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The Quantum Chemistry of Unusual Oxidation States of the Lanthanides and Actinides

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The electronic structure and properties of the actinides in unusual oxidation states have been examined within the framework of quantum-chemical ideas. Hartree-Fock atomic calculations for the actinide series, and molecular orbital calculations for the octahedral oxyanions of uranium, neptunium, plutonium, and americium in high and highest oxidation states, and for the octahedral chloro-complexes of the actinides(III) and (IV) from protactinium to einsteinium, have been carried out. These calculations have been used to examine the possible existence of various new oxidation states of the actinides.
A cation-cation interaction mechanism has been proposed. The characteristic features of the *trans*-effect in the chemistry of the actinides have been examined. New possibilities for using the Mössbauer isomer shifts at the actinide nuclei to interpret chemical properties have been demonstrated. The influence of relativistic effects on the chemical properties of the actinides has been analysed. In particular, it has been shown that the high value of the spin-orbit splitting is responsible for the gradual stabilisation and stability of the bivalent state at the end of the actinide series, the significant difference in the stability of the lanthanides(IV) and actinides(IV), and the possibility in principle of obtaining lanthanyl groups at the end of the lanthanide series.
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I. INTRODUCTION

In recent years there has been a marked increase in interest in compounds of the *f*-elements, because of their varied practical applications. Practical requirements are making it necessary to carry out more detailed studies of "classical" compounds of the bivalent and tervalent lanthanides and actinides, and to prepare new compounds in new oxidation states. Lanthanides and actinides are interesting objects of research studies, since the question of the discovery of new oxidation states can now be raised for only a few elements of Mendeleev's periodic system.

Quantum chemistry plays an important role in the study of extremal oxidation states. The evaluation of the present state of valence theory depends on the field of chemistry. Several thousand molecular orbital calculations have been carried out for organic systems, slightly fewer for inorganic systems, and only about thirty for actinide

molecules. This is due to a number of factors, primarily the fact that the experimental data which are usually employed in theoretical calculations are not available for the actinides; many are highly radioactive and difficult to obtain. To this must be added the significant mathematical difficulties: the carbon atom has six electrons, whereas the curium atom has ninety six, and the quantum-chemical study of a system of sixteen carbon atoms involves less difficulty than the study of any curium molecule.

The use of computers has led to considerable progress in lanthanide and actinide valence theories. Overall, however, the progress resulting from the use of computers has been less than seemed likely in the nineteen-sixties, when calculations by the Roothaan method began to be carried out for the first time in the Soviet Union. The existence of computers and their availability make the ideological content of quantum-chemical calculations and their relation to experiment of primary importance, since computers only process ideas. The mathematical apparatus of quantum mechanics is most effective in those cases where the chemical model of the phenomenon is clarified in collaboration with experimentalists, and afterwards an apparatus is selected using a computer, calculator, or slide rule, adequate for the problem being posed and effective for its solution. When applied to the study of extremal oxidation states of the lanthanides and actinides, this approach means not only the use of up-to-date quantum-mechanical atomic and molecular orbital calculations but also the search for various correlations on the basis of the experimental results obtained.

The Soviet experimental school has accumulated a large amount of experience in the study of extremal oxidation states of the lanthanides and actinides: Cm(VI),[1] Md(I),[2] Pu(II),[3] Pu(VII),[4] Am(VII),[5] Np(VII),[6] and Tm(IV) [7] have been discovered. This makes it possible to raise the question of the quantum-chemical prediction of the existence of both higher and lower oxidation states of the lanthanides and actinides: univalent lanthanides and actinides, plutonium(VIII) and americium(VIII), oxidation states of 5+, 6+, and 7+ for curium, 5+ and 6+ for californium and berkelium, and 4+ for holmium, erbium, and thulium. The prediction of a given oxidation state is an important aspect of the problem. The study of the electronic structure and properties of the lanthanides and actinides in unusual oxidation states is a no less important and apparently more complex question, including a number of problems: the determination of redox potentials, ionic radii, the geometry of molecular systems, and the study of reaction mechanisms, energy structure, etc.

The present review is devoted to the theoretical study of new oxidation states of the lanthanides and actinides and the investigation of the regular features of their structure in relation to Mendeleev's periodic law.

II. STABILITY OF THE LOWER OXIDATION STATES OF THE *f*-ELEMENTS

1. Characteristics of the Univalent State

A number of experimental studies have been devoted to the attempt to obtain lanthanides or actinides in univalent or singly-charged states. Fong[8] studied the reduction of lathanides to the singly-charged state in crystalline lattices. In particular, the broad absorption band in the thermoluminescence spectra of γ-irradiated Sm^{2+}/KCl specimens has been assigned to the electronic transition $4f^6 6s^1 \cdot\cdot 4f^5 6s^2$, corresponding to the reduction of Sm^{2+} to the univalent state. Similar experiments were carried out[9] for Sm^{2+}/KCl and Eu^{2+}/KCl specimens; no evidence in support of the formation of Eu^+ was obtained. Subsequently, experiments were carried out[10] including the additional high-temperature treatment of Sm^{2+}/KCl and Eu^{2+}/KCl specimens in potassium vapour. This gave fundamentally new (at T = 4.2 K) absorption bands in the thermoluminescence spectra of these specimens, which were assigned to the univalent states Sm^+ and Eu^+. Fong's data on the preparation of univalent europium were confirmed in 1978.[11]

A series of unique studies in the synthesis of univalent lanthanides has been carried out.[12–15] The compounds LnX, where Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu; and X = Cl, Br, were synthesised. The compounds obtained have a layer structure, and are isostructural with ZrCl or ZrBr.[15] Zirconium chloride has the sodium chloride structure with alternating layers of Zr and Cl atoms parallel to the (001) face. The coordination polyhedron of the Ln atom is an antiprism of Ln_3–Cl_3 atoms.[15] A characteristic feature of the structure is the presence of a bond between the metal atoms, so that these compounds have the properties of two-dimensional metals.

Among actinide atoms, an attempt has been made to obtain mendelevium(I); the conclusion that mendelevium(I) exists was based on its ability to cocrystallise with potassium hexachloroplatinate.[2]

In all the experiments, the crystal lattice acts as an additional factor stabilising the univalent state (KCl or K_2PtCl_6); in the compounds prepared in the works cited,[12–15] the corresponding factor is the formation of Ln_6 metal clusters. The methods of high-temperature chemistry have detected the existence of many neutral molecules with the formula LnF.[16] These are unstable molecules, analogous to the univalent alkaline earth metal halides; they have similar dissociation energies, for example: E_d(CaF) = 125.5 kcal mole^{-1}, E_d(SmF) = 127 kcal mole^{-1}, E_d(SrF) = 129.5 kcal mole^{-1}, and E_d(NdF) = 130 kcal mole^{-1}. Stable compounds of the univalent lanthanides and actinides have not been obtained in solution or the gas phase.

Experiments on the study of solid specimens raise a number of important theoretical problems regarding the electronic structure of these elements in the univalent state, namely: 1) the nature of the electron configuration of the *f*-elements; 2) the stability of the lower oxidation states in the actinide series; 3) the analogy between the actinides in lower oxidation states and other elements of the periodic system.

The valence possibilities of an atom are determined by the number of unpaired electrons, unshared electron pairs, unfilled atomic orbitals (AO), and the energy of excitation from one electronic state to another. For most elements of the lanthanide and actinide series, the electron configuration of the ground state is $f^n s^2$, so that the univalent state is realised when one *s*-electron is involved in chemical bond formation, and the other remains localised, as in the univalent alkaline earth metal halides. In contrast to the elements of group II, however, in the singly-charged lanthanides and actinides there may be rearrangement of the electron configuration, stabilising this state: $M^+(f^n s) \rightarrow M^+(f^{n+1})$ or $M^+(f^n s) \rightarrow M^+(f^{n-1} s^2)$, where M = Ln, An. For the group II elements there is no "inner" atomic orbital which might have been involved in a stabilisation process.

It is of interest to compare the excitation energies E_1 of the transition $f^n s \rightarrow f^{n+1}$ for singly-charged lanthanides and actinides (Table 1). Using the Hartree–Fock Hamiltonian as the zeroth approximation and applying perturbation theory to the calculation of the correction to the kinetic energy operator and to take account of spin–orbit coupling, and also the Darwin correction, the present

authors calculated the excitation energies for the singly-charged lanthanides and actinides.[18,19] The data in Table 1 lead to the following conclusions.[23]

Table 1. Promotion energies of the transition $f^n s \rightarrow f^{n+1}$ for singly-charged actinide and lanthanide ions (kcal mole^{-1}).[18-22]

An$^+$	[20, 21]	[18, 19]	[22]	Ln$^+$	[20, 21]	[22]
Ac$^+$	81.00	—	109.8	La$^+$	118.00	118.29
Th$^+$	94.00	91.2	85.52	Ce$^+$	98.00	96.79
Pa$^+$	86.00	83.58	78.37	Pr$^+$	91.00	97.82
U$^+$	78.00	77.17	72.36	Nd$^+$	94.00	99.73
Np$^+$	63.00	54.29	50.91	Pm$^+$	74.00	79.71
Pu$^+$	40.00	29.28	27.46	Sm$^+$	52.00	52.63
Am$^+$	92.00	86.61	81.23	Eu$^+$	166.00	162.60
Cm$^+$	68.00	57.02	53.48	Gd$^+$	137.00	134.20
Bk$^+$	46.00	35.67	33.46	Tb$^+$	114.00	115.66
Cf$^+$	46.00	34.76	32.61	Dy$^+$	126.00	122.24
Es$^+$	49.00	35.06	32.89	Ho$^+$	132.00	130.02
Fm$^+$	40.00	17.08	16.02	Er$^+$	123.00	113.08
Md$^+$	17.00	8.23	7.72	Tm$^+$	97.00	87.83

Note. Numbers in square brackets denote references (Ed. of Translation).

1. The energies of excitation into the univalent state for the singly-charged actinide ions are lower than those of the corresponding lanthanide ions.
2. The energies of excitation into the univalent states are lower for the second half of the actinides than for the first half, with the exception of Pu^+, which also has a low excitation energy $f^6s \rightarrow f^7$.
3. For the second half of the actinides, with increase in the atomic number, the excitation energy decreases, and the lowest excitation energy is shown by Md, at which the f^{14} shell is filled.
4. Of the lanthanides, Sm^+ ($f^6s \rightarrow f^7$ transition) and Pm^+ have the lowest excitation energies.

In addition to the electron configuration $f^n s$, an atom may be univalent in the electron configurations $f^n d$ and $f^n p$. The energy E of excitation into these states, however, is much greater than that into the state $f^n s$, and $E(f^n p) > E(f^n d) > E(f^n s)$. For all singly-charged actinides, the values of $E(f^n p)$ are greater than $E(f^n s)$ by ~3 eV. For U^+, Np^+, and Pu^+, the energy of the $f^n d$ electron configuration is higher than that of $f^n s$ by 1.0–1.5 eV; for the other elements of the actinide series, this difference gradually increases, reaching 3 eV for Md. These data indicate that for the univalent actinides, bond formation involves chiefly the 7*s* orbital; the 6*d* orbitals may play a small part in bond formation in the middle of the series (for U, Np, and Pu), but the 7*p* orbitals remain excited for all the univalent actinides; the 5*f* orbitals, like the other valence configurations ($f^n ds^2$, $f^n s^2$, $f^n sd$, etc.), remain core orbitals, deeper than the *s* orbital. Thus in the electron configuration $f^n s$ for the singly-charged actinide ions An^+, it is more difficult to remove an electron from an *f* orbital than from the *s* orbital; the difference in the ionisation energies $I_f - I_s$ is 2.1 eV for Pu, 3.3 eV for Am, 0.6 eV for Cm, 1.4 eV for Bk, 2.4 eV for Cf, 2.5 eV for Es, 2.1 eV for Fm, and 3 eV for Md.[20-22]

A second way in which the univalent state is stabilised is associated with the transfer of an *f* electron to the *s* level, that is $f^n s \rightarrow f^{n-1} s^2$. With a low excitation energy, a filled s^2 electron shell is formed. The data in Table 2 show that the values of the excitation energies $E_2(f^n s \rightarrow f^{n-1} s^2)$ are low, except for samarium and europium. It may be assumed that in the previously synthesised[12-15] monohalides LnCl, Ln = La, Ce, Pr, Nd, Gd, Tb, Ho, Er, the second route to the stabilisation of the univalent state is followed. They therefore have a distorted CdI_2 or $Mg(OH)_2$ structure, in which the central atoms also have an unshared pair of s^2 electrons. At the same time, samarium and europium differ from the other lanthanides: univalent europium should be the analogue of the alkaline earth elements, but Sm^+ can be stabilised by the first mechanism.

