# Chemical Theory

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# Progress in heavy-element research: results from relativistic quantum theory

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The production of the heaviest elements was recently marked with new achievements: longer lived isotopes of elements 112 and 114 suitable for chemical investigations were produced in hot-fusion reactions [1]. This allowed for the first successful chemical identification of element 112 as a homolog of Hg with the use of the gas-phase chromatography technique [2,3]. Around the same time, elements 107 and 108 were chemically identified by studying volatility of their compounds with oxygen and chlorine [4,5] using the same approach. New experiments were conducted on aqueous chemistry separations of element 104 [6].

Traditionally, theoretical assistance was rendered to all those important experimental works: detailed predictions of the experimental behavior had been made on the basis of relativistic atomic and molecular calculations, as well as various physico-chemical models. In its turn, the relativistic quantum theory has further developed with respect to the accuracy of the calculated properties, as well as it moved to the description of various new systems of the heaviest elements not yet studied experimentally. Accurate calculations were performed for atoms till Z=122, molecules till Z=118 and very recently for the heaviest atoms interacting with metal clusters with the use of the best available modern quantum-chemical codes. A study of relativistic effects on the electronic structure and properties of these heaviest elements has been an indispensable aspect of those theoretical works. Results of the recent theoretical investigations of the electronic structures and properties of the heaviest elements and their homologs are overviewed in the presentation. A special attention is paid to the predictive power of those theoretical works for chemical experiments.

*Atomic calculations*. Electronic configurations have accurately been defined for elements up to Z=122 with the use of the Dirac-Fock-Breit Coupled Cluster Single Double excitations (DFB CCSD) method [7]. The multiconfiguration DF (MCDF) calculations for the ground and excited states were performed for elements 104 through 108 [8]. Both types of the calculations have shown that the relativistic stabilization of the 7s electrons of the transactinides results in the stability of the $7s^2$ electron pair in the ground and first ionized state over the entire $7^{th}$ row of the Periodic Table, which is different from the states of some elements of the $6^{th}$ row. The relativistic stabilization of the 8p electrons manifests itself in some ground states different than those of the lighter homologs: for example, the $8s^28p$ state of element 121 differs from the $8s^27d$ state of the lighter group-3 homologues, or the $8s^27d8p$ ground state of element 122 differs from the $7s^26d^2$ state of Th. These new DF CCSD results are in agreement with the old single-configuration DF and Dirac-Slater (DS) results of [9].

Ionization potentials (IP) were accurately defined by the DF CCSD calculations for elements up to Z=115, and 119 through 122. Multiple IPs were calculated using the MCDF method for elements 104 through 108 [8]. These calculations have shown the multiple IP to decrease within the transition element groups. The reason for that is the proximity of the relativistic valence 7s and 6d levels. This makes excitation energies of the 6d elements smaller than those of the lighter 4d and 5d homologues, resulting in an enhanced stability of the maximum oxidation states. Due to the same reason lower oxidation states at the beginning of the 6d series will be unstable.

Ionic radii (IR) of elements 104 through 108 have been defined on the basis of the MCDF calculations [8]. The values indicate that for the elements in the maximum oxidation state the IR of the transactinides

are about 0.05 – 0.06 Å larger than the IR of the lighter 5d homologs. The IR of the lighter 6d elements are, however, smaller than the IR of the actinides, since the latter undergo the actinide contraction of 0.030 Å which is mostly a relativistic effect. The calculated radii of the radial charge density $R_{max}$ show that the maximum of the relativistic 7s orbital contraction falls on element 112.

*Molecular calculations*. Relativistic calculations have by now been performed for all the compounds of the heaviest elements studied experimentally. Two recent works on predictions of the electronic structure and volatility should be mentioned: on $MO_3Cl$ (M=Tc, Re and Bh) [10] and $MO_4$ (M=Ru, Os and Hs) [11]. In those papers, volatility was predicted for specific gas-phase experiments on the basis of the fully relativistic (four-component) density function theory (DFT) calculations with the use of the physisorption models. It was shown that the volatility of the $MO_3Cl$ species should change as Re > Tc > Bh due to increasing dipole moments in this row. The calculations for the group-8 tetroxides have shown that $HsO_4$ should be very similar in its electronic structure and properties to $OsO_4$. On the basis of these calculations using models of physisorption it was predicted that $OsO_4$ and $HsO_4$ should have similar adsorption enthalpies on a quartz surface of the chromatography column. Using thermodynamic models of adsorption, the temperature of the deposition of $HsO_4$ on the quartz surface was predicted to be slightly above that of $OsO_4$ [12]. Experiments [4] have confirmed the predicted behavior of the group-7 oxychlorides on adsorption, while they disagreed in the $T_{ads}$ for the group-8 tetroxides [5]. The analysis of this disagreement will be given in the talk.

