Russian Chemical Reviews **78** (12) 1173 – 1181 (2009) © 2009 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2009v078n12ABEH004075

Relativistic pseudopotential model for superheavy elements: applications to chemistry of eka-Hg and eka-Pb

A V Zaitsevskii, C van Wüllen, A V Titov

Contents

I.	Introduction	1173
II.	Relativistic pseudopotentials for superheavy elements	1174
III.	Chemical properties of elements 112 and 114	1176
IV.	Conclusion	1179

Abstract. Relativistic pseudopotential approach to the electronic structure simulation of superheavy elements (SHE) compounds is presented. Advanced formulations of this approach leaving both valence and outer-core electronic shells for explicit treatment give rise to simple and efficient computational techniques ensuring highly accurate description of most chemical properties of SHE. At present, the errors due to the use of approximate methods for solving the correlation problem for a subsystem of valence electrons are much larger than those stemming from the pseudopotential approximation itself. Recent applications to the studies of the chemistry of elements 112 (eka-Hg) and 114 (eka-Pb) are reviewed; properties of these elements and their lighter homologues, Hg and Pb, are compared. The bibliography includes 54 references.

I. Introduction

Since the discovery of the Periodic Law of the chemical elements, finding new elements and correct placing them into the Periodic Table has attracted attention of many chemists. For superheavy elements (SHE), the rapidly diminishing half-lives of the newly synthesized nuclides have blocked the possibility of their chemical investigations, so their identification had become exclusively the field of nuclear physics up to the end of the 20th century. The recent successful synthesis of relatively long-lived SHE isotopes from the island of stability (see, *e.g.*, Refs 1 – 3 and references cited therein) has made experimental studies of their chemistry possible.

Probably, the most attention for more than forty years has been paid to elements 112 (eka-mercury or eka-Hg below) and 114 (eka-lead or eka-Pb), which are (at least formally, according to their atomic shell structure) heavy homologues of mercury and lead, respectively. This was due to the expectation that the top of the island of stability should be located at the nuclide with proton number $Z = 114$ and neutron number $N = 184$. In the 1970s,[4] the periodicity of the properties of these elements was called into question because of the very strong relativistic contraction of the 7s and huge spin-orbit splitting of the $7p_{1/2}$ shells and, up to the last years, the theoretical predictions and experimental data were contradictory. In 2006, the combination of the nuclear physical synthesis/detection setup with the chemical thermochromatography of the synthesized elements has led experimentalists to the first reliable identification of the long-lived $^{283}112$ isotope.[5] At that time, the chemical inertness of eka-Hg was also rejected in accurate quantum chemical calculations[6 – 9] and agreement between the results of thermochromatography and the corresponding estimates derived from theoretical data was finally attained.[10, 11] Gas-phase chemistry was also employed in studies of several isotopes of eka-lead ($^{287}114$, $^{288}114$ and $^{289}114$) in 2007 – 2008; the results were interpreted as indicative of the particular chemical inertness of this element similar to those of heavy rare gases.[12, 13]

The experimental study of new SHE is extremely laborious and expensive, and only a few superheavy atoms per week can be produced. Therefore, careful planning of chemical experiments is required based on the results of comparatively inexpensive quantum chemical calculations and the theoretical analysis of physicochemical properties of the SHE.

Theoretical chemistry of superheavy elements is far outside of the domain of applicability of the conventional tools of quantum chemistry based essentially on a non-relativistic quantum many-body theory and considering relativistic effects as corrections.[14] A straightforward approach to the simulation of the electronic structures of SHE compounds employing a sufficiently accurate relativistic many-electron Hamiltonian normally requires huge

A V Zaitsevskii Institute of Hydrogen Energetics and Plasma Technologies, Russian Research Centre 'Kurchatov Institute', Kurchatov pl. 1, 123182 Moscow, Russian Federation. Fax/tel. (7-499) 196 99 92, e-mail: zaitsevskii@kintech.ru
C van Wüllen Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Deutschland. Fax (49-0631) 205 27 50, tel. (49-0631) 205 27 51, e-mail: vanWullen@Chemie.Uni-KL.de
A V Titov B P Konstantinov Petersburg Nuclear Physics Institute, Russian Academy of Sciences, 188300 Gatchina, Leningrad Region, Russian Federation. Fax (7-813) 714 61 06, e-mail: titov@pnpi.spb.ru