Table 2. Excitation energies for Ln^+ and An^+.[21]

An	$10^{-3} E_2$, cm^{-1}	Ln	$10^{-3} E_2$, cm^{-1}	An	$10^{-3} E_2$, cm^{-1}	Ln	$10^{-3} E_2$, cm^{-1}
Ac	−28.20	La	−6.75	Cm	−2.09	Gd	3.44
Th	−17.50	Ce	5.52	Bk	5.00	Tb	5.50
Pa	−8.00	Pr	16.00	Cf	12.00	Dy	12.336
U	−4.66	Nd	17.50	Es	12.00	Ho	10.00
Np	2.00	Pm	17.00	Fm	9.00	Er	7.00
Pu	8.19	Sm	24.00	Md	17.00	Tm	12.50
Am	18.50	Eu	33.00				

The univalent state in solution is characterised by the oxidation potential of the reaction

$$An^+_{aq}(f^{n+1}) \rightarrow An^{2+}_{aq}(f^n) + e$$

or

$$An^+_{aq}(f^{n-1}s^2) \rightarrow An^{2+}_{aq}(f^{n-1}s^1) + e$$

The factors determining the stability of the univalent state can be considered. The energy balance of the reaction is determined by the difference between the ionisation energy of the actinide ion in the univalent configuration and the energy of excitation from the univalent to the bivalent state $\varepsilon_1 = I - E_1$, and also by the difference in the free energies of hydration for these oxidation states, δF_n.

Table 3. Ionisation energies of singly-charged lanthanide and actinide ions in the electron configuration $f^{n-1}s^2$.[24,25]

Configuration	Term	Ln	$10^{-3} I'$, cm^{-1}	An	$10^{-3} I'$, cm^{-1}
f^0s^2	^1S	La	17.5	Ac	18.0
f^1s^2	^1F	Ce	33.8	Th	27.9
f^2s^2	^3H	Pr	47.9	Pa	47.2
f^3s^2	^4I	Nd	45.7	U	59.0
f^4s^2	^5I	Pm	44.6	Np	66.5
f^5s^2	^6H	Sm	55.5	Pu	101.4
f^6s^2	^7F	Eu	68.9	Am	88.0
f^7s^2	^8S	Gd	7.9	Cm	59.3
f^8s^2	^7F	Tb	24.4	Bk	91.7
f^9s^2	^6H	Dy	34.7	Cf	108.0
$f^{10}s^2$	^5I	Ho	32.5	Es	118.7
$f^{11}s^2$	^4I	Er	27.4	Fm	136.7

Factors increasing the stability of the univalent state are a high value of the ionisation energy of the singly-charged ion and a low excitation energy. From data on the ionisation energies of $An^+(f^n s)$, calculated in the relativistic Hartree–Fock approximation,[19] and from the excitation energies E_1 (Table 1), it follows that in the second half of the actinide

series, the most stable univalent state, corresponding to the minimum value of E_1, is shown by mendelevium. For univalent states stabilised by the second mechanism with the production of the electron configuration $f^{n-1}s^2$, the stability of the univalent state to oxidation is also determined by the quantity $\varepsilon_2 = I' - E_2$, where the corresponding values relate to the electron configuration $f^{n-1}s^2$. Table 3 gives the values of the ionisation energies for the electron configuration $f^{n-1}s^2$.[24,25] Comparison of the values of E_2 and I' shows that: 1) in the lanthanide series, the stability of the univalent state in solution with respect to oxidation is low; 2) in the actinide series, the stability of the univalent state in solution is higher than for the corresponding lanthanides.

2. Ionic Radii

The determination of the ionic radii of the actinides in lower oxidation states is important for establishing the similarity in the properties of the actinide elements and the elements of other groups of Mendeleev's periodic system. The solution of this problem is difficult, because of high radioactivity and the difficulty of obtaining the heavy actinides. At present, californium is apparently the last element for which ionic radii can be calculated from structural data. There are extremely few published data on the ionic radii of the actinides in lower oxidation states. Of the bivalent actinide compounds, americium di-iodide has been prepared; the measured interatomic distance in this compound, $R_{Am-I} = 3.28-3.40$ Å, indicates that the ionic radius of americium is 1.12–1.24 Å.[26]

Comparison of the lattice parameters of AmI_2 and EuI_2 [27] indicated that $R_{Am^{2+}} = 1.1$ Å, $R_{Eu^{2+}} = 1.09$ Å, and comparison of the lattice parameters of $EuBr_2$, $CfBr_2$, and $SrBr_2$ showed that $R_{Cf^{2+}} = 1.08$ Å. The similarity in the crystallisation coefficients of Sr^{2+} and Fm^{2+} with $SmCl_2$ indicates that the ionic radii of these elements differ by not more than 5%. Finally, comparison of the behaviour of Sr, Ca, and No in extraction and ion-exchange systems[28] indicated that the ionic radius of nobelium(II) lies in the range of the ionic radii of strontium and calcium.

Quantum-chemical methods make it possible to calculate the distance from the nucleus to that part of the ion where there is the maximum electron density R_{max}. Slater[30] has shown that the value of R_{max} for singly-charged ions is related to the crystal ionic radius by the simple relationship $R_{cr} = c_n R_{max}$, where c_n is a coefficient which depends on the principal quantum number n of the outer valence shell of the ion. For the f-elements of a given series, existing in the same charge state and therefore having the same valence f-orbital, the value of c_n apparently remains constant for the elements of the entire series. The Slater functions are crude approximations for the f-elements; better agreement can be obtained using the Hartree–Fock radii of the maximum electron density, calculated in the relativistic approximation.[24,25]

The Hartree–Fock values of R_{max} for the lanthanides and the crystal ionic radii of these elements in the tervalent state have been used[29] to calculate the coefficients c_n, which were found to be constant for all elements of the 4f series ($c_n = 1.257$). Similarly, the coefficients remain constant for the tervalent actinides from plutonium to einsteinium ($c = 1.21$). Pauling's relationship for isoelectronic ions[31] has been used to calculate the ionic radii for univalent and bivalent actinides;[30] the following values were obtained for the ionic radii of the doubly-charged actinide ions (Å):

Am^{2+}	Cm^{2+}	Bk^{2+}	Cf^{2+}	Es^{2+}	Fm^{2+}	Md^{2+}	No^{2+}
1.17	1.16	1.14	1.06	1.05	1.05	1.04	1.02

The ionic radii of the doubly-charged actinides calculated in this way agree with available experimental data. Thus the value of $R_{No^{2+}}$ lies in the range between the ionic radii of strontium and calcium.[32] The ionic radius of Fm^{2+} is close to the ionic radii of Sr^{2+} and Sm^{2+}; the ionic radius of Cf^{2+} agrees with the experimental data, which show that CfI_2 and CdI_2 are isostructural, and is close to the suggested[27] value of 1.08 Å.

The value obtained for the ionic radius of Am^{2+} shows good agreement with the experimental internuclear distance R_{Am-I} in AmI_2. Published data[27] on the ionic radius of americium, $R_{Am^{2+}} = 1.1$ Å, do not agree with the Hartree–Fock calculations, since the proportional relationship between $R_{max}(Am^{2+})$ and $R_{cr}(Am^{2+})$ breaks down. The value 1.21 Å was obtained[30] for $R_{cr}(Md^{+})$; the ionic radius of Md^{+} calculated in this way is close to that of Ag^{+} (1.13–1.26 Å).

III. HIGHER OXIDATION STATES OF THE LANTHANIDES AND ACTINIDES

1. Relationship Between the Oxidation Potentials and the Electronic Structure of the Central Atom

The marked increase in interest in compounds of the f-elements in unusual oxidation states can be attributed to two factors. Firstly, the discovery of nuclear decay and the subsequent development of nuclear energy have led to the detailed study of the chemistry of the lanthanides, the principal fission products found in the nuclear reactor, and of the chemistry of the transuranium elements, which are also formed at the same time. Secondly, there has been an increase in the role of the lanthanides and actinides in industry and a consequent increase in the need to study their properties and predict nontrivial oxidation states.[34]

It has been suggested[33] that einsteinium(IV) should exist in compounds with the fluorite structure. French workers, using thermochromatography, were the first to prove the existence of einsteinium(IV) fluorides,[35] and also curium(V) and (VI).[138] The behaviour of EsF_4 in the gas phase is analogous to that of CmF_4, BkF_4, and CfF_4.

It has been suggested that einsteinium(IV), fermium(IV) and mendelevium(IV) can exist as the double salts $Li_3.AnF_7$,[36] and berkelium(V), californium(V), and einsteinium(V) as the oxygen compounds Li_7AnO_6.[34] It has also been suggested that einsteinium(VI) and fermium(VI) can be obtained as the hexafluorides.[37] These suggestions, which undoubtedly contain elements of new ideas, have not been confirmed by calculations, estimations, or other evidence.

French workers,[38] on the basis of a calculation of the thermodynamic characteristics of the 5f elements, estimated the stability of berkelium(V) and californium(V), and showed that Cf(V) should be stable, and Bk(V) unstable, in aqueous solutions. The stability of a given oxidation state is determined by the oxidation potential of the reaction $An^{z+}(m) \rightarrow An^{z'+}(m+1) + e$, which in turn is determined by all the changes taking place when the central ion with effective charge z and oxidation number m is converted into a state with oxidation state $m+1$ and charge z'. The free

energy change F in the oxidation, $F = \pm\varepsilon + I + \Delta F_h$, includes the ionisation energy I, the energy $\pm\varepsilon$ used in the rearrangement of the electron configuration of the ion An^{z+} in the change from the state with oxidation number m to the state with oxidation number $m + 1$, and ΔF_h is the change in the free energy of hydration.

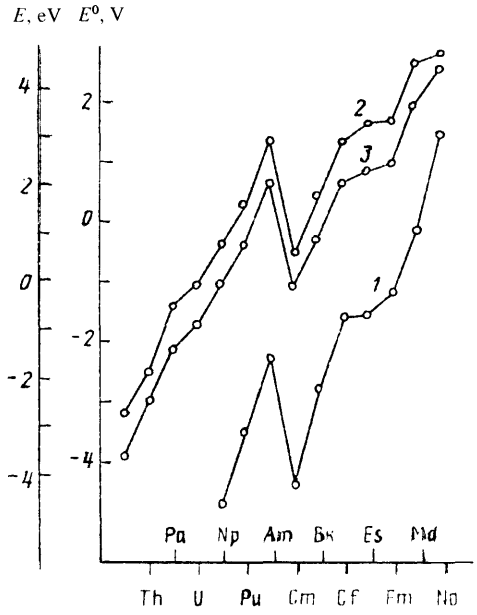


Figure 1. Dependence of the oxidation potentials E^0(II–III) (*1*) and the excitation energies $E = \varepsilon(f^n) - \varepsilon(f^{n-1}d)$ (*2*) and $E = \varepsilon(f^n s^2) - \varepsilon(f^{n-1}ds^2)$ (*3*) on the atomic number of the element.[107]

Within the framework of the covalent model, the electron configurations of the bivalent state $f^n s^2$ and the tervalent state $f^{n-1}ds^2$ in the approximation of the ionic model are f^n and $f^{n-1}d$ respectively. In both approximations, the value of ε changes in the same sense as the potentials E^0(II–III).[57] Fig. 1 gives the dependence on the atomic number of the elements of the oxidation potentials E^0(II–III) and the excitation energy, calculated for the two electron configurations from published data.[20–22] The main regular features of the dependence of other oxidation potentials on the atomic number of the element are also determined by the energy used up in the rearrangement of the electron levels of the actinide atoms or ions.[57,59] Change in the heats of hydration leads to renormalisation of the oxidation potentials, without changing their course. The linear relationship between the oxidation potentials and the energy of excitation of an f-electron into the d-level (Figs. 2 and 3) makes it possible, from the correlation rules alone, to judge whether a transition into the next oxidation state takes place. In this connection, an important role is acquired by calculations of the energy of the f- and d-levels in actinide and lanthanide atoms and ions.

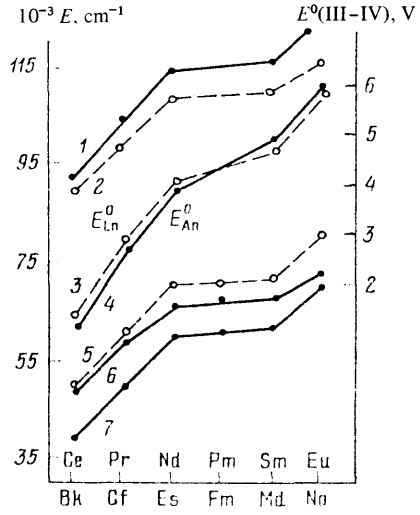


Figure 2. Change in the same sense in the oxidation potentials E^0(III–IV): *3*) Ln, *4*) An, and excitation energies for triply-charged lanthanide and actinide ions:[107] *1*) $An(f^n \to f^{n-1}p)$, *2*) $Ln(f^n \to f^{n-1}s)$, *5*) $Ln(f^n \to f^{n-1}d)$, *6*) $An(f^n \to f^{n-1}s)$, *7*) $An(f^n \to f^{n-1}d)$.