Due to the importance of experiments with element 112, predictions of its experimental behavior have been of a particular value. Early predictions of volatility were made via extrapolations over the lighter homologs in group 12 [13-15]. Predictions of adsorption behavior of element 112 on various metal surfaces from the electronic structure calculations have been of a particular importance. Recently, calculations of intermetallic compounds of element 112 and Hg (HgX and 112X, where X=Cu, Ag, Au, Pd and Pt) were performed using the DFT method [16]. Results of the calculations did not reveal an expected dramatic decrease in the binding energies from the Hg to the 112 compounds. They have shown that element 112 should form compounds with metals like Cu, Ag, Au and particularly Pd, with the bond strength being only 10-15 kJ/mol weaker than that of the respective Hg compounds. Results of the first calculations of adsorption energy of Hg and element 112 on metal clusters of Au and Pd [17] have shown about the same difference in the bond strength between Hg and 112 with gold clusters as that obtained from the dimer calculations [16].

A number of theoretical predictions were made for experiments with aqueous solutions of the heaviest elements. For Rf and its group-4 lighter homologs, predictions of hydrolysis and complex formation in the HF and HCl solutions were made on the basis of the DFT calculations [18]. It was shown that Rf should hydrolyse to a less extent than Zr and Hf. The complex formation in very diluted HF solutions was shown to change as Zr ≥ Hf > Rf, which will result in the following sequence Zr ≤ Hf < Rf by the extraction of the positively charged complexes of these elements by an AIX (anion exchange) column. Experiments [19] on the AIX separation of group-4 elements from HF solutions have confirmed those predictions.

For element 106, Sg, along with Mo and W, predictions of hydrolysis and complex formation in HF solutions were made on the basis of the DFT calculations [20]. Hydrolysis of Sg was shown to be a complex process depending on pH of the solution. At low pH, i.e. for the formation of positively charged complexes, the decreasing trend in hydrolysis of group-6 elements is continued with Sg, so that the trend in the complex formation is Mo > W > Sg. At higher pH, i.e. for the formation of negatively charged complexes, the trend in reversed in the group: Mo > Sg > W. The former trend proved to be in agreement with experiments on the separation of Sg from aqueous $HNO_3$ solutions by a cation exchange column: Sg having a positive change was sorbed on the column, while the neutral complex of W was not retained [21]. The complex formation of Sg in HF solutions was shown to be even a more complex process than hydrolysis and trends in group 6 were predicted to be different at various pH and HF concentrations.

Much attention was paid to the study of relativistic effects on the properties of the elements at the end of the 6d-series and at the 7p-series. A series of calculations using the relativistic pseudo-potential (PP) method was performed for compounds of elements 111 through 114 which are expected to have strong relativistic effects on their properties [22]. Energies of decomposition reactions of hydrides, fluorides and some chlorides of those elements were calculated. A most important conclusion of those works is that the relativistic stabilization and contraction of the 7s orbital in the $7^{th}$ row results in the smallest bond lengths of the 111X and 112X compounds in groups 11 and 12, respectively. On the other hand, relativistic destabilization of the 6d orbitals leads to their larger involvement in bonding for high-coordination compounds, so that the stability of higher oxidation states increases in those groups, like for example of the 5+ state of element 111, or of the 4+ state of element 112. The calculations for the decomposition reactions of the 112 compounds have confirmed its inertness.

Molecular calculations with the use of the relativistic effective core potentials (RECP) for a series of hydrides of the 7p elements [23] have demonstrated a large influence of the 7p orbital spin-orbital (SO) splitting on molecular spectroscopic properties. A large bond contraction was observed in the compounds of element 113 with the predominant contribution of the relativistically contracted $7p_{1/2}$ orbital in bonding (for example in 113H), while for compounds of the other 7p elements, e.g. 115 through 118, the properties are influenced by a relativistically expanded $7p_{3/2}$ orbital. This results in an increase in the bond length of compounds of these elements. The calculations have confirmed a relative inertness of element 114 showing decreasing binding energies of compounds like 114X (X=F, Cl, Br, I, O, $O_2$) [24] in comparison with those of the lighter homologs. The PP calculations of the decomposition reactions of $MX_4$ and $MX_2$ (X=H, F, Cl) have shown a decreasing stability of the 4+ state and increasing stability of the 2+ state for element 114 [22].

The RECP calculations for the reactions $M + F_2 \rightarrow MF_2$ and $MF_2 + F_2 \rightarrow MF_4$, where M=Xe, Rn and element 118 [25] confirmed an increase in the stabilities of the 2+ and 4+ oxidation states in group 18. The SO effects were shown to stabilize $118F_4$ by a significant amount of about 2 eV, though they elongate the bond by 0.05 Å. Thus, increasing trends in bond length and bond strength are continued with element 118. The influence of the SO interaction on the geometry of $MF_4$ was also investigated [25,26]. It was shown that a $D_{4h}$ geometrical configuration for $XeF_4$ and for $RnF_4$ becomes slightly unstable for $118F_4$. A $T_d$ configuration was shown to be more stable than the $D_{4h}$ in $118F_4$ by about 0.2 eV. The reason for that was the availability of only stereochemically active $7p_{3/2}$ electrons for bonding. Trends in molecular stability were predicted for a number of simple compounds of element 118 as compared to those of elements 112 and 114, as well as to those of Rn. So far, elements heavier than 118 were not studied at the MO level. For a complete review, the following references can be recommended [23,27-29]. Prospects for future theoretical studies are also presented in the talk.