Received 13 May 2009
Uspekhi Khimii **78** (12) 1263 – 1272 (2009)

computational efforts, and applications to more or less complex systems of practical importance often requires compromises (such as using small basis sets or simplistic models), which easily result in inacceptable losses in the accuracy of the predicted physical and chemical properties. The relativistic pseudopotential (effective core potential) theory [15–19] offers a simple and efficient way to avoid such compromises. The relativistic all-electron problem for an atom or a molecule is replaced by a simpler one restricted to a small subsystem of electrons, usually referred to as valence shell (let us underline that the meaning of this term can differ from that generally assumed by chemists). Moreover, in the majority of formulations of the pseudopotential theory the valence shell many-electron problem formally resembles that for non-relativistic many-electron system, since the kinetic energy of explicitly treated electrons and electron–electron interactions are described by corresponding non-relativistic operators. However, through the presence of spin-dependent one-electron pseudopotential operators the spin-orbit interaction is included and the non-relativistic symmetry no longer applies. From the viewpoint of a computer implementation, this is the essential difference from the non-relativistic case.

Several decades ago, the pseudopotential approach was generally considered as a basis for the development of intermediate accuracy techniques of electronic structure calculations. However, it was shown quite recently that the proper choice of the electron subsystem explicitly treated, the use of somewhat sophisticated Ansätze for the pseudopotentials and the extraction of their parameters from high-level relativistic calculations on free atoms can ensure remarkable accuracy in predicting various properties of molecular and supramolecular systems and chemical reactions; errors arise from approximations that should be necessarily introduced to solve the valence-electron problem rather than from the pseudopotential model *per se* (see Ref. 19 and references cited therein). The domain of applicability of this approach covers the whole Periodic Table, including actinides and transactinides. Numerical experiments have demonstrated that no significant differences appear between the results of all-electron and advanced pseudopotential calculations, provided that the approximation for the all-electron relativistic Hamiltonian is accurate enough and the same method of electron correlation treatment is employed in both cases.

As a consequence, the relativistic pseudopotential approach is becoming extremely popular in theoretical studies of the chemistry of superheavy elements. In particular, *ab initio* and density functional theory (DFT) calculations performed with accurate relativistic pseudopotentials provided a considerable amount of valuable information on the chemical properties of elements 112 and 114.

The present review provides a brief survey of the relativistic pseudopotential theory, focusing on the models that have proven its usefulness in electronic structure calculations on superheavy element compounds. The results of recent applications of these models to studies of eka-mercury and eka-lead chemistry are summarized and discussed.

II. Relativistic pseudopotentials for superheavy elements

The most straightforward approach to electronic structure calculation on molecular systems comprising superheavy atoms is to approximately solve the eigenvalue problem for an appropriate relativistic many-electron Hamiltonian using four-component one-electron spinors to construct many-electron wavefunctions (see, *e.g.*, Ref. 20). However, this is not an easy task even for rather small molecules because of the large number of core electrons (and thus the total number of electronic variables), the complicated structure of relativistic wave functions, and their rapid variations in the vicinity of the atomic nuclei. An attractive alternative consists in invoking the concept of relativistic pseudopotentials (also known as relativistic effective core potentials, RECP) originally suggested by Lee *et al.* in 1977,[15] which offers the possibility of achieving a remarkable accuracy of electronic structure simulation for superheavy element compounds with moderate computational efforts.

The pseudopotential approach is based on replacing the all-electron problem by its effective analogue for a subsystem of electrons associated with outer (low-energy) shells. This is usually referred to as a valence subsystem; however, hereinafter we shall not adhere to this convention using the term 'valence electrons' in accordance with chemical intuition. Since it is convenient to discern the cases where this subsystem comprises only valence electrons (large-core pseudopotential model) and where outermost core shells are also treated explicitly (small-core pseudopotentials). Let us restrict our consideration to the case where the effective Hamiltonian for the subsystem is written in the form