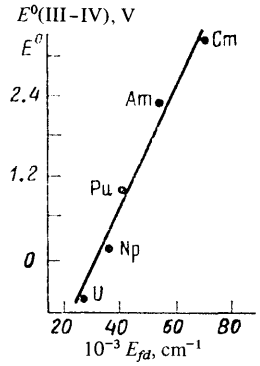


Figure 3. Linear relationship between the oxidation potentials E^0(III–IV) and the excitation energy.[107]

2. The Approximation Based on Calculations for Free Atoms and Ions

Atomic calculations give the first representations of the energy levels of atoms, and characterise the radial wavefunctions. These calculations can be used to reach important chemical conclusions about the possible oxidation states of atoms, the regular features of the change in stability, the specific features of the behaviour of the

actinide ions in solids, etc. Although calculations for molecules are used to reach definite chemical conclusions, calculations for atoms and ions are rarely used to interpret chemical data. These calculations may be useful, however, for an understanding of qualitative chemical regularities.

Atomic calculations for the actinides have an extensive history. Herman and Skillman[39] found solutions of the Hartree–Fock–Slater equation for all atoms up to element 103. Almost simultaneously,[40] the Hartree equation was solved with an exchange correction to the total energy. The first relativistic calculations for atoms, including uranium, were carried out[41] without allowance for exchange. Subsequently,[42] relativistic calculations were carried out with allowance for exchange by Slater's method, and account was taken of the effect of the finite dimensions of the nuclei.[43] Unfortunately, these calculations do not always correlate with the chemical properties. In Ref. 43, for berkelium and fermium, the electron configurations f^8ds^2 and $f^{11}ds^2$, corresponding to a more stable tervalent state, were obtained, whereas in fact they are more stable in the bivalent state. The difference in the energies of the 5*f*-orbitals of californium and einsteinium should not be so large as found in Ref. 43, since the oxidation potentials E^0(II–III) for these elements are similar.[44]

The use of the Slater exchange potential for large radii is an approximation, since the potential tends to zero according to an exponential law, and not as r^{-1}. The use of different coefficients[45–47] in the exchange potential improves the results, although the crude asymptotic form of the approximation is preserved. A number of authors have studied the question of why the local approximation is crude for large radii.[48–50] In Ref. 51, a first-order correction was introduced into the local approximation, using as the functions of the zeroth approximation the functions obtained in Ref. 52. The results[51] also show some lack of agreement with experiment. For the plutonium atom, the calculated energy of the 5*f* orbital is higher than that of the 7*s* orbital, whereas the opposite relationship should be observed. The energy parameters obtained[51] for americium indicate a very low ionisation energy (2.885 eV), and also show that it should be stable in the univalent or tervalent states, but not in the bivalent state; the energy parameters of berkelium correspond to stable tervalent and quinquevalent states. None of this agrees with experiment. Moreover, for Cf, the difference between the energy of the 5*f* and 7*s* orbitals is so small that its electron configuration should lead to a stable sexavalent state, which again does not agree with experiment. Beginning from einsteinium, however, adequate qualitative agreement between the calculated and experimental parameters is observed.

Hartree–Fock calculations of the electronic structure of atoms have been carried out by Mann.[53] Although these were non-relativistic calculations, exchange terms were taken into account without approximation; it was found that the 7*s* orbital (6*d* orbital in Refs. 43 and 51) is responsible for the ionisation energy. Although the values of the energy of the 6*d* orbitals obtained by Mann[53] are slightly low, the energies of the 5*f* orbitals give qualitatively the regular chemical features relating to the stability of the bivalent and tervalent states of the actinides. The absolute values of the energies of the 5*f* orbitals obtained in Ref. 53 differ by a factor of 2–2.5 from those obtained in Refs. 43, 51, and 54. In Ref. 53, these energies are systematically too low, possibly due to the neglect of relativistic effects.

In a series of calculations by Desclaux, the Dirac–Fock equation was solved without approximations for the exchange terms; the nuclei were regarded as spheres with uniform charge distribution,[54] in accordance with the published procedure.[55,56] A noteworthy feature is the small difference in the orbital energies of the 6*d* and 7*s* levels, which explains many experimental facts. In the thorium atom, the 6*d* orbital is deeper than the 7*s* orbital, that is thorium is an analogue of the transition elements; for protactinium, uranium, neptunium, and curium, on the other hand, the 7*s* orbital is lower than the 6*d* orbital, and this explains the stabilisation of the electron configuration f^ns of their singly-charged ions.[54]

In the first half of the series, the energies of the valence 5*f* orbitals differ little from the energies of the 6*d* and 7*s* orbitals, indicating that the elements of the first half of the series tend to form higher oxidation states. In the second half of the series, this difference gradually increases, again in agreement with the experimentally observed stabilisation of the bivalent state in the second half of the actinide series. The absolute values of the energies of the 5*f* orbitals explain their participation in chemical bond formation and the sequence in the arrangement of the molecular orbitals in actinide molecules and complexes.

Thus many atomic calculations give correctly the regular features of the electronic structure of the lower oxidation states of the actinides An(II) and An(III), and this gives grounds for using these calculations for the higher oxidation states also. The present authors carried out a series of calculations for the atoms of the 5*f* elements in excited configurations with the participation of the 6*d* orbitals and positively charged ions by the Hartree–Fock method with allowance for relativistic corrections.[61] According to these calculations, carried out for actinide ions in the electron configuration f^n,[19] the energy of removal of the last *f*-electron (Ry) increases sharply on going from Ac to Pu:

Ac	Th	U	Np	Pu
1.53068	2.70432	5.43696	6.97975	8.63445

The correlation of these ionisation energies with the known oxidation potentials corresponding to the change to higher oxidation states leads to a high potential for plutonium: E^0(VII–VIII) ≅ 4 V.

When applied to the change to a higher oxidation state, it may be assumed that the relative depth of the potential well for the $5f^1$ electron configuration is determined by the energy of splitting of the ^2F term as a result of spin–orbit coupling. Using the calculated[19] spin–orbit coupling constants for the actinides in the f^1 electron configuration from the actinium atom to the americium atom (cm^{-1})

Ac	Th	Pa	U	Np	Pu	Am
707	960	1211	1472	1747	2038	2337

for correlation with the known potentials also gave a high oxidation potential for plutonium: E^0(VII–VIII) ≅ 4 V; the oxidation potential obtained for the americium couple was even higher: E^0(VIII–IX) ≅ 5.8 V.

An important factor in the comparative estimation of the stability of f^n electron configurations with $n > 1$ is the interelectronic interaction, determined by the Racah parameters E^0, E^1, E^2, E^3. The ionisation energy[62] of an *f*-element in the electron configuration f^n can be expressed in terms of the Racah parameters and *W*, the Coulomb energy in the field of the positively charged core, imitating the cloud of the inert gas radon (Table 4).

The change in the energy of the electrostatic interaction with change in the number of electrons determines the binding energy of the valence electrons with the core. For example, exchange interaction increases the ionisation energy in the electron configuration f^{10} by $+12E^3$, makes no contribution to the electron configuration f^{11}, and decreases the ionisation energy in the electron configuration f^{12} by

$-12E^3$. The parameter W also changes with change in the number of electrons, but these changes are not so great for the lanthanides as for the actinides; thus for the 4*f*-elements, the parameter E^3 can influence the relative stability of a given oxidation state along the series. The stabilities of the 4+ oxidation states of the lanthanides show interesting regular features. From the experimental values of the oxidation potentials E^0(III–IV), it follows[58,75] that the stability of the 4+ oxidation state decreases on going from cerium to neodymium in the first half of the series and from terbium to dysprosium in the second. In other words, the stability of the 4+ oxidation state decreases towards the end of the series.

Table 4. Ionisation energy of actinides with the electron configuration f^n.[62]

n	$I=E(f^{n-1})-E(f^n)$	n	$I=E(f^{n-1})-E(f^n)$
1	W	8	$W-7E^0-9E^1$
2	$W-E^0+9E^3$	9	$W-8E^0-9E^1+9E^3$
3	$W-2E^0+12E^3$	10	$W-9E^0-9E^1+12E^3$
4	$W-3E^0$	11	$W-10E^0-9E^1$
5	$W-4E^0-12E^3$	12	$W-11E^0-9E^1-12E^3$
6	$W-5E^0-9E^3$	13	$W-12E^0-9E^1-9E^3$
7	$W-6E^0$	14	$W-13E^0-9E^1$

When the change in the parameter E^3 for the electron configurations f^{10}, f^{11}, and f^{12}, corresponding to triply-charged holmium, erbium, and thulium, is taken into account, the opposite trend in the stabilities of the 4+ oxidation state can be expected for these elements: Ho < Er < Tm. This is confirmed by the fact that for holmium, erbium, and thulium, there is a decrease in the energies of excitation from the f^n (n = 10, 11, 12) to the $f^{n-1}d$, $f^{n-1}p$, and $f^{n-1}s$ states.[19] For the actinides, there is a gradual increase in the corresponding energies from californium to nobelium (Fig. 4). These facts indicate that the stability of the 4+ oxidation state increases towards the end of the lanthanide series from holmium to thulium, and decreases towards the end of the actinide series from einsteinium to nobelium, that is in the actinide series on going from Es to No, the most stable 4+ oxidation state is shown by einsteinium, whereas in the lanthanide series it is shown by thulium. The preparation of compounds of thulium(IV) [7] and einsteinium(IV),[35] Cs_3TmF_7 and EsF_4, confirmed these theoretical predictions.

The sharp increase in the ionisation energy for the half-filled f^7 electron configuration compared with the f^8 configuration is due to the appearance of the term $-9E^1$ for n = 8. When applied to Cm, this means that it gives up an electron with greater difficulty in the tervalent state than in the quadrivalent state, but in the quinquevalent state the binding of the remaining five electrons to the core is decreased as a result of electrostatic repulsion, so that Cm(V) should be more readily converted into Cm(VI), compared with the conversion of Cm(IV) into Cm(V). Finally, Cm(VI) and Cm(III) are analogues in the sense that the interelectronic interaction parameter E^3 does not make a contribution to the binding energy of the remaining electrons to the core. Thus the potential E^0(VI–VII) for Cm should be high, like E^0(III–IV). Even this qualitative approach determines the chemical properties. For a quantitative estimate of the oxidation potentials, the correlation with the energies of the *fd*-transitions can be used.[64–68]

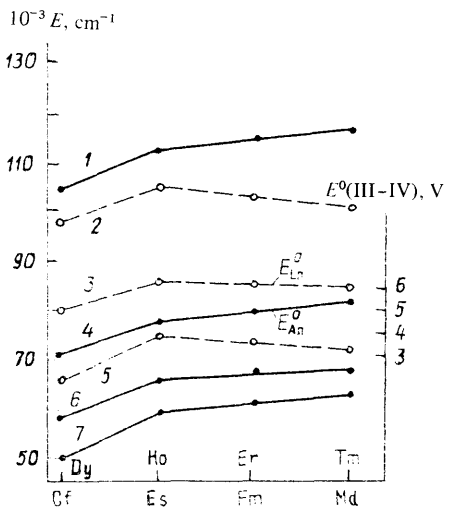


Figure 4. Change in the opposite sense in the oxidation potentials E^0(III–IV): *3*) Ln, *4*) An, and the excitation energies for triply-charged actinides and the corresponding lanthanides:[107] *1*) An($f^n \rightarrow f^{n-1}p$), *2*) Ln($f^n \rightarrow f^{n-1}s$), *5*) Ln($f^n \rightarrow f^{n-1}d$), *6*) An($f^n \rightarrow f^{n-1}s$), *7*) An($f^n \rightarrow f^{n-1}d$).

Published data on the transition energies have been obtained from the atomic spectra and the spectra of multiply ionised ions,[20,21,69,70] from thermochemical data for metals,[20,21] the electronic spectra of compounds,[71,72] the spectra of actinide ions in matrices, from Hartree–Fock calculations for free atoms and ions with allowance for relativistic corrections,[39–43,45–47,51–56] and finally by linearisation of the parameters of Coulombic and spin–orbit interactions.[22] The absolute magnitudes of these quantities do not always coincide, due chiefly to the marked broadening of the bands in the spectra as a result of spin–orbit coupling. Thus for uranium with a charge of 5+ in the electron configuration f^1, the terms of the ground state ^2F and the first excited state ^2D are split by spin–orbit coupling $^2F \rightarrow {}^2F_{5/2} + {}^2F_{7/2}$, $^2D \rightarrow {}^2D_{3/2} + {}^2D_{5/2}$ by 7609 cm^{-1} and 9511 cm^{-1}.[69] In accordance with the increase in the atomic number, the splitting energy of the ^2F term for Np^{6+} and Pu^{7+} increases. There is an analogous increase in the splitting energy of the ^2D term.[69] Thus for the transuranium elements it is possible to speak only of a qualitative charge dependence of the energy of the *fd* transition. On the basis of available experimental data on the energies of *fd* transitions, the present authors calculated the difference in the energies of the f^n and $f^{n-1}d$ states for the multiply ionised ions from actinium to curium; the data obtained are given in Table 5.[19,63,68] The correlation of the values of E_{fd} obtained with the known oxidation potentials indicates that curium(VI) is stable in solution: E^0(V–VI) = 5.1 V, whereas E^0(IV–V) = 1.7 V and E^0(VI–VII) = 2.7 V. The preparation of curium(VI) [1] confirmed these theoretical predictions. This approach indicated that californium(V)

is stable,[73] as confirmed experimentally,[74] and also that einsteinium(VI) is stable, E^0(V–VI) = 1.5 V. According to these estimates, berkelium(V) and californium(VI) should be unstable in solution.