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# Improved density-functional calculations for molecules and calculation of adsorption of the heaviest elements on surfaces

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In 1964 Hohenberg and Kohn [1] were able to show that the total energy of any system in an external field can be described by a functional of its density only. This pioneer work is the basis of the Density Functional Theory (DFT) and provides an incentive for many theoreticians to find this functional. In the last three decades many approximations for the energy density functional were made which gave quite good results, but the 'exact' form of the functional is still unknown.

DFT calculations depend on the choice of the exchange-correlation functional and the treatment of the kinetic energy. The spectrum of the different approximations of the kinetic energy starts with a purely non-relativistic approach with or without spin-orbit interaction, continues with the Zeroth-Order Regular Approximation (ZORA) [2, 3] and ends with a full-relativistic description. A comparison of these approximations and corresponding results can be found in [4, 5].

An important difference between various density functionals is the treatment of the spin of the electrons. In the simplest form of non-relativistic density functionals spin is completely neglected. This approximation works quite well for closed-shell systems but leads to wrong results for open-shell molecular as well as atomic systems. A very important improvement was achieved by extending these functionals to spin-polarized (SP) forms [6]. In a relativistic description the spin should actually be included in the relativistic form of the density functionals, which directly depend on the four current density, but this approach is not yet suitable for practical applications. Alternatively, the spin can be included into the relativistic form of the density functionals in a theoretically consistent way via the magnetization density using a fictitious external magnetic field which is set to zero in the end formulas (for more details see [7, 8]).

In this case the exchange and/or correlation functionals depend not only on the density but also on the magnetization density (see details in [7, 8, 9]). The magnetization density at any point in space is defined as magnetic moment per volume [10]. Following this, it is a vector which, in general, points to different directions at different points in space. In order to simplify the calculations in most implementations the magnetization density is aligned to the axis of the highest symmetry (z-axis), which in the literature is called the collinear approximation. There are only few implementations of the non-collinear approximations for atoms and solids known in the literature [9, 11, 12]. Only one of them reports an implementation for molecules where the authors used a scalar-relativistic description [13]. In a recent letter [14] we were able to present the first four-component implementation of the non-collinear density functionals for the diatomic molecule $Pt_2$. The accuracy which is achieved with this method is better than 0.2 eV in contrast to the old type of calculations without the inclusion of the magnetization density.

In the context of the very first molecular calculations which include transactinide elements with this new method we present results for $RfCl_4$ and its homologues. Again the difference between the theoretical and the experimental results of $ZrCl_4$ and $HfCl_4$ indicate a maximal error of 0.2 eV. This gives us hope that this method can be used as calculational tool with chemical relevant accuracy.

A second improvement for future calculations of very heavy systems will be demonstrated in the adsorption of single atoms on surfaces. In order to detect a very heavy element atom like e.g.112 thermographic chromatography is a method which often is used. The physical quantity which determines the adsorption of the single atom on a surface is the binding energy. For this element 112 we present our first results where the surface is either determined by a cluster or alternatively by an embedding procedure which simulates the surface. Comparison with the homologue Hg leads to a good prediction of the adsorption energy of element 112.

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# Electronic properties for the superheavy elements 111 to 119 from relativistic ab-initio calculations

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Relativistic effects scale approximately with $Z^2$ (Z=nuclear charge), hence very large relativistic effects are expected for the trans-actinides, the elements beyond nuclear charge 103, the so-called superheavy elements. The heaviest element discovered so far is the superheavy element 116 with a half-life of about 33 ms for the isotope 289[1]. For chemical studies at an atom-at-a-time scale half-lives within at least the second range are required. The recent discoveries of superheavy isotopes in the second-range of stability open the way for atom-at-a-time chemistry of 108 (Hs), 110, 112 or even 114 [2]. A major drawback in the synthesis is the small production cross-section which drops rapidly with increasing nuclear charge. Thus, for the prediction of periodic trends and the chemical behaviour for elements including the 7th period of the periodic table and beyond, the use of theoretical methods are currently the only way to gain useful chemical information. This talk gives an overview on properties for the elements with nuclear charge 111 (eka-Au) to 119 (eka Fr) [3]. It is shown that relativistic effects significantly influence chemical properties of these elements (see figure below). In contrast, quantum electrodynamic effects are small and can be neglected for chemical properties. We also address the current problem of identifying new isotopes and suggest K-inversion spectroscopy as a useful tool [4].

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# High-accuracy calculations for heavy and superheavy elements

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Accurate calculations for very heavy elements require high-order inclusion of both relativity and electron correlation. The framework of our method is the Dirac-Coulomb-Breit Hamiltonian, which includes relativistic terms up to second order in $\alpha$, the fine-structure constant. This model is adequate for all atoms, as long as they are not highly ionized. The one-electron four-component Dirac-Fock-Breit spinors are obtained first, playing the same role as the Hartree-Fock orbitals in nonrelativistic quantum mechanics. Correlation is included via the coupled cluster method, which may be interpreted as infinite-order summation of large classes of perturbation terms, and has emerged as the most accurate approach for this purpose.

