) [a]
62. D V Fischer, W L Baun *Anal. Chem.* **37** 902 (1965)
63. J Merrit, E J Agazzi *Anal. Chem.* **38** 1954 (1966)
64. G P Kostikova, Yu P Kostikov, D V Korol'kov *Vestn. Leningradsk. Gos. Univ.* (1) 42 (1986)
65. J A Tossell, in *The 179th ACS National Meeting, Houston, TX, (Abstracts of Reports)* (Washington, DC: American Chemical Society, 1980) p. 113
66. A V Kondratenko, L N Mazalov, K M Neiman *Opt. Spektrosk.* **48** 1072 (1980)
67. I I Nefedov *Zh. Strukt. Khim.* **12** 303 (1971) [a]
68. V A Fomichev *Fiz. Tverd. Tela* **9** 3167 (1967)
69. R A Mattson, R C Ehlert *J. Chem. Phys.* **48** 5465 5471 (1968)
70. J A Tossell *Inorg. Chem.* **19** 3328 (1980)
71. V D Yumatov, L N Mazalov, A V Okotrub, I A Topol' *Zh. Strukt. Khim.* **25** 43 (1984) [a]
72. L I Molkanov, K Ya Mishin, Yu S Grushko, V K Isupov *Eksperimental'noe Issledovanie Elektronnoi Valentnoi Struktury Soedinenii Ksenona (Preprint LIYaF Akad. Nauk SSSR 1979)* [Experimental Investigation of the Electronic Valence Structure of Xenon Compounds (Preprint of the Leningrad Institute of Nuclear Physics of the Academy of Sciences of the USSR, 1979)] No 521
73. Yu S Grushko, L I Molkanov, I M Band, A V Oleinik *Usp. Fiz. Nauk* **113** 362 (1974) [g]
74. L I Molkanov, Yu S Grushko, I M Band, A Shadrina, M B Trzhaskovskaya *Zh. Eks. Teor. Fiz.* **70** 2218 (1976)
75. E M Shustorovich *Koord. Khim.* **2** 435 (1976) [d]
76. E M Shustorovich *Inorg. Chem.* **17** 2648 (1978)
77. K H Johnson *Adv. Quant. Chem.* **7** 143 (1973)
78. J A Tossell *J. Am. Chem. Soc.* **97** 4840 (1975)
79. F Kein, W Kutzelnigg *J. Am. Chem. Soc.* **97** 3623 (1975)
80. G M Schwenzer, H F Schaefer *J. Am. Chem. Soc.* **97** 1393 (1975)
81. M A Ratner, J R Sabin *J. Am. Chem. Soc.* **93** 3542 (1971)
82. W R Rodwell *J. Am. Chem. Soc.* **100** 7209 (1978)
83. K Siegbahn *ESCA Applied to Free Molecules* (Amsterdam: North-Holland, 1971)
84. K Siegbahn *ESCA. Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy* (Upsala: Upsala University, 1967)
85. V I Nefedov, V I Vovna *Elektronnaya Struktura Khimicheskikh Soedinenii* (The Electronic Structure of Chemical Compounds) (Moscow: Nauka, 1987)
86. G P Kostikova, V S Strykanov, Yu P Kostikov, D V Korol'kov *Teor. Eksp. Khim.* **18** 279 (1982)
87. V I Nefedov *Stroenie Molekul i Khimicheskaya Svyaz' T. 3 (Ser. Itogi Nauki i Tekhniki)* [The Structure of Molecules and the Chemical

Bond, Vol. 3 (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1975)
88. J A Connor, I H Hillier, V R Saunders, M Barber *Mol. Phys.* **23** 81 (1972)
89. G L Gutsev, A E Smolyar *Izv. Akad. Nauk SSSR, Ser. Khim.* 939 (1981) [h]
90. G M Bancroft, P A Malmquist, S Svensson, E Basilier, U Gelius, K Siegbahn *Inorg. Chem.* **17** 1595 (1978)
91. V I Nefedov *Stroenie Molekul i Khimicheskaya Svyaz' T. 1 (Ser. Itogi Nauki i Tekhniki)* [The Structure of Molecules and the Chemical Bond, Vol. 1 (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1973)
92. G P Kostikova, M I Raitsina, Yu P Kostikov, D V Korol'kov *Koord. Khim.* **20** 565 (1994) [d]
93. W L Jolly *Coord. Chem. Rev.* **13** 47 (1974)
94. W B Perry, T F Scaaf, W L Jolly *J. Am. Chem. Soc.* **97** 4899 (1975)
95. S Cradok, E A V Ebsworth, A Robertson *Chem. Phys. Lett.* **30** 413 (1975)
96. R Shong-yuan, W X Ching *Phys. Rev. B, Condens. Matter* **23** 5454 (1981)
97. K Siegbahn *Rev. Mod. Phys.* **54** 709 (1982)