Table 5. Excitation energies from the f^n electron configuration to $f^{n-1}d$ (10^{-3} E_{fd}, cm^{-1}).[63]

n	Ac	Th	Pa	U	Np	Pu	Am	Cm
1	—20.0	5.0	31.0	57.5	82.5	—	—	—
2	—	—15.1	17.5	52.5	87.5	120.0	—	—
3	—	—	—5.0	27.0	55.0	82.5	112.5	—
4	—	—	—	0.5	35.0	70.0	104.0	—
5	—	—	—	—21.0	9.1	40.0	70.0	100.0
6	—	—	—	—	—12.5	17.5	51.0	82.5
7	—	—	—	—	—	—5.0	24.0	57.5

3. Molecular-Orbital Analysis of Octahedral Complexes

Since the discovery of septavalent neptunium, plutonium, and americium,[4–6] a large amount of experimental material has accumulated,[76] and the problems still to be solved have become clear. These problems are related primarily to the study of the electronic structure of compounds of neptunium(VII), plutonium(VII), and americium(VII), and cover a wide range of questions: the electron density distribution, the structure of the energy levels, the regular features of the change in the ionisation energies and electron affinity, the determination of the oxidation potentials, and the interpretation of the electronic spectra. The discovery of the highest oxidation state of neptunium raised the question of the possible existence of plutonium(VIII), which can be resolved only by a systematic study of the high oxidation states of uranium, neptunium, plutonium, and americium.

To resolve these problems, Pershina[77,78,95] carried out a a series of molecular orbital calculations for octahedral oxyanions UO_6^{7-}, UO_6^{6-}; NpO_6^{7-}, NpO_6^{6-}, NpO_6^{5-}; PuO_6^{6-}, PuO_6^{5-}, PuO_6^{4-}; AmO_6^{6-}, AmO_6^{5-} [77–80] by the semi-empirical molecular orbital method[81] using numerical Hartree–Fock functions.[53] The choice of objects of study is not accidental: most compounds of the actinides in the highest oxidation states in solution, and also those obtained by solid-phase synthesis, are oxygen compounds.

It follows from molecular orbital calculations that the effective charges on the central atoms do not exceed 2+ (Table 6). For isoelectronic anions they decrease with increase in the atomic number of the central atom. Table 6 shows that the populations of the 5*f* orbitals differ considerably from those given by crystal field theory. The population of the 6*d* orbitals corresponds to approximately two electrons. This is an interesting fact, since the ground state of the neutral atoms does not contain more than one 6*d* electron. With increase in the oxidation state of the actinide, the population of the 6*d* orbital increases; at the same time the population of the 5*f* orbital decreases, that is the oxidation is accompanied by the excitation of an electron into the 6*d* level. The population of the 7*s* orbital is low, and changes little from one compound to another.

A typical energy level diagram for octahedral oxyanions is shown in Fig. 5 for the UO_6^{7-} ion. The low-lying energy levels correspond to the interaction of the 2*s* and 2*p*σ orbitals of the oxygen atoms and the 7*s*, 6*d*, and 5*f* orbitals of the actinide atom. These are predominantly ligand orbitals. The next group of levels corresponds to pure σ or mixed (σ–π) molecular orbitals. In all the anions studied, the system of bonding levels is completed by quasi-degenerate molecular orbitals (MO), corresponding to oxygen atomic orbitals (AO), which are separated from the antibonding MO by an energy gap of width ΔE. For the diamagnetic ions UO_6^{6-}, NpO_6^{5-}, and PuO_6^{4-}, the values of ΔE are low, indicating the possible existence of polarisation temperature-independent paramagnetism.

Table 6. Populations of the *s*-, *d*-, and *f*-orbitals (*e*).[77,78]

Orbital	U(V)	U(VI)	Np(VI)	Np(VII)	Pu(VI)	Pu(VII)	Pu(VIII)	Am(VI)	Am (VII)
s	0.29	0.28	0.28	0.26	0.27	0.25	0.23	0.26	0.25
d	2.10	2.30	2.21	2.34	2.10	2.25	2.40	2.08	2.21
f	1.75	1.47	2.80	2.70	4.04	3.92	3.84	5.19	5.11

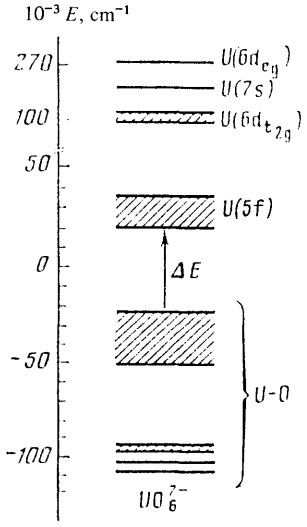


Figure 5. Typical energy level diagram for octahedral oxyanions of the actinides: the uranium(V) oxyanion.[107]

In the isoelectric ions, the magnitude of the crystal field splitting increases from U(VI) to Np(VII) and Pu(VIII) (Fig. 6). The magnitude of the splitting increases with increase in the oxidation state of the central ion; for example, for PuO_6^{6-}, PuO_6^{5-}, and PuO_6^{4-}, the magnitude of the splitting is 18030, 23260, and 28080 cm^{-1} respectively.[77–80]

In the highest oxidation states, the ionisation potential is determined by the molecular orbital t_{1u}. The energy of this MO decreases on going from U(VI) to Np(VII) and Pu(VIII) in accordance with the decrease in the effective negative charge on the ligands. As a result of the stabilisation of the 5*f* orbitals of the actinide atoms with increase in the atomic number in the isoelectronic anions,

the energy of the non-bonding $2\Gamma_7^-$ level decreases in the order U(VI) > Np(VII) > Pu(VIII), so that the electron affinity for PuO_6^{5-} is ~5.8 eV. This is apparently one of the main reasons for the instability of plutonium(VIII) in the oxyanion form. In anions with the $(2\Gamma^-)^1$ configuration, this level is also stabilised with increase in the atomic number of the actinide; thus U(V) is readily converted into U(VI), whereas plutonium(VII) is not oxidised.

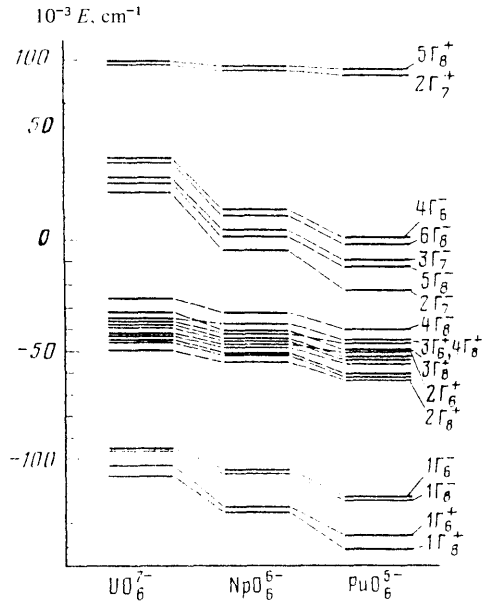


Figure 6. Change in the energy levels in isoelectronic oxyanions with increase in the atomic number of the actinide.[107]

Usually, three groups of bands are interpreted in the electronic spectra of actinide compounds: *ff*, *fd*, and charge-transfer transitions. This interpretation has been carried out in detail for uranium, neptunium, and plutonium hexahalides,[82-88] for actinyl ions,[89] and for a number of complexes.[90-93] The *ff* transitions in various octahedral oxyanions have been assigned.[94] A complete analysis of the electronic spectra on the basis of molecular orbital calculations for the entire series of octahedral oxyanions from U to Am has not been carried out. In the diamagnetic anions of U(VI), Np(VII), and Pu(VIII), the lowest transitions take place from the molecular orbitals $3\Gamma_6^+$ and $4\Gamma_8^+$ into antibonding MO with symmetry Γ_7^- and Γ_8^-. This leads to the existence of seven charge-transfer transitions allowed by the dipole selection rules (Table 7). Seven fine-structure bands appear in the absorption spectrum. This absorption band is displaced towards longer wavelengths in the series U(VI) → Np(VII) → Pu(VIII).

Additional absorption bands may also appear in the spectrum, since many of the MO are practically non-bonding. Two such additional bands are formed by transitions from the orbitals $2\Gamma_6^+$, $3\Gamma_8^+$ and $1\Gamma_6^+$, $2\Gamma_8^+$ (Table 7).

Table 7. Energies of the charge-transfer bands (10^{-3} *E*, cm^{-1}).[78]

Transition	UO_6^{6-}	NpO_6^{5-}	PuO_6^{4-}
$3\Gamma_8^+ \rightarrow 5\Gamma_8^-$	45.6	32.3	26.6
$3\Gamma_6^+ \rightarrow 6\Gamma_8^-$	57.7	45.2	39.8
$4\Gamma_8^+ \rightarrow 2\Gamma_7^-$	40.2	25.1	15.6
$4\Gamma_8^+ \rightarrow 5\Gamma_8^-$	45.6	32.3	26.6
$4\Gamma_8^- \rightarrow 3\Gamma_7^-$	51.2	35.6	31.4
$4\Gamma_8^+ \rightarrow 6\Gamma_8^-$	57.7	45.2	39.8
$4\Gamma_8^- \rightarrow 4\Gamma_6^-$	58.2	46.2	43.7
$2\Gamma_6^+ \rightarrow 5\Gamma_8^-$	51.9	38.2	32.0
$2\Gamma_6^+ \rightarrow 6\Gamma_8^-$	64.0	51.1	45.2
$3\Gamma_8^+ \rightarrow 2\Gamma_7^-$	42.1	30.3	23.5
$3\Gamma_8^+ \rightarrow 5\Gamma_8^-$	47.6	37.6	34.5
$3\Gamma_8^- \rightarrow 3\Gamma_7^-$	53.1	40.8	39.3
$3\Gamma_8^+ \rightarrow 6\Gamma_8^-$	59.4	50.5	47.7
$3\Gamma_8^- \rightarrow 4\Gamma_6^-$	60.2	51.4	51.6
$2\Gamma_8^+ \rightarrow 2\Gamma_7^-$	56.2	41.9	33.0
$2\Gamma_8^+ \rightarrow 5\Gamma_8^-$	61.6	49.2	43.9
$2\Gamma_8^- \rightarrow 3\Gamma_7^-$	67.2	52.5	48.8
$2\Gamma_8^+ \rightarrow 6\Gamma_8^-$	73.7	62.1	57.2
$2\Gamma_8^+ \rightarrow 4\Gamma_6^-$	74.2	63.1	61.0

Extensive experimental material has been published[76] on the electronic absorption spectra of actinides(VII) (Pu, Am) in alkaline solutions. The regular features in the spectra, corresponding to charge-transfer bands, are the same as for the highest oxidation states. Fine structure of the main band is observed, apparently as a consequence of spin–orbit coupling of the energy levels in the complex, particularly the levels with a large contribution from the 5*f* orbitals of the atoms. For systems with the $5f^1$ electron configuration of the actinide (UO_6^{7-}, NpO_6^{6-}, PuO_6^{5-}), transitions of the *ff* type appear, with calculated energies lying in the ranges 4170–14340, 5944–17020, and 9070 to 22040 cm^{-1} respectively.[77,78] The energies of the *fd* transitions in these complexes and the experimental values of the oxidation potentials E^0(V–VI) for uranium and E^0(VI–VII) for neptunium[76] make it possible to estimate the oxidation potential for plutonium: E^0(VII–VIII) = 3.7 V. This confirms the conclusion, based on atomic calculations, that plutonium(VIII) is unstable in solution.[78]

A similar analysis of the electronic structure and properties has been carried out for the octahedral chloro-anions of actinides(III) and (IV) $AnCl_6^{z-}$.[95,96] In the An(IV) complexes, the populations of the 6*d* orbitals decrease with increase in the atomic number of the element, smoothly on going from Pa to Np and then more sharply on going to Pu, and the populations of the 5*f* orbitals increase in the same direction. The energies of the charge-transfer transitions pass through an extremal value for curium (Table 8). The calculations of the energies of the *ff* transitions give good agreement with experiment (Table 9);

this makes it possible to use the calculated values of the energy for those complexes for which there are no experimental data. The energies of the *fd* transitions and their correlation with known oxidation potentials have been used to determine the oxidation potential E^0(IV–V) for californium, which indicated that californium(V) is stable.[80]

Table 8. Energies of the charge-transfer bands (10^{-3} E, cm^{-1}) for octahedral chloro-complexes $AnCl_6^{2-}$.