We are usually interested in studying a large number of states of a given atom. Since most of these states cannot be described, even approximately, by a single determinant, multireference coupled cluster methods are required. The essence of multireference methods is the partitioning of the function space into a small *P*, which comprises all the important determinants, and a large *Q*, the rest of the function space. The effect of *Q* is included by the CC scheme in an effective Hamiltonian constructed in *P*. This $H_{\mathrm{eff}}$ is then diagonalized, yielding the energies of all desired states simultaneously. Since the effect of *Q* is included approximately, whereas *P* is solved exactly by diagonalization, extending *P* will improve results. However, convergence of the CC iterations puts severe limitations on the structure and size of *P*. A new approach, the intermediate Hamiltonian coupled cluster, has recently been developed, allowing larger model spaces and greater flexibility in their construction, thereby extending the scope of the method and increasing its accuracy.

The method has been applied to many atoms, calculating energies of numerous states for each. Agreement with available experimental values was usually within a few hundredths of an eV. This makes the method a useful tool for reliable prediction of energy levels of superheavy elements.

Applications to transactinides include, *inter alia*:

- The ground state of Rf (E104) has been determined to be $7s^26d^2$, in contrast with previous predictions of $7s^27p^6d$. Correlation, which favors the $d^2$ configuration over dp, wins over relativity, which prefers the former configuration, leading to structure similar to that of Hf.
- E111 (eka-gold) is predicted to have a $6d^97s^2$ ground state, vs. the $(n-1)d^{10}ns$ structure of lighter coinage metals.
- The dication of E112 (eka-mercury), unlike Hg2+, shows very strong mixing of the $d^8s^2$, $d^9s$, and $d^{10}$ levels in its low electronic states. The E112+ cation has the same electronic ground state as E111.
- E113 (eka-thallium) has a large (0.6eV) electron affinity, raising the possibility of $E113^-$ compounds. The $d^9s^2$ level of the dication is a mere 0.1 eV above the $d^{10}s$ ground state; this energy difference in Tl is over 8 eV. Di- and trivalent compounds of E113 with an open 6d shell could therefore exist.

- The ionization potential of E114 is 1.1 eV above that of Pb; in fact, it is higher than the IPs of all group-4 elements except carbon. This indicates that E114 will be less metallic and more inert than Pb.
- E118, a rare gas, is predicted to have positive electron affinity of 0.064(2) eV. QED effects on this value were calculated and found to decrease the EA by 9% or 0.0059(5) eV.
- The EA of E119 (eka-francium) is predicted to be 662 meV, much higher than for Cs (491 meV) or any other alkali atom.
- The ground state of E121 (eka-actinium) is $8s^2 8p$, vs. $ns^2(n-1)d$ of other group-3 elements.
- E122 (eka-thorium) will have an $8s^2 7d^8 p$ ground state, vs. the $7s^2 6d^2$ of Th.

These and other examples will be described.

# Spin-orbit coupling in transactinide chemistry: secondary periodicity and effects in high-symmetry ligand fields

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Extreme spin-orbit coupling extant for the transactinides is known to have dramatic effects on the valence electronic structure of 6d-block and 7p-block elements. We will examine the consequences of these severe spin-orbit effects on the nature of the transactinide ligand field of 6d transactinide coordination compounds and discuss their implications on their structure, bonding, and spectra vis-à-vis analogs of lower periods. In addition, we will address the question of what constitutes a closed-shell or chemically satisfied valence in light of the secondry periodicity wrought by spin-orbit effects. In particular, we will discuss the effect of spin-orbit coupling on dispersion interactions in dimers of nominally closed-shell 7p-block elements. To further this end, we introduce a modified version of the Bernardi-Boys counterpoise-correction scheme which reduces the calculated overcorrection of the basis set superposition error typical of this method at the correlated level.

# Valence-shell QED effects in heavy-element compounds

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Valence-shell quantum-electrodynamical terms (QED), whose two leading terms, of opposite sign, are the self-energy (SE) and vacuum polarization (VP), are of interest for three different reasons: 1) To the extent that they are small, this smallness justifes the current Dirac-level models, 2) Actually the accuracy of present quantum chemistry, in the domain from water to the superheavies, is now approaching the level where not only relativistic, but QED effects will soon be seen in a head-on comparison between ab initio theory and experiments, 3) These terms may have been 'the last train from physics to chemistry' at the level of fundamental Hamiltonians.

A large number of careful studies of these effects exist for few-electron atoms. A few examples will be shown. The fundamental way of treating these terms is to first create a complete basis of one-particle states and to then evaluate the relevant Feynman diagrams. This can also be done for the SE of valence electrons in neutral, or nearly neutral atoms, to the extent that an effective one-electron potential is available [1]. For the lowest-order VP term, a local potential by Uehling and Serber in 1935 is available. Various approximate methods have also been tried [2].

To give an idea of the orders-of-magnitude, for heavy elements ($Z > 50$), the QED effects cance about -1% of the Dirac-level relativistic effects [1], for the energy shifts of *ns* valence electrons. For the ionization potential of the gold atom this means about -0.3% of the total value. Here it should be mentioned that the very first estimates for Cs and Fr were published by Dzuba et al. [3] already in 1983.