98. W L Jolly, D N Hendrickson *J. Am. Chem. Soc.* **92** 1863 (1970)
99. J M Hollander, W L Jolly *Acc. Chem. Res.* **3** 193 (1970)
100. M E Dyatkina, E L Rozenberg *Stroenie Molekul i Khimicheskaya Svyaz' T. 2 (Ser. Itogi Nauki i Tekhniki)* [The Structure of Molecules and the Chemical Bond, Vol. 2 (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1974)
101. J H Schofield *J. Electron Spectrosc.* **8** 129 (1976)
102. S L Ruby, G K Shenoy, in *Mössbauer Isomer Shifts* (Eds G K Shenoy, F E Wagner) (Amsterdam: North-Holland, 1978) p. 617
103. S I Bondarevskii, Yu P Kostikov, S A Timofeev *Teor. Eksp. Khim.* **20** 89 (1984) [e]
104. G P Kostikova, Yu P Kostikov, D V Korol'kov *Dokl. Akad. Nauk SSSR* **280** 663 (1985) [f]
105. G P Kostikova, Yu P Kostikov, D V Korol'kov *Koord. Khim.* **20** (10) 735 (1994) [d]
106. Ya V Salyn', K V Titova, E N Loginova, V I Nefedov *Zh. Neorg. Khim.* **22** 2998 (1977) [b]
107. D N Hendrickson, J M Hollander, W L Jolly *Inorg. Chem.* **8** 2642 (1969)
108. V I Nefedov *Koord. Khim.* **4** 1283 (1978) [d]
109. M Lax *Phys. Rev.* **119** 1502 (1960)
110. G M Mikhailov, Yu G Borod'ko *Poverkhnost'* **6** 85 (1982)
111. V I Vovna *Zh. Strukt. Khim.* **28** 166 (1987) [a]
112. G L Gutsev, A A Levin *Zh. Strukt. Khim.* **20** 771 (1979) [a]
113. G L Gutsev, A I Boldyrev *Zh. Strukt. Khim.* **26** 2353 (1981) [a]
114. Yu A Teterin, S G Gagarin, Yu P Dikov, G L Gutsev *Teor. Eksp. Khim.* **19** 256 (1983) [e]
115. G P Kostikova, Yu P Kostikov, D V Korol'kov *Dokl. Akad. Nauk SSSR* **296** 914 (1987) [f]
116. G P Kostikova, Yu P Kostikov, D V Korol'kov *Koord. Khim.* **20** (8) 573 (1994) [d]
117. A N Chekhlov, S P Ionov *Teor. Eksp. Khim.* **18** 682 (1982) [e]
118. I B Bersuker *Elektronnoe Stroenie i Svoistva Koordinatsionnykh Soedinenii* (The Electronic Structure and Properties of Coordination Compounds) (Leningrad: Khimiya, 1986)
119. J V Seeley, T M Miller, A A Vaggiano *J. Chem. Phys.* **105** 2127 (1996)
120. V V Pinyas'kin, I V Stankevich, A L Chistyakov, I S Akhrem, S V Gudima, M E Vol'pin *Izv. Akad. Nauk, Ser. Khim.* 1116 (1996) [h]
121. E Ruiz, D R Salahub, A Vella *J. Phys. Chem.* **100** 12265 (1996)
122. Y Yamaguchi, Y Hie, S Kim, H F Schaefer *J. Phys. Chem.* **105** 1951 (1996)
123. M N Glukhovtser, A Dransfeld, P von R Schleyer *J. Phys. Chem.* **100** 13447 (1996)
124. A L Chistyakov, I V Stankevich, I S Akhrem, R P Gambaryan, M E Vol'pin *Izv. Akad. Nauk, Ser. Khim.* 886 (1996) [h]
125. I P Beletskii, A G Grebenyuk, V E Klimenko *Koord. Khim.* **22** 174 (1996) [d]
126. A Stromberg, U Wahlgren, L Petersen, P Siegbahn *Chem. Phys.* **89** 323 (1984)
127. A N Chekhlov, S P Ionov *Koord. Khim.* **7** 34 (1981) [d]
128. A N Chekhlov, S P Ionov *Koord. Khim.* **11** 19 (1985) [d]
129. J A Tossell, D J Vaughan, K H Johnson *Chem. Phys. Lett.* **20** 329 (1973)
130. P S Bagus, C J Nelin, in *New Challenges in Computational Quantum Chemistry* (Eds R Broer, P J C Aerts, P S Bagus) (Groningen: University of Groningen, 1994) p. 165

[a] — *J. Struct. Chem. (Engl. Transl.)*
[b] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[c] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[d] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[e] — *Theor. Exp. Chem. (Engl. Transl.)*
[f] — *Dokl. Chem. (Engl. Transl.)*
[g] — *Physics-Uspekhi*
[h] — *Russ. Chem. Bull.*