An	Pa	U	Np	Pu	Am	Cm	Cf
Theory (Ref.131)	46.07	38.70	34.30	28.00	22.60	12.60	22.10
Experiment (Ref.97)	—	39.00	33.10	27.90	—	—	—

Table 9. Energy of the *ff* electronic transitions (10^{-3} E, cm^{-1}).

$\Gamma_\mu - \Gamma_\nu$	Complex	$\Gamma_7 - \Gamma_8$	$\Gamma_7 - \Gamma_8'$	$\Gamma_7 - \Gamma_7'$
Theory (Ref.131)	$PaCl_6^{2-}$	8.410	7.260	5.650
Experiment (Ref.97)	$(NEt_4)_2PaCl_6$	8.011	7.022	5.330

4. Cationic Forms of the Highest Oxidation States of Uranium, Neptunium, and Plutonium

Since plutonium(VIII) is unstable as PuO_6^{4-},[107] the question of its possible existence as molecules or cations arises. The PuO_4 molecule with tetrahedral or square coordination of the ligands should have an even greater electron affinity than the oxyanion. The cationic form of high oxidation states of neptunium and plutonium, in particular NpO_2^{2+} and PuO_2^{3+}, have been regarded as realistic by a number of authors,[97] so that the existence of PuO_2^{4+} might also be assumed.

The change in the stability of the isoelectronic ions in the series PaO_2^+, UO_2^{2+}, NpO_2^{3+}, PuO_2^{4+} can be considered.[98] In the maximum overlap model, linear spatial coordination of the nuclei corresponds to either *fd* or *fs* hybridisation, and angular coordination corresponds to *ds* hybridisation. This means that if in the actinide ion An^{z+} in the electron configuration of the ground state there is a closely-lying *d* or *s* level, the dioxo-cation AnO_2^{z+} obtained will be stable in the linear coordination. The energies ε of the transfer of an *f*-electron from the ground state to the excited electron configuration of lowest energy can be compared for the isoelectronic ions Pa^+, U^{2+}, Np^{3+}, and Pu^{4+} (Table 10). For Pa^+, excitation into the electron configuration f^3d or f^3s requires a greater expenditure of energy than excitation into the configuration f^2ds, corresponding to an angular molecule.[20–22] The preference for angular coordination distinguishes the protactinium ion from other actinyl ions. For the U^{2+} ion, the electron configuration of the ground state is $f^3d(^5L_6)$. It coincides with the electron configuration of the U^{2+} ion in the uranyl group.[99,100] Thus the doubly-charged uranium ion is able to adopt linear coordination without the expenditure of energy on *fd* hybridisation and without the participation of inner 6*p* orbitals (Table 10).

Table 10. Excitation energies (10^{-3} E, cm^{-1}) for An^{z+} in AnO_2^{z+}.[98,107]

Electron configuration	PaO_2^+	UO_2^{2+}	NpO_2^{3+}	PuO_2^{4+}
f^3d	18.04	0.00	31.60	47.00
f^2ds	1.20	—	—	—
		UO_2^+	NpO_2^{2+}	PuO_2^{3+}
f^1d		12.50	4.10	44.00
f^2ds		0.289	41.00	—
			NpO_2^+	PuO_2^{2+}
f^2d			12.80	9.80
f^1ds			0.49	57.00

It is of interest to compare the geometry of the UO_2^{2+} ion with that of the MoO_2^{2+} or WO_2^{2+} ions. Thus for the doubly-charged molybdenum ion [ground state $d^4(^5D)$], the first excited state $d^3s(^5F)$ corresponds to angular coordination and $\varepsilon \cong 30000$ cm^{-1}, whereas the excited d^3p state corresponding to linear coordination, is higher, $\varepsilon \cong 75000$ cm^{-1}.[101] Thus the dioxo-cations of the transition elements and the corresponding actinides evidently have different geometries.

The electron configuration of the ground state of the triply-charged neptunium ion and the quadruply-charged plutonium ion is $f^4(^5I)$. The energy of excitation of an *f*-electron into the *d*-level is $(38 \pm 7) \times 10^3$ cm^{-1} for Np^{3+} and 47×10^3 cm^{-1} for Pu^{4+}.[20–22] This leads to the qualitative conclusion that for the isoelectronic linear actinyl ions UO_2^{2+}, NpO_2^{3+}, and PuO_2^{4+}, the stability decreases on going from uranium to plutonium. The high excitation energy and the high electron affinity, greater than for the PuO_6^{4-} oxyanion and the PuO_4 molecule, make the cationic form of plutonium PuO_2^{4+} unstable. The published range of values for the energy of excitation of Np^{3+} into the f^3d-state is fairly wide, however: 31×10^3 $cm^{-1} \leqslant \varepsilon \leqslant 45 \times 10^3$ cm^{-1}.[20,21] Attempts to measure this quantity have a long history. In 1960, Carnall and Cohen[102] found from the absorption spectra of Np^{3+} in 1 M $HClO_4$ that the value of ε ($f^4 \rightarrow f^3d$) lies in the range 31×10^3–43×10^3 cm^{-1}. In 1965, Marcus and Shiloh[103] detected in the absorption spectra of neptunium(III) in concentrated solutions two intense bands at 26040 cm^{-1} and 32050 cm^{-1}, which they assigned to the $f^4 \rightarrow f^3d$ electron transition. The absorption and emission spectra of single crystals of $LaCl_3$ containing $NpCl_3$ were obtained in 1967.[104] A large group of bands, assigned to *ff* transitions, was detected in the range 5000–25000 cm^{-1}, and it was concluded that the energy of the $f^4 \rightarrow f^3d$ transitions lies above 25000 cm^{-1}. Recently, Carnall and co-workers[105] recorded the low-temperature absorption spectrum of $NpCl_3$ and $NpBr_3$ in the range 3300–43000 cm^{-1}. The spectra of both compounds showed broad intense bands in the range 26000–32 000 cm^{-1}, assigned to *fd* transitions. Nugent and co-workers,[22] on the basis of a systematic treatment of low-lying electron configurations, calculated the energy of excitation into different electronic states of the actinides and their ions. According to their calculations,

the excitation energy of the $f^4 \rightarrow f^3d$ transition for Np^{3+} is 31600 cm^{-1}. Finally, Carnall, Fried, and Wagner,[106] on the basis of the recorded spectra of the triply-charged ions of the elements from U to Cf in matrices, concluded that the lowest energy of excitation into the f^3d state for Np^{3+} is 26000 cm^{-1}. For comparison, it may be noted that the excitation energy of the transition $f^7 \rightarrow f^6d$ for Am is 23.9×10^3 cm^{-1} [22] or $(24 \pm 3) \times 10^3$ cm^{-1}.[20,21] Since AmO_2^+ exists, although it is less stable than other doubly-charged actinyl ions, it might be thought that NpO_2^{3+} might exist. There are two factors, however, determining stability: the ratio of the energies of the AO of the central atom and the ligands and their degree of overlap. The present authors[107] calculated the radial wavefunctions and energies of the valence AO for An^{z+} ($z = 0-5$) using a relativistic version of the Hartree–Fock method, and obtained the following results.

1. For the doubly-charged ions of the elements of the first half of the actinide series, the energy of a 5*f* orbital lies in the range 15–20 eV, that is it is close to the energy of the 2*s* and 2*p* orbitals of the oxygen atom.
2. The energy of a 5*f* orbital of the triply-charged actinide ions is much lower than that of the 2*s* and 2*p* orbitals of the oxygen atom.
3. The overlap integrals of the valence AO of the triply-charged actinide ions with the AO of oxygen are small, since the 5*f* orbitals are greated contracted, and the 5*f* electrons tend to remain localised.

All this prevents the formation of a stable NpO_2^{3+} cation, not to mention PuO_2^{4+}, since with further increase in the charge, the 5*f* electrons are localised to an even greater extent.

The isoelectronic series UO_2^+, NpO_2^{2+}, and PuO_2^{3+} can be considered. It has been established experimentally[21] that for the singly-charged uranium ion the ground state is $f^3s^2(^4I_{9/2})$; its first excited state $f^3ds(^6L_{11/2})$ lies only 289 cm^{-1} above the ground state, that is it almost coincides with the ground state, but the next excited state $f^4s(^6I_{7/2})$ lies 4664 cm^{-1} above the ground state.[20-22]. The linear coordination of the nuclei in UO_2^+ can apparently be non-rigid under certain conditions; the main condition is a low effective charge on the uranium atom, not exceeding +1.5. It may be assumed that in compounds with a uranyl group containing uranium(VI) and donor ligands, which decrease the effective charge on the uranium atom, possible deviation from the linear structure is not excluded. The energies of the transition for the doubly-charged neptunium ion into excited states correspond to a stable state and linear coordination of the nuclei in NpO_2^{2+}. The plutonyl ion PuO_2^{3+} is unstable for the same reason as NpO_2^{3+}.

A noteworthy feature is that the cationic forms examined here are three-atom systems which do not have ligands (or solvent molecules) in the equatorial plane. Donor ligands, which increase the electron density on the central atom and decrease the effective charge, would lead to stabilisation of the triply-charged cationic forms.

In a number of experimental papers[108] it has been suggested that in acidic media, septavalent Np exists as the singly-charged cation NpO_3^+. It was of interest to use quantum-chemical ideas to examine different geometric forms of this cation and to estimate the possibility of its existence as an independent oxo-group.[109] The method used was the X_α scattered wave method in the model of touching spheres. The criterion for the central metal atom being chemically combined with the oxyger atoms surrounding it is the existence of a minimum on the potential energy curve. This is equivalent to the statement that in a certain range of interatomic distances there is a strictly determined set of filled molecular levels, determined by the symmetry point group of the molecule. Since the dependence of the total energy of a molecule on the interatomic distance cannot be determined reliably in the X_α method, the possibility of existence and the stability of the NpO_3^+ cation being considered was estimated from the viewpoint of the existence of the correct standard electronic structure.[109] Three geometric configurations of NpO_3^+ were examined:[109] a *T*-shaped structure with symmetry C_{2v}, a pyramidal structure with symmetry C_{3v}, and a planar triangular structure with symmetry D_{3h}. The calculation showed that NpO_3^+ cannot exist as an independent stable oxo-group of septavalent Np, in contrast to the analogous oxo-cations of the septavalent *d* transition metals, for which both the planar triangular configuration and the pyramidal configuration exist.

5. The Use of the Principle of Orbital Symmetry to Explain the Mechanism of Cation–Cation Interactions

After Woodward and Hoffmann had demonstrated the effectiveness of the application of the principle of orbital symmetry to explain reaction mechanisms in organic chemistry, this principle became a fundamental theoretical concept.[110] The present authors attempted to apply the principle of preservation of orbital symmetry to cation–cation reactions in the chemistry of the actinides.

It has been established that actinides(V) AnO_2^+, where An = U, Np, Pu, and Am, tend to react with various "active" cations, in particular UO_2^{2+}, Fe^{3+}, In^{3+}, and Th^{4+}.[110-115] A number of regular features have been established experimentally, and can be explained on the basis of quantum-chemical considerations: only actinyl ions containing actinides(V) tend to undergo cation–cation interaction (CCI); the PuO_2^{2+} ion, isoelectronic with NpO_2^+, does not react with UO_2^{2+} ions even in 3 M uranyl perchlorate solution; the degree of CCI of UO_2^{2+} with AnO_2^+ decreases with increase in the atomic number in the series: $UO_2^+ > NpO_2^+ > PuO_2^+ > AmO_2^+$; CCI between AnO_2^+ and active cations is accompanied by a change in the electronic absorption spectrum of AnO_2^+ and by the appearance of new bands; the interaction of NpO_2^{2+} with AnO_2^+ is weaker than for UO_2^{2+}; and the degree of CCI increases with decrease in the energy corresponding to the maximum of the charge-transfer band in the absorption spectrum of the aquo-complex of the active cation.[116] In the present review, a mechanism of CCI is proposed, and a quantum-chemical explanation is given for the experimental regular features.