The VP part is to lowest order a local potential, a property of space, same for all elements. Would it be possible to find an effective potential, simulating the SE terms? For energy-only this can be done. Probably any 'broad δ-function' at the nucleus with a right norm will do the job. An example is the work by Fricke in 1971 [4]. For several simultaneous properties such an effective potential has not been attempted, to our knowledge, before Pyykkö and Zhao [5], who fitted the SE effects on the energy and the magnetic-dipole hyperfine integrals of 2s states. Note that both the relativistic and the QED effects are smaller for the 1*s* states than for the higher states. The $V_{SE}$ used was a simple Gaussian, $B \exp(-\beta r^2)$. Finally, a quadratic fit of the height $B$ and the width parameter $\beta$ to the nuclear charge was made for the fitting range Z=29 - 83. The final results were tested over this range and above it, up to the superheavy alkali metal E119. Recent, more fundamental results are available for the hyperfine effects of the alkali metals Li-Fr by Sapirstein and Cheng [6]. For properties close to a threshold, the percental QED effects can become very large. An example is the electron affinity of eka-radon, E118, where a decrease of -9% is obtained [7]. The final calculated EA is -0.064(2) eV.

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# Electronic structure of molecules containing very heavy & superheavy elements

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Relativistic computations that include both relativistic and electron correaltion effects such as complete active space multi-configuration interaction (CAS-MCSCF) followed by multi-reference configuration interaction (MRSDCI) computations that included up to 50 million configurations of molecules containing very heavy and superheavy elements reveal surprising trends compared to their lighter analogs in the periodic table. We shal discuss these unusual features and trends concerning structure and properties of these very heay to superheavy molecules. We have computed not only the ground electronic states, but also several excited electronic states. It is shown that Jahn-Teller distortion is quenched by spin-orbit coupling in these very heavy species. We have carried out relativistic computations for the electronic states of the newly discovered superheavy elements and yet to be discovered elements such as 113 (eka-thallium) 114 (eka-lead) and 114+. Many unusual periodic trends in the energy separations of the electronic states of the elements 114, 113, 114+, (113)H, 114H, etc., and unusual features in electronic state compositions are found due to relativistic effects. The potential energy surfaces of $(114)H_2$ exhibit unusual trends compared to $PbH_2$ due to relativity and break-down of singlet and triplet features of the electronic states due to spin-orbit coupling. Unusual features have been computed for the Lawrencium and Nobelium compounds. All of these species will be considered with emphasis on unusual periodic trends.

# Relativistic effects on the electronic structure and volatility of the group-8 tetroxides $MO_4$ (M=Ru, Os and Hs)

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Element 108 was identified chemically by studying volatility of its tetroxide $HsO_4$ along with that of the osmium tetroxide, $OsO_4$ [1]. The $MO_4$ molecules were adsorbed on/desorbed from a quartz surface of a chromatography column and the temperatures of the 50% of the chemical yield of the products that passed through the column, $T_{50\%}$, provided an information about their volatilities in a comparative study. Theoretically, volatility, as the adsorption enthalpy, $\Delta H_{ads}$, of the tetroxides on a quartz surface of the column, was predicted using a model of physisorption, with molecular spectroscopic properties being *ab initio* calculated using the fully relativistic (four-component) density functional theory (DFT) method [2]. On the basis of these predicted $\Delta H_{ads}$ with the use of thermodynamic models of adsorption, $T_{50\%}$ of $HsO_4$ was expected to be about 2 degrees lower than $T_{50\%}$ of $OsO_4$, which means that $HsO_4$ should be more volatile [3]. Experiments have, however, observed a larger $T_{50\%}$ for $HsO_4$, which was interpreted as $HsO_4$ having a lower volatility than that of $OsO_4$ [1]. The reasons for this disagreement will hopefully be found by the future research, while those from the theoretical point of view are analyzed in [3].

Theoretically, results of the DFT calculations [2] and the thermodynamic considerations [3] indicate that $HsO_4$ should be more volatile than $OsO_4$ due to its larger molecular size (i.e. large molecule-surface interaction distance) and a larger molecular weight. To investigate the influence of relativistic effects on the electronic structure and properties of $MO_4$ (M=Ru, Os and Hs), especially on volatility, non-relativistic calculations for these molecules have been performed by us in addition to our former relativistic calculations [2].

Comparison of the obtained non-relativistic with relativistic values shows that relativistic effects, as expected, increase binding energies and decrease bond lengths in those compounds, as they decrease molecular polarizabilities. Results of those recent investigations with respect to the influence of relativistic effects on molecular volatility and on the trend in Group-8 are discussed.