In the symmetry point group $D_{\infty h}$, the 5*f* atomic orbitals of an actinide atom are split into σ_u, π_u, δ_u, and Φ_u orbitals, and the 6*d* orbitals are split into σ_g and π_g orbitals. Thus for UO_2^{2+}, which has 12 valence electrons, the electron configuration of the energy levels has the form $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\Phi_u\delta_u\pi_u^*\sigma_u^*$. This configuration is preserved in all other actinyl ions AnO_2^{z+}, but with different filling numbers for the non-bonding Φ_u and δ_u levels. In solution, actinyl ions have tetragonally distorted octahedral geometry $AnO_2L_4^{z+}$ (where L represents a ligand) with symmetry point group D_{4h}. Fig. 7 shows the form of the molecular orbitals and the correlation of the symmetry of the orbitals for both point groups. On going from the free ion AnO_2^{z+} to $AnO_2L_4^{z+}$, splitting of the Φ_u level takes place, and new orbitals are added, corresponding to the interaction of the actinide with the ligands L in the equatorial plane.

The reaction between UO_2^+ and UO_2^{2+} can be considered. This interaction takes place by the overlap of the occupied molecular orbitals of UO_2^+ with unoccupied orbitals of UO_2^{2+},

and conversely. To interact, these orbitals must have the same symmetry.[110] Molecular orbital calculations for octahedral complexes containing actinides(V) and actinides(VI), AnO_6^{7-} and AnO_6^{6-}, where An = U, Np, Pu, and Am, showed showed[117] that the last occupied molecular orbital has t_{1u} symmetry. For the point group D_{4h} this corresponds to the interaction of e_{2u} and a_{2u} orbitals, and for the symmetry group $D_{\infty h}$ it corresponds to the interaction of occupied σ_u orbitals and unoccupied or partly occupied δ_u orbitals. According to calculation,[100] the energy of the occupied σ_u orbital in UO_2^{2+} is −17.75 eV, whereas the energies of the unoccupied Φ_u and δ_u orbitals in UO_2^{2+} are lower and amount to −22.88 eV and −22.72 eV respectively. This important feature determines all the specific characteristics of the interaction of the ion-containing actinides(V) and actinides-(VI), since the occupied σ_u orbital in UO_2^+ will donate electron density to the unoccupied δ_u orbital in UO_2^{2+}. The analogous interaction between the UO_2^{2+} (σ_u^2) and UO_2^+ (δ_u) orbitals is energetically unfavourable, since the donor orbital in UO_2^{2+} is much lower than the acceptor orbital in UO_2^+.

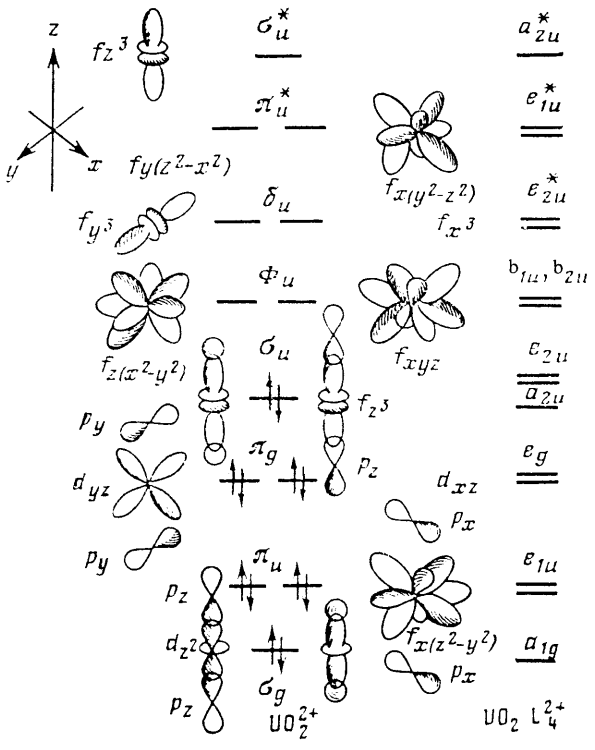


Figure 7. Qualitative energy level diagram for the uranyl ion. The change in the levels on formation of bonds with ligands L in the equatorial plane is shown on the right.[107]

This interaction scheme assumes that the ligand L in the equatorial plane is replaced, and that a U(VI)–O–U(V)–O bond is formed. The mechanism of the removal of L from $UO_2L_4^{2+}$ can be represented in terms of orbital symmetry theory.[110] Fig. 8*a* shows the symmetry of the intermediate state, which is obtained by the interaction of the antibonding orbital e_{2u}^* in $UO_2L_4^{2+}$ and the bonding orbital a_{2u} in $UO_2L_4^+$. The intermediate state symmetry requirements make necessary the rupture of the U(VI)–L bond and the formation of the U(VI)–O–U(V) bond, in which the oxygen atom of the actinyl ion containing the actinide(V) is the bridging atom. After the removal of the ligand L, the bridging oxygen atom will undergo a bonding interaction with both uranium atoms through both $f\sigma$ and $f\pi$ bonds (Fig. 8*b*).

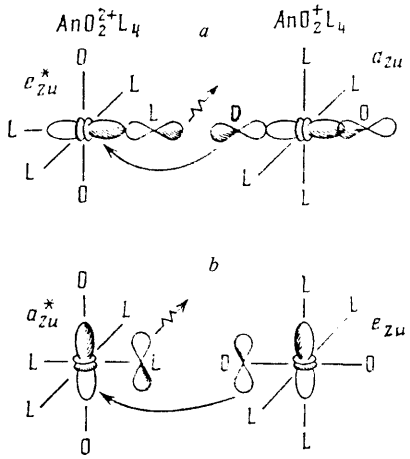


Figure 8. Interaction of the donor–acceptor type between unoccupied molecular orbitals of a uranyl complex containing uranium(VI) and the occupied orbitals of an actinyl complex containing an actinide(V):[107] *a*) σ-bond interaction, *b*) π-bond interaction.

Thus in the complexes AnO_2^+–UO_2^{2+}, the quantitative characteristic of CCI is the magnitude of the energy gap between the donor a_{2u} (or σ_u) and acceptor e_{2u}^* (or δ_u) orbitals, that is

$$E_{\sigma_u}(AnO_2^+) - E_{\delta_u}(UO_2^{2+}) = \Delta, \quad E_{a_{2u}} - E_{e_{2u}^*} = \Delta'$$

The greater Δ or Δ′, the more energetically favourable the cation–cation interaction of the donor–acceptor type. When Δ is negative, that is when the acceptor levels lie above the donor levels, CCI does not take place. On going from UO_2^+ to NpO_2^+, PuO_2^+, and AmO_2^+, the occupied σ_u^2 orbital is lowered, approaching the δ_u orbital of UO_2^{2+}, that is the magnitude of Δ decreases and the strength of the CCI decreases in the same direction.

This approach immediately explains why the PuO_2^{2+} ion, which is isoelectronic with NpO_2^+, does not react with the uranyl ion containing uranium(VI). Interaction between two UO_2^{2+} ions obviously does not take place, because $\Delta < 0$. The electron configuration of PuO^{2+} has the form $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2 \cdot \Phi_u^1\delta_u^1$. The donor level σ_u^2 in PuO_2^{2+} lies even lower than in UO_2^{2+}, and $\Delta < 0$, while $|\Delta_{PuO_2^{2+}-UO_2^{2+}}| > |\Delta_{UO_2^{2+}-UO_2^{2+}}|$, that is the UO_2^{2+}–PuO_2^{2+} interaction is even less favourable than UO_2^{2+}–UO_2^{2+}. The fact that PuO_2^{2+} and NpO_2^+ are isoelectronic does not lead to reaction, since the two *f* electrons

above the occupied "core" cloud, situated in the Φ_u and δ_u orbitals, do not interact with UO_2^{2+}, and from symmetry considerations remain non-bonding. In PuO_2^{2+}, the acceptor levels δ_u and Φ_u each contain one unpaired electron, and although these levels, as in UO_2^{2+}, are lower than the donor levels σ_u^2 in AnO_2^+, their ability to attract electron density from the O atom is lower, because of electron–electron repulsion. Thus the actinyl ions NpO_2^{2+} and PuO_2^{2+} containing actinides(VI) interact with AnO_2^+ less strongly than UO_2^{2+}. The mechanism of formation of the dimeric cation–cation complex $(NpO_2^+)^2$ ($\Delta = 0$) is fundamentally different, and involves mainly covalent interaction. Complex formation between AnO_2^{2+} and AnO_2^+ involves the modification of all the molecular orbitals in AnO_2^+. If the bond An(VI)–O with the bridging atom is sufficiently strong, the change involves both the core bonding levels and the antibonding levels of the *f* type. The change in the latter can be considered for the case of the dinuclear system UO_2^{2+}–NpO_2^+. Complex formation leads to practically no change in the positions of the b_{1u} and b_{2u} levels. Thus the ligands L take part in the formation of σ-bonds, so that the b_{2u} orbital will be non-bonding, and the b_{1u} orbital remains non-bonding from symmetry considerations. The positions of the subsequent e^*_{2u}, e^*_{1u}, and a^*_{2u} levels is influenced primarily by the non-equivalence of the Np(V)–O bonds in NpO_2^+. The internuclear distance to the bridging oxygen atom increases, the lengths of the equatorial bonds also increase, and the bond Np(V)–O with the terminal oxygen atom becomes shorter. These changes are due to the specific manifestation of the *trans*-effect in the actinides,[59,118,119] which is the opposite of the *trans*-effect in the transition elements. As a result, the energy of the e^*_{2u} level corresponding to $f\sigma$ interaction of Np(V) with the ligands of the equatorial plane, increases. The energy of the level $\sigma_u = f_z^3 + \phi_1 + \phi_2$ decreases, since one ϕ_2 orbital will correspond to interaction with a terminal oxygen atom, and the other will correspond to interaction with a bridging oxygen atom. The influence of these effects on the position of a level of the $f\pi$ type is less than that for the $f\sigma$ type, so that the splitting of the e^*_{1u} molecular orbital is slight, although its energy should decrease as a result of the decrease in the strength of the bond with the bridging oxygen atom. These changes influence the transitions of the *ff* type (Fig. 9). When the published interpretation[89] of the electronic absorption spectrum of NpO_2^+ is taken into account, it must be concluded that the main transitions take place from the non-bonding Φ_u and δ_u levels into the antibonding π^*_u and σ^*_u orbitals. The lowering of the e^*_{1u} level leads to a displacement of the most intense band with energy $\nu = 10\,200$ cm^{-1} towards the red range of the spectrum, and the splitting of the e^*_{1u} and e^*_{2u} levels leads to the appearance of a new band in the energy range 12000–13 000 cm^{-1}. This qualitative picture becomes much more complicated when allowance is made for the effect of spin–orbit coupling.

In the electronic spectrum of the combined UO_2^{2+} complex, the modification involves mainly charge-transfer bands. The absorption spectrum of the combined NpO_2^+ complex shows additional absorption bands, not related to *ff* transitions, since splitting of various levels takes place in the system of core orbitals, leading to a lowering of the symmetry of the complex from D_{4h} to C_{4v}.

According to this mechanism of CCI, the extent of this interaction should correlate with a number of parameters. It has already been noted that in the interaction UO_2^{2+}–AnO_2^+, where An = U, Np, Pu, and Am, the magnitude of the energy gap determines the degree of interaction. For the values of Δ, the position of the unoccupied $\sigma_u(UO_2^{2+})$ level can be used as the starting point for the measurement, so that the energy of the σ_u level in AnO_2^+ will be the principal determining parameter. The lower the energy of this level, the smaller the negative charge on the oxygen atoms, and the lower the degree of cation–cation interaction. At the same time, the lower the energy of this level, the smaller (for $\Delta > 0$) the magnitude of Δ, and the degree of CCI decreases. In the actinyl ions containing actinides(V), the effective negative charge on the oxygen atoms decreases on going from UO_2^+ to AmO_2^+. According to a published calculation[9] the electron density distribution in UO_2^+ is as follows: O(−0.915)–U(+2.83)–O(−0.915). According to calculations carried out by the present authors[120] for the octahedral oxyanions of the highest oxidation states AnO_6^{7-} or AnO_6^{6-}, where An = U–Am, with increase in the atomic number of An, the magnitude of the negative charge decreases by approximately 0.02–0.05 *e* on each oxygen atom.[120] It may be assumed[117] that in the americyl ion containing americium(V), the electron density distribution has the form: O(−0.8)–Am(+2.6)–O(−0.8).

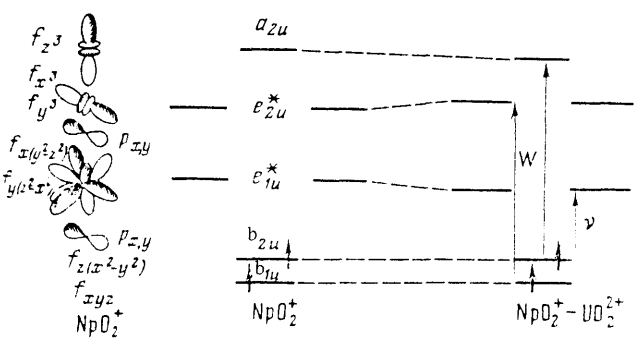


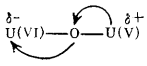
Figure 9. Splitting of the energy levels of the *f*-type in the cation–cation interaction in NpO_2^+.[107]

Thus the chemical ideas based on the electron density distribution[115] and the theoretical molecular orbital ideas about CCI coincide. The presence of an effective negative charge on the oxygen atoms in AnO_2^+ is an insufficient condition for CCI, however. In the actinyl ions AnO_2^{2+} containing actinides(VI), the oxygen atoms again have a fairly high negative charge, O(−0.27)–U(+2.54)–O(−0.27) [100] [or O(−0.3)–U(+2.6)–O(−0.3) [99]], which might have led to the transfer of electron density to the U(VI) atom and the formation of the dinuclear system ...U(VI)–O–U(VI)... The presence of an excess of negative charge on an oxygen atom of one of the actinyl ions also does not lead to interaction; thus on the basis of effective charges alone, CCI might have been expected between O(−0.3)–U(+2.6)–O(−0.3) and O(−0.1)–Am(+2.2)–O(0.1) when the uranyl ion is a ligand relative to the americyl ion. Since this interaction has not been detected experimentally, it must be assumed that the charge should be not only negative or in excess in one cation compared with the other, but that it must ensure an energetically favourable arrangement of the donor and acceptor levels σ_u and δ_u.

The degree of cation–cation interaction should correlate with other parameters in addition to the effective charges. The degree of cation–cation interaction increases with

decrease in the energy corresponding to the charge-transfer band in the aquo-complexes of the active cations.[116] Thus in the series $E_{UO_2^{2+}} < E_{Fe^{3+}} < E_{In^{3+}} < E_{Th^{4+}}$, where E is the energy of the charge-transfer band, the degree of CCI increases in the opposite direction. Thus the quantity E in the aquo-complexes is defined as $E = E_L - E^*$, where E_L is the energy of the ligand level L in ML_6^{2-} or $AnO_2L_4^{2+}$, and E^* is the energy of the orbitals of the central atom. In UO_2^{2+}, the energy E^* corresponds to the position of the acceptor level. If E_L is assumed to be approximately constant in all the complexes, the energy of the charge-transfer band will depend on the position of the level E^*, which also determines the degree of CCI: the lower this level, the lower the energy of the charge-transfer band and the greater the degree of CCI. The nature of the solvent should have a definite influence on the CCI, since the position of the levels of the central atom in the active cations depends on the interaction with solvent molecules.

Since the position of the donor level σ_u in AnO_2^+ determines to some extent the energy of the charge-transfer band in AnO_2^+ and the potential E^0(V–VI), a qualitative correlation should be observed between the degree of CCI and these quantities. The correlation can be only qualitative, since these quantities also depend on the position of the f-levels, which in AnO_2^+ have no significant influence on the CCI. A correlation between the degree of CCI and the oxidation potentials E^0(V–VI) [116] in the AnO_2^+–AnO_2^{2+} system is apparently justified, since the transfer of electron density δ in the complex (A)



corresponds to the partial reduction of the actinide(VI) atom.

In conclusion it may be noted that the position of the ions containing actinides(V) does not appear exceptional from the viewpoint of CCI. Cation–cation interaction takes place if the energy of an unoccupied acceptor orbital in one system is lower than the energy of a donor orbital in the other system, and the acceptor orbital is predominantly an orbital of the central atom. This situation may arise not only between cations, although if the acceptor system is a cation, it is known that the first unoccupied level is fairly low.

One of the criteria for the existence of CCI in complexes with identical central atoms M is apparently the ability of M to form mixed-valence compounds. Essentially, PtF_3 or $CsAuCl_3$, which in the crystalline state are made up of M(II)–M(IV) and M(I)–M(III) ions, to some extent model CCI in a crystal. About 40 elements in Mendeleev's periodic system form mixed-valence compounds,[121] in many of which an ordered arrangement of the cations with different oxidation states is produced below the critical temperature or pressure.[122] The established[123–127] criterion for the existence of a charge-ordered state $I - 2mV < 0$, where I is the energy of the one-centre electron repulsion, V the energy of the electron repulsion between centres, and m the number of nearest neighbours, also determines the stability of the cation–cation complex: in a complex of type (A), the electron–hole attraction $-2V\delta$ should be greater than the electron repulsion $I\delta$.

It can apparently be assumed that other types of cation–cation interaction will be found among the transition elements, among the actinides, and between them. If triply-charged AnO_2^{3+} cations existed, they would interact with AnO_2^{2+} according to the same regular features as AnO_2^{2+} with AnO_2^+. Three model systems with the same geometry can be considered: UO_2^{2+}, UO_2^+, and UO_2. The UO_2^{2+}–UO_2 interaction is most favourable, since for this interaction, $\Delta = 12.8$ eV;[100] the presence of two f electrons has no influence on the interaction, since in UO_2 they remain non-bonding. In the UO_2^+–UO_2 interaction, the acceptor level in UO_2^+ is partly occupied; thus the cation–cation interaction UO_2^+–UO_2 would be weaker than UO_2^{2+}–UO_2.

In the molecules of the same type UF_6, NpF_6, and PuF_6, the acceptor level in UF_6 is higher than the ligand levels in NpF_6 and PuF_6.[128] Comparison of the positions of the levels in UF_6 and UF_6^- shows, however, that the unoccupied acceptor level in UF_6 is lower than the donor level of the same symmetry in UF_6^-.[85]

6. The *trans*-Effect in the Chemistry of the Actinides

The specific features of the *trans*-effect in the chemistry of the actinides has recently attracted the attention of a number of workers.[59,118,129] Thus *trans*- and *cis*-configurations have been detected in $Cs_2UO_2Cl_4$ and $Cs_2WO_2Cl_4$ respectively. This difference was first explained[59] using the maximum overlap model. Other workers[118,129] raised the question of the fundamental difference in the *trans*-effects in $MoCl_5^-$, where M = Mo, or W, and in $UOCl_5$ (Fig. 10). The *trans*-effect observed in the uranium compounds is the direct opposite of the *trans*-effect in the analogous transition metal complexes: in the first compounds, the metal–halogen *trans*-bond is longer than the equatorial bonds, whereas in the second case the uranium–halogen *trans*-bond is shorter than the equatorial bonds.

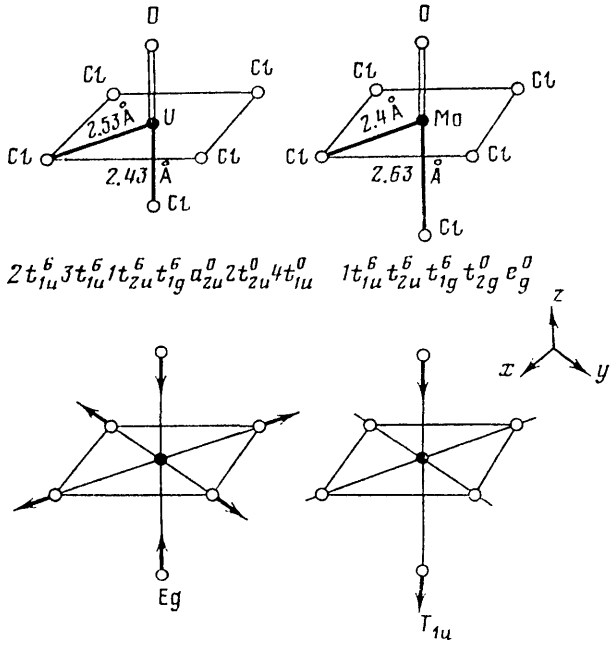


Figure 10. Comparison of the *trans*-effects in compounds of the same type formed by actinide and transition elements.[59]

Systematic MO calculations carried out by the present authors[117,119,131,132] make it possible to explain this fundamental difference using the electronic–vibrational

model of heteroligand inorganic complexes.[129] The energy of the substituted and deformed complex is represented in the form of a series with respect to powers of the normal coordinates q_ν characterising the deformation. If the energy of the non-substituted complex in the equilibrium configuration is taken as the zeroth term of the expansion, the expansion will contain a term which is linear with respect to q_ν and which leads to a change in the geometry of the non-substituted complex. In the MO method, the energy component linear with respect to q_ν has the form:[129]

$$E = 4 \sum_{\nu,o,u} \frac{\langle \psi_o H \psi_u \rangle \left\langle \psi_o \left| \frac{\partial H}{\partial q_\nu} \right| \psi_u \right\rangle}{\Delta_{ou}} q_\nu \quad \text{or} \quad E = kq_\nu$$

Here, ψ_o and ψ_u are the wavefunctions of the occupied and unoccupied MO respectively, Δ the magnitude of the energy gap between these MO, and H the one-electron substitution operator.

The main qualitative difference between actinide complexes and transition metal complexes of the same type is the difference in the sequence of the MO (see Fig. 10). As a result, the active mode leading to distortion will be a mode of E_g symmetry in the actinide complexes, and a mode of T_{1u} symmetry in the complexes of d transition elements. Using calculations for oxygen compounds, in particular UO_6^{6-}, it can be shown that the coefficient k in the expression for E is greater than zero in those cases where the $1t_{2u}$ and $2t_{2u}$ molecular orbitals mix as a result of the influence of the vibrational mode E_g. This means that when four substituents are introduced into UO_6^{6-} along the x and y axes, that is $UO_2L_4^{n-}$, the decrease in the total energy corresponds to $q_\nu < 0$, or in Cartesian coordinates: $q_\nu = 1/\sqrt{12}\ (2z_1 - 2z_4 - x_2 + x_5 - y_3 + y_6)$. A negative value for q_ν corresponds to an increase in the length of the equatorial bonds and a decrease in the length of the axial bonds.

This conclusion is confirmed by X-ray diffraction data for compounds containing the uranyl group. In UO_6^{6-}, the U–O distance is 2.08 Å, and in $UO_2L_4^{n-}$ this distance is 1.7–1.8 Å, whereas the U–L distances are much greater than 2.08 Å, for molecules with different ligands: NO_3^-, H_2O, $(Et_2ONCO)^-$, $MeCOO^-$, CO_3^{2-}.[133] Using the same approach in an examination of mono-substituted $UOCl_5^-$, the present authors took UCl_6 as a basis and obtained an increase in the length of the equatorial internuclear distances U–Cl compared with the U–Cl *trans*-bond.[59] In the d^0 complexes of molybdenum and tungsten, the last occupied t_{1u} and t_{2u} orbitals are mixed with the unoccupied t_{2g} orbital by a vibrational mode of symmetry T_{1u}, leading to the opposite change in the distances. In systems with the electron configuration f^n, the *trans*-effect should decrease with increase in the number of f-electrons. For those complexes for which the f-levels are occupied, the *trans*-effect should be the same as in compounds of the d-elements. In complexes with partly occupied f-levels, both vibrational modes may be active, so that the resulting effect may be extinguished.

IV. INFLUENCE OF RELATIVISTIC EFFECTS ON THE PROPERTIES OF THE COMPOUNDS OF THE HEAVY ELEMENTS

It is only in recent years that objective conditions have been created for studying the influence of the relativistic effect on the properties of the compounds of the heavy elements. A stimulus for this study was provided by the development of calculation methods and computing techniques, and also the practical interest in compounds of the heavy elements. It has been suggested[134,135] that the main anomalies in the second half of Mendeleev's table are due to the relativistic effect. These anomalies are the unique properties of gold compared with copper and silver, and of mercury compared with cadmium and zinc, the lanthanide contraction, the inert pair effect, the unique properties of the 6+ oxidation state of uranium, neptunium, and plutonium, the influence of spin–orbit coupling on magnetic properties, for example in Os(VI) compounds, the tendency towards stabilisation of the oxidation states from III to I in the indium subgroup and from IV to II in the carbon subgroup on going to the heavy elements, etc.

When it becomes necessary to take account of a given effect, attempts to explain many regular chemical features on the basis of this effect appear quite natural. This was the case, for example, with the excited *nd* orbitals of the atoms of phosphorus, sulphur, chlorine, and xenon. It was later found that the part played by *nd* orbitals for the atoms of these elements had been greatly overestimated.

Another outstanding example relates to the problem of the localisation and delocalisation of electrons. The extensive application of MO methods in calculations for molecules and the zone scheme for the solid state has practically displaced calculation schemes in which account is taken of localised states. A step back has now been taken, and the Heitler–London scheme is again beginning to be used.