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# Ionic radii of heavy actinide(III) cations

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Filling of the 4*f* orbitals in the lanthanide series and 5*f* orbitals in the actinide series is accompanied by a significant decrease in the atomic and ionic radii. This effect, called lanthanide (actinide) contraction, is the consequence of incomplete shielding of the outermost *p* orbitals from nuclear charge by the 4*f* and 5*f* electrons, respectively. In addition to the increase of the effective nuclear charge, relativistic effects contribute considerably to the actinide contraction[1,2]. Relativistic effects influence the contraction of the lanthanide(III) and actinide(III) ionic radii in two ways: by splitting the outermost *p* orbitals and stabilisation of $p_{1/2}$ orbitals, and by expanding the $f_{5/2}$ and $f_{7/2}$ orbitals. The latter results in less effective shielding from the nuclear charge. For the heaviest actinides this may lead to much smaller ionic radii than in the absence of relativistic effects. For example, in the case of $Fm^{3+}$ the relativistic calculations give $r_i$ 8 pm smaller than nonrelativistic, whereas in the case of $Er^{3+}$ (homologue in the lanthanides series) - only 2.5 pm.

For the five heaviest members of the lanthanide series, the spacing between ionic radii of the adjacent elements decreases regularly from 1.3 to 1.0 pm (Table 1). Unexpectedly, in the case of end actinides the spacings between $r_i$ of the neighbouring elements change irregularly. For example, the difference in $r_i$ between $Es^{3+}$ and $Fm^{3+}$ is 1.7 pm, whereas that between $Md^{3+}$ and $No^{3+}$ only 0.2 pm.

Table 1. Ionic radii of heavy lanthanides and actinides, CN=6

| $Ln^{3+}$ ion | $r_i$ , pm [3] | $An^{3+}$ ion | $r_i$ pm |
|---|---|---|---|
| $Ho^{3+}$ | 89.4 | $Es^{3+}$ | 92.8 |
| $Er^{3+}$ | 88.1 | $Fm^{3+}$ | 91.1 |
| $Tm^{3+}$ | 86.9 | $Md^{3+}$ | 89.6 |
| $Yb^{3+}$ | 85.8 | $No^{3+}$ | 89.4 |
| $Lu^{3+}$ | 84.8 | $Lr^{3+}$ | 88.1 |

Ionic radii are usually obtained from X-ray diffraction data for oxides or fluorides [4]. In the case of heavy actinides from $Bk^{3+}$ to $Es^{3+}$ $r_i$ were determined from lattice parameters of sesquioxides measured by electron diffraction [5]. Unfortunately, elements heavier than einsteinium are produced in non-weighable amounts, so that the experimental structural data for these elements are not available. For $Fm^{3+}$, $Md^{3+}$, $No^{3+}$ and $Lr^{3+}$, the values of $r_i$ were determined only by the chromatographic method [6,7,8]. The ionic radii of $Fm^{3+}$, $Md^{3+}$ and $Lr^{3+}$ were estimated by comparing their elution positions with the positions of rare earth tracers and of actinides of known ionic radii on strong acidic cation exchange resin with α-hydroxyisobutyrate solution as eluent [6,8]. In the case of No, which is unstable in the +3 oxidation state, $r_i$ was also determined chromatographically but on the cryptomelane $MnO_2$ - inorganic ion exchanger which shows strong oxidizing properties. The $HNO_3$-$H_5IO_6$ solution was used both as oxidant and eluent [7].

In order to understand the sources of irregularity in the contraction of ionic radii of heavy actinides we compared the experimental $r_i$ with the radii of the maximum charge density, $R_{max}$, of the outermost orbital radii in these cations. Linear correlations of $r_i$ on $R_{max}$ and on expectation values of orbital radii, $\langle r \rangle$, were found for cations of the same charge in many groups of the periodic table [9,10]. These

correlations are suitable to predict $r_i$ of ions in case when experimental measurements are difficult or impossible [9,11,12].

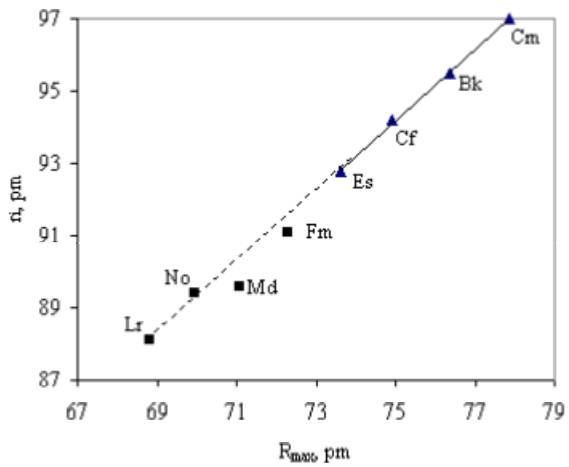


Figure 1. The ionic radius as a function of the 2j+1 weighted in the heavy actinides. Triangles present ionic radii determined from electron diffraction data, squares ionic radii from elution experiments.

Figure 1 presents the dependence of the ionic radius on $R_{max}$ of the outermost shell in the ions of the heavy actinides. The orbital radii have been calculated by V.Pershina using the Dirac-Slater method [13]. As the outermost shell radii we used the 2j+1 weighted $R_{max}$. The ionic radii of $Cm^{3+}$ $Bk^{3+}$, $Cf^{3+}$ and $Es^{3}$ are those of Templeton and Dauben radii [3], whereas the ionic radii of the last four actinides where obtained from elution experiments by comparing with Templeton and Dauben radii of lanthanides. As shown in Figure 1 a linear dependence of $r_i$ on $R_{max}$ of the outermost shell is observed for +3 actinides from Cm to Es. For these cations the experimental $r_i$ were determined from electron diffraction on oxides. It is important to note that the chromatographically determined ionic radii of $Lr^{3+}$ and $No^{3+}$ also fit the extrapolated part of the straight-line plot. As shown in Table 2. large differences between the extrapolated and experimental radii are observed for $Md^{3+}$ and $Fm^{3+}$.