The part played by relativistic effects is undoubtedly important, but it apparently should not be overestimated. In the discussion of the influence of relativistic effects on the properties of the heavy elements, it seems appropriate to distinguish three cases, where the relativistic effect: 1) completely determines the property or feature; 2) increases its strength; and 3) acts in a direction opposite to the orbital effect. In the properties of the heavy elements, the relativistic effect appears through the relativistic contraction of the $s_{1/2}$ and $p_{1/2}$ clouds, spin–orbit splitting, and destabilisation of d- and f-electrons.[134] The first effect is due to the fact that the mass of an electron depends on its velocity, the second is due to the splitting of the energy levels corresponding to the quantum numbers j, and the third is due to the high values of the angular momenta of the d- and f-electrons, the weaker attraction to the nuclei, and the more diffuse character. These effects lead to the high stability of the uranyl ion and the sexavalent forms of uranium, neptunium, and plutonium.[135]

Generally speaking, the high stability of the uranyl ion is also explained within the framework of the simple MO method, since this system contains 12 valence electrons, which occupy all the bonding MO, and the antibonding orbitals remain unoccupied. In the series of U(VI) compounds there are stable and less stable systems: on going along the series UO_4^{2-}, UO_6^{6-}, UO_2^{2+}, the stability increases, although the relativistic contraction of the 7*s* orbital and the opening of the 5*f* orbitals are everywhere the same. The properties of the compounds of U, Np, and Pu in the 6+ oxidation state can also be explained within the framework of relativistic approximations, that is they do not belong to those "specific" properties which cannot be understood even qualitatively without allowance for relativistic effects.

The influence of the relativistic spin–orbit effect on the stability of lanthanides and actinides in the 2+, 3+, and 4+ oxidation states and the tendency to form mixed-valence compounds and new oxidation states has been examined.[95,96,136,137] It was shown above that the oxidation potentials correlate with the excitation energy $E(f^n \rightarrow f^{n-1}d)$: a

high excitation energy "hinders" the oxidation, and the ion remains in the original configuration f^n, and a low excitation energy facilitates oxidation and the change to the state with the electron configuration $f^{n-1}d$. Thus a high spin–orbit splitting energy, E_{so}, in the f^n electron configuration, which brings the f^n and f^{n-1} electronic states "closer together", increases the tendency for the oxidation state to increase.

Table 11 gives the values of E_{so} and E_{fd} for the f^n electron configuration of the doubly-charged actinides. For uranium and neptunium, $E_{so} > E_{fd}$, so that the excited f^{n-1} states overlap with the terms of the f^n states. This leads to unstable bivalent forms for uranium and neptunium. For plutonium, the bivalent state is more stable, since for it, $E_{so} < E_{fd}$. For americium, $E_{so} \ll E_{fd}$, and the stability of the bivalent form reaches a maximum value in the first half of the actinide series. For curium, as for uranium and neptunium, $E_{so} > E_{fd}$, so that the bivalent state is unstable. For berkelium, $E_{so} \cong E_{fd}$, which corresponds to an increase in the stability of the bivalent form. For californium, $E_{so} < E_{fd}$, and for einsteinium, fermium, mendelevium, and nobelium, as a result of the decrease in E_{so} and the increase in E_{fd}, this inequality is preserved and increases. This leads to an increase in the stability of the bivalent state in the second half of the actinide series.

Table 11. Energies E_{so} and E_{fd} and the oxidation potentials E^0(II–III).[137]

An	n	Term	$10^{-3}E_{so}$, cm^{-1} (Ref.24)	$10^{-3}E_{fd}$, cm^{-1} (Ref.96)	E^0(II-III), V (Ref.58)
U	4	$^5I_{4-8}$	14.27	0.00	4.7
Np	5	$^6H_{5/2-15/2}$	13.74	4.10	4.7
Pu	6	$^7F_{0-6}$	9.87	13.70	3.5
Am	7	$^8S_0$	0.00	23.90	2.3
Cm	8	$^7F_{6-0}$	12.24	7.10	4.4
Bk	9	$^6H_{15/2-5/2}$	19.76	18.90	2.8
Cf	10	$^5I_{8-4}$	24.84	27.80	1.6
Es	11	$^4I_{15/2-11/2}$	21.71	30.20	1.3
Fm	12	$^3H_{6-4}$	15.25	40.10	1.1

Table 12. Energies E_{so} and E_{fd} and the oxidation potentials E^0(II–III).[137]

Ln	n	Term	$10^{-3}E_{so}$, cm^{-1}	$10^{-3}E_{fd}$, cm^{-1}	E^0(II-III), V
Nd	4	$^5I_{4-8}$	6.305	13.88	2.6
Pm	5	$^6H_{5/2-15/2}$	6.189	14.85	2.6
Sm	6	$^7F_{0-6}$	4.540	23.48	1.6
Eu	7	$^8S_0$	0.000	34.62	0.3
Gd	8	$^7F_{6-0}$	5.789	−2.19	3.9
Tb	9	$^6H_{15/2-5/2}$	10.208	8.97	3.7
Dy	10	$^5I_{8-4}$	13.497	17.52	2.6
Ho	11	$^4I_{15/2-11/2}$	15.035	16.87	2.9
Er	12	$^3H_{6-4}$	10.313	15.80	3.1

The stabilities of Ln(II) and Ln(III) can be compared analogously (Table 12). The successive decrease in E_{so} in the first half of the series and the increase in E_{fd} indicate gradual stabilisation of the bivalent state. This approach makes it possible not only to understand the regular features of the change in the oxidation potentials but also to answer the question of why they have different absolute values for corresponding lanthanides and actinides. Thus in the first halves of the series (U–Am and Nd–Eu), the relationship $E^0(\text{II–III})_{Ln} < E^0(\text{II–III})_{An}$ is preserved. For neodymium and promethium, $E_{so} < E_{fd}$, whereas for uranium and neptunium, $E_{so} > E_{fd}$. The difference $E_{fd} - E_{so}$ is much smaller for plutonium than for samarium, and E_{fd}(Am) < E_{fd}(Gd).

In the second half of the actinide series, gradual stabilisation of the bivalent states takes place, whereas in the second half of the lanthanide series this regular feature is not observed, the break in the trend taking place at holmium. Comparison of holmium and einsteinium shows a vast difference: for holmium, $E_{so} \cong E_{fd}$, whereas for einsteinium, $E_{fd} - E_{so} \cong 10000$ cm^{-1}. Similarly, for fermium, $E_{fd} - E_{so} \cong 25000$ cm^{-1}, whereas for erbium this quantity is ~5000 cm^{-1}. This difference is responsible for the difference in the oxidation potentials E^0(II–III) for the lanthanides and actinides. In addition to the difference in the oxidation potentials, this leads to the situation where states with mixed oxidation numbers are not observed in the second half of the actinide series, whereas at the end of the lanthanide series, thulium shows mixed oxidation states Tm(II)–Tm(III) in many compounds.

Table 13. Energies E_{so} and E_{fd} for the triply-charged lanthanides and the oxidation potentials E^0(III–IV).[137]

An	$10^{-3}E_{so}$, cm^{-1} (Ref.24)	E^0(III-IV), V (Ref.58)	$10^{-3}E_{fd}$, cm^{-1} (Ref.22)	Term	$10^{-3}E_{fd}$, cm^{-1} (Ref.22)	E^0(III-IV), V (Ref.58)	$10^{-3}E_{so}$, cm^{-1} (Ref.24)
Th	11.000	3.7	—	^2F	49.4	−1.8	—
Pa	11.482	2.00	26.7	$^3H_{4-6}$	61.3	−3.4	5.054
U	15.541	−0.63	27.1	$^4I_{9/2-15/2}$	70.4	−4.6	6.953
Np	17.552	−0.15	31.6	$^5I_{4-8}$	71.6	−4.9	7.982
Pu	16.625	−0.97	35.6	$^6H_{5/2-15/2}$	72.5	−5.2	7.687
Am	11.770	−2.34	45.0	$^7F_{0-6}$	81.0	−6.4	5.542
Cm	0	−3.1	55.1	$^8S_0$	92.0	−7.9	0
Bk	14.305	−1.64	38.3	$^7F_{6-0}$	55.1	−3.3	6.966
Cf	22.424	−3.2	50.0	$^6H_{15/2-5/2}$	66.6	−5.0	12.181
Es	27.466	−4.5	58.8	$^5I_{8-4}$	74.6	−6.2	15.979
Fm	24.850	−4.9	61.1	$^4I_{15/2-11/2}$	73.9	−6.1	17.678
Md	17.358	−5.4	63.0	$^3H_{6-4}$	72.7	−6.7	11.359

For the triply-charged ions of the lanthanide series, E_{fd} is much greater than E_{so}, so that the energy of spin–orbit splitting should not have a significant influence on the oxidation potentials (Table 13). The situation is completely different in the actinides: for protactinium, E_{so} is close to E_{fd}; for uranium, $E_{fd} > E_{so}$, but they are similar; for Np and Pu, E_{fd} increases slowly, and at the same time E_{so} also changes little. This corresponds to gradual destabilisation of the 4+ oxidation state. On going to curium, E_{so} decreases, and E_{fd} increases sharply, leading to a further decrease in the potential E^0(III–IV). As a result of the decrease in E_{fd} and the increase in E_{so}, the 4+ oxidation state is more stable for berkelium than for curium and americium. E_{fd} for californium is intermediate between the values for Am and Cm, but E_{so} is much larger than for

these elements. The absolute magnitude of the potential E^0(III–IV) for californium should apparently be less than 3.2 V.

The magnitude of the spin–orbit splitting of the ground state term of the f^n electron configuration can be related to the stability and geometry of the actinyl groups. It was shown above that if an actinide ion An^{z+} has closely-situated *d*- or *s*-levels, the resulting dioxo-cation will be stable for linear coordination of the nuclei. A high value of E_{so} for An^{2+} corresponds to stability of the linear AnO_2^{2+} system. On going from U^{2+} to Am^{2+}, both effects, orbital and relativistic, act in the same direction: E_{so} decreases, and E_{fd} increases, that is the stability of the actinyl groups decreases. For doubly-charged uranium, the most favourable situation is created for the formation of the dioxo-cation: $E_{fd} = 0$, and E_{so} is greater than for Np, Pu, Am, and Cm. UO_2^{2+} does not contain antibonding electrons. All this together determines the stability of the uranyl group. Beginning from NpO_2^{2+}, the number of antibonding electrons increases, so that CmO_2^{2+} should have the electron configuration $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\Phi_u^4\delta_u\pi_u\sigma_u$, when the antibonding Φ_u level is completely occupied. In CmO_2^{2+}, however, the antibonding effect due to the four electrons in the Φ_u level is to some extent quenched by the marked spin–orbit effect and the small expenditure of energy in *fd* hybridisation, so that the CmO_2^{2+} cation is stable.

A comparative analysis of E_{so} and E_{fd} helps to explain why lanthanyl groups are not obtained. For doubly-charged neodymium, promethium, and samarium, the values of E_{so} are small, and $E_{fd} > E_{so}$, whereas for their analogues uranium, neptunium, and plutonium, on the contrary, $E_{fd} < E_{so}$. The values of E_{so} and E_{fd} are similar only at the end of the lanthanide series (Gd, Tb, Ho, Er). Although in the lanthanyl groups of these elements after gadolinium the next antibonding level δ_u is occupied, decreasing the strength of the bond, the decrease in strength should be less than that for their actinide analogues, since the crystal field splitting for the 4*f* levels is less than that for the 5*f* levels. In any case, the formation of lanthanyl groups in the second half of the lanthanide series cannot be regarded as impossible.

Thus on the basis of a scheme taking account of the relativistic splitting of the f^n electron configuration and the excitation energy E_{fd}, it is possible to explain a number of important regular features of the electronic structure of the lanthanides and actinides: the gradual stabilisation of the bivalent state in the first half of the lanthanide series and in the second half of the actinide series; the absence of gradual stabilisation of the bivalent state in the second half of the lanthanide series; the marked difference in the oxidation potentials E^0(II–III) in the first halves of the lanthanide and actinide series; the formation of states with mixed valence at the end of the lanthanide series, and the absence of these states at the end of the actinide series; the fundamental difference in the stability of the 4+ oxidation state for the actinides and lanthanides; and possible stabilisation of lanthanyl groups at the end of the series.

In all cases examined, the two effects act in the same direction. The relativistic effect is greater for the lower oxidation states E^0(II–III), since the values of E_{so} and E_{fd} are comparable. The two effects separately give qualitatively the change in the oxidation potentials, but the orbital effect also gives the quantitative relationship. It can apparently be stated that the relativistic effect does not determine the regular features, although it makes a significant contribution to the quantitative characteristics. The influence of the relativistic effect on the states of atoms in higher oxidation states is weakened, since the orbital effect suppresses the relativistic effect, particularly for the tervalent lanthanides. For the actinides, however, the relativistic effect may be significant in the estimation of the oxidation potentials E^0(III–IV), as clearly confirmed for californium.

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Thus quantum chemistry is finding the most varied applications in the study of the electronic structure and properties of the actinides, from the prediction of the possibility of existence of unusual oxidation states to the explanation of reaction mechanisms. In spite of considerable progress, however, many unsolved problems remain, particularly in the study of unique oxidation states in the second half of the actinide series, where experimental studies are made difficult by the high radioactivity and the difficulty of obtaining the elements.

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