Table 2. Experimental and extrapolated $r_i$ for heaviest actinides, CN=6

| $An^{3+}$ ion | $R_i$(pm) experimental | $r_i$(pm) extrapolated |
|---|---|---|
| $Fm^{3+}$ | 91.1 | 91.5 |
| $Md^{3+}$ | 89.6 | 90.3 |
| $No^{3+}$ | 89.4 | 89.2 |
| $Lr^{3+}$ | 88.1 | 88.1 |

As mentioned earlier the ionic radii of $Fm^{3+}$, $Md^{3+}$ and $Lr^{3+}$ were determined only by the chromatographic method. The linear dependence of the logarithm of distribution coefficients ,$K_d$, on $r_i$ for the tripositive ions of heavy lanthanides and actinides in α-hydroxyisobutyrate solutions was the basis for the $r_i$ determination of the heaviest actinides [6,8]. However, in complexing solutions strong deviations from linearity of the log $K_d$ vs. $r_i$ plot are observed [4,15]. This effect called double-double or tetrad consist in the division the lanthanide and actinide series into two subgroups by the $f^7$ configuration and futher division of each subgroup into two segments by the $f^3$-$f^4$ and $f^{10}$-$f^{11}$ pairs [16]. Stabilization of the $f^3$, $f^4$, $f^7$ ,$f^{10}$ and $f^{11}$ configurations depends on the environment and decreases with increasing ability of the ligand to expand the *f* electrons cloud. In water, where the nepheloauxetic effect is very low the

delocalization of *f* electrons is insignificant. In α-hydroxyisobutyrate solution where water molecules in the solvation sphere are exchanged for the ligand which shows high nepheloauxetic effect, the cations with $f^3$, $f^4$, $f^7$, $f^{10}$ and $f^{11}$ configurations form less stable complexes than expected from ionic radii.

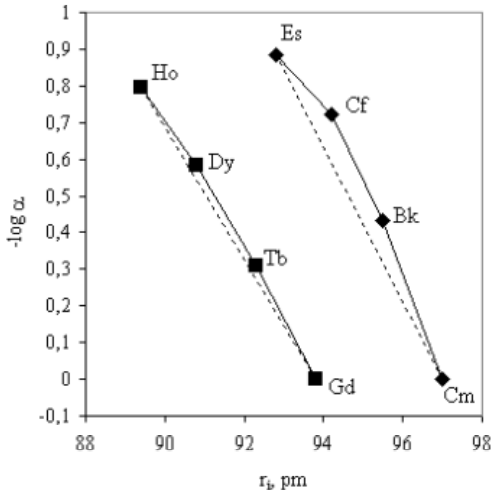


Figure 2. Dependence of the logarithm of the separation factor (α) on $r_i$ for the third segment ($f^7$-$f^{10}$) in lanthanide ($Gd^{3+}$-$Ho^{3+}$) and actinide ($Cm^{3+}$-$Es^{3+}$) series in the α-hydroxyisobutyrate ~V strong acidic cation exchange resin system.

Figure 2 presents the dependence of the logarithm of the separation factor (α) on $r_i$ for the third segment ($f^7$-$f^{10}$) in both lanthanide ($Gd^{3+}$-$Ho^{3+}$) and actinide ($Cm^{3+}$-$Es^{3+}$) series in the α-hydroxyisobutyrate ~V strong acidic cation exchange resin system. The separation factor α is defined as $K_d(Ln^{3+})/K_d(Gd^{3+})$ or as $K_d(An^{3+})/K_d(Cm^{3+})$ for lanthanides and actinides, respectively. Figure 2 shows that for the third segment the dependence of log α on $r_i$ for lanthanides(III) does not deviate much from linear. However, in the case of actinides(III) strong deviations from linearity due to the tetrad effect are observed. This is because greater radial extent expansion of 5*f* in comparison with 4*f* orbitals results in stronger participation of 5*f* orbitals in metal to ligand bonding. Similar effect should be observed in the fourth segment ($f^{11}$-$f^{14}$) of the lanthanide ($Er^{3+}$-$Lu^{3+}$) and actinide ($Fm^{3+}$-$Lr^{3+}$) series. In the case of lanthanides(III) small deviations from linearity are indeed observed [17], whereas for $Fm^{3+}$- $Lr^{3+}$ strong tetrad effect is to be expected. This means that ionic radii of the heaviest actinides can not be determined from linear dependence of log $K_d$ or log α on $r_i$ in experiments based on the α-hydroxyisobutyrate ~Vcation exchange system, as there is no way to get rid of the tetrad effect in the stability constants. The only way seems to be extrapolation of the linear dependence of $r_i$ (ionic radius based on crystal data) on $R_{max}$, which is valid for the Cm-Es interval, to the Fm-Lr interval, see Figure 1. From this extrapolation one gets $r_i$ equal to 91.5 and 90.3 pm for $Fm^{3+}$ and $Md^{3+}$, respectively.

The question remains, why the ionic radii of $Lr^{3+}$ and $No^{3+}$, determined from elution positions, are the same ($Lr^{3+}$) or almost the same ($No^{3+}$) as those calculated from orbital radii. In the case of $Lr^{3+}$ participation of the *f* orbitals in the metal to ligand bonding is negligible because the 5*f* shell is filled and the nepheloauxetic effect in 5*f* electrons does not affect stability constant of the α-hydroxyisobutyrate complex. As far as the $No^{3+}$ is concerned it should be noted that it has been determined chromatographically by comparison of its $K_d$ with $K_d$ of heavy lanthanides on cryptomelane-$MnO_2$ cation exchanger [7]. The selectivity of cryptomelane-$MnO_2$ for the cations is due to steric effects and depends on the radii of the cations and of the tunnel (280 pm) in the sorbent [18]. The hydrated +3 metal cations with diameters much larger than 280 pm must be dehydrated before entering the ion exchange phase.

Therefore, the selectivity of the cyptomelane $MnO_2$ depends nearly linearly on the free energy of hydration which, in turn, is a linear function of the reciprocal of the ionic radius. The linear dependence of the free energy of hydration on the reciprocal of the ionic radius for the whole $Ln^{3+}$ series and for those actinides for which the $\Delta G_{hydr}$ is available, indicates that in the hydration energy the tetrad effect is, as expected, insignificant.

## Conclusion

The tetrad effect in complexation of actinide(III) cations by α-hydroxyisobutyrate gives underestimated values for $Fm^{3+}$ and $Md^{3+}$ ionic radii comparing with the ionic radii obtained from the linear dependence of ionic radii on orbital radii. With the calculated $r_i$ for $Fm^{3+}$ 91.5 pm and $Md^{3+}$ 90.3 pm, the ionic radii of $An^{3+}$ at the end of the series decrease regularly like in the radii of the lanthanide (III) cations (Fig.3).

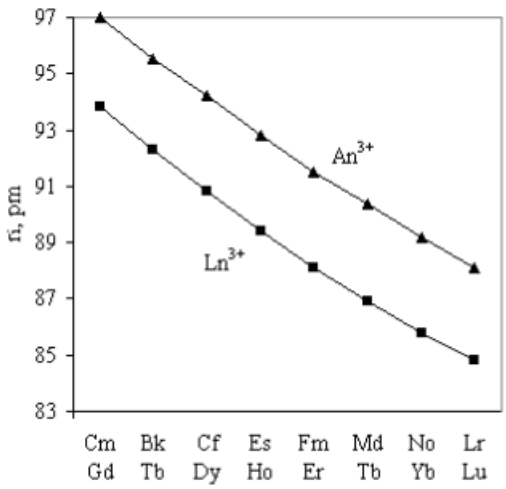


Figure 3. Contraction of ionic radii of the heavy lanthanides(III) and actinides(III). The radii of $Fm^{3+}$ and $Md^{3+}$ are calculated from $R_{max}$ by extrapolation procedure.

## Acknowledgments

The author thanks Prof. Slawomir Siekierski for helpful discussion and Dr. Valeria Pershina (GSI Darmstadt) for calculation of orbital radii of actinides cations. The research was supported by the grant from the State Committee for Scientific Research of Poland nr. 7 T09A 073 20.

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# Adsorption of element 112 on Au surface

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The adsorption of element 112 on a gold surface is studied using the full relativistic four– component ab initio density functional (DFT) cluster calculations. The binding energy and bond length is determined, as well the adsorption position relative to the surface atoms sites. The use of optimized numerical atomic wave functions in the MO-LCAO procedure in the DFT method offers a flexible basis for the expansion of the MO orbitals. Because the adsorption phenomenon is dominantly local, we use clusters of different sizes to approximate the surface. In addition we apply the embedded cluster method. This procedure uses an inner part of 22 and 28 atoms (depending of the symmetry of the adsorbate–cluster surface) which is made self consistently. The surrounding atoms which account for the environmental influences to the inner cluster, is divided in two parts (transition environment and external environment) which are treated in different ways in the description of the interaction with the inner part. Finally potential energy curves and diagrams for the density of states for the system under consideration are presented. The results from size convergent cluster calculations are compared with the results of the embedding calculations.

# Relativistic mixed-sector intermediate hamiltonian coupled cluster method: theory and applications

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Newly developed mixed-sector relativistic multireference Coupled Cluster (CC) scheme based on Intermediate Hamiltonian formulation is presented. This formulation widely extends possibilities of the traditional Fock-space and Hilbert–space CC approaches and could be regarded as a bridge between the two approaches. High-precision calculations of some heavy and super-heavy atomic systems are presented. The new method yields converged results for states not accessible by traditional Relativistic Fock-space coupled cluster approach. Moreover, states calculated by both methods exhibit much better accuracy in the mixed-sector intermediate Hamiltonian (MSIH) formulation.