$$H = \sum_i \Big(T(i) + U(i) \Big) + \sum_{i>k} \frac{1}{r_{ik}}, \qquad (1)$$

Here the summations run only over the indices of valence (or valence and outermost core) electrons, $T(i)$ is the conventional non-relativistic kinetic energy operator and r_{ij} stands for the separation between the electrons i and j so that the two-body terms describe the instantaneous Coulomb repulsion of explicitly treated electrons. The interactions of these electrons with the atomic nuclei and the core electrons that are not explicitly treated are simulated by the spin-dependent pseudopotential operators $U(i)$ bearing all information about the effects of relativity (possibly including those of quantum electrodynamics) and the spatial distribution of the nuclear charge [19, 21] (let us recall the importance of properly accounting for finite nuclear sizes in the electronic structure calculations on SHE compounds). The Hamiltonian (1) acts upon the wave functions built of two-component one-electrons spinors; the two components are normally associated with spin up and spin down. A separation of one-electron functions into two classes (spin up and spin down), as in the non-relativistic case, is no longer possible because U is spin-dependent.

The assumed form of the effective Hamiltonian imposes certain restrictions on the accuracy of the model. For instance, it cannot directly describe magnetic and retarded interactions between the explicitly treated electrons [in contrast, the corresponding interactions involving the excluded core electrons can efficiently be simulated by the one-electron operators $U(i)$]. Fortunately, the latter limitation is not important for most applications to the chemistry of SHE because of the relatively slow increase in the amplitudes of the missed interactions within the outer electronic shells as functions of nuclear charges.

Pseudopotentials for polyatomic systems are normally constructed as superpositions of atomic contributions. The

latter entities are defined in such a way that atomic calculations with a pseudopotential reproduce the main features of low-lying atomic states obtained in fully relativistic all-electron calculations. This approximation is pretty accurate, especially for small-core models, because the excluded inner core shells are localized in the vicinity of the corresponding nuclei and the corresponding charge distributions are almost non-overlapping; furthermore, these shells are not affected by low-energy processes such as chemical reactions.

Various Ansätze for relativistic pseudopotentials of atomic cores have been proposed. In most cases, one assumes that the same spherically symmetric potential is acting on all one-electron atomic states with the same orbital (l) and total (j) angular momenta (semilocal or radially-local pseudopotential). The most popular form of the semilocal atomic pseudopotential in the relativistic case is written [15] as

$$U = u(r) + \sum_{lj}^{l<L} \Big(u_{lj}(r) - u(r)\Big) P_{lj}, \qquad (2)$$

where r is the distance from the given nucleus, function $u(r)$ defines the local part of the pseudopotential operator, P_{lj} projects onto the subspace of spinors with the orbital momentum l and total momentum j and $u_{lj}(r)$ is the potential acting on these spinors. In the above expression, the difference between the potentials with $l > L$ is neglected (see Ref. 22 for details), so the local part acts uniformly on all these high-angular-momentum one-electron states.

Operator (2) can readily be split into the spin-independent part (averaged over all possible couplings of orbital and spin momenta) and the spin-dependent part, usually referred to as the effective spin-orbit interaction. This is the most popular representation of relativistic pseudopotentials used in molecular calculations since it allows one to include the spin-dependent terms only at the last stages, frequently as a perturbation. Replacing the full operator $U(i)$ in Eqn (1) by a combination of atomic averaged pseudopotentials, one arrives at the scalar relativistic pseudopotential model; the corresponding Hamiltonian has high non-relativistic (spin and point group) symmetry, which can efficiently be exploited to simplify the calculations, whereas the effective spin-orbit interaction destroys it requiring the use of the relativistic symmetry and thus leading to more complicated and expensive calculations. One should notice that the above splitting of the Hamiltonian is not very useful for the electronic structure simulation of SHE compounds: because of huge amplitudes of effective spin-orbit interactions, the scalar relativistic approximation provides a rather poor starting point.

Because of the radially local nature of the pseudopotential (2), the corresponding lowest-energy one-electron solutions of the atomic SCF problem (pseudospinors) do not have radial nodes observed for the true outer core and valence spinors oscillating in the vicinity of heavy-atom nuclei. The elimination of these oscillations (smoothing of one-electron spinors) in the core region corresponds to the decrease in kinetic energy (this can be interpreted as a dramatic 'slowing' of the motion of explicitly treated electrons near the nuclei), counterpoised by the increase in the potential energy (*i.e.*, by adding a certain repulsive component to the potential) in order to preserve the one-electron energies. As has been pointed out by Lee *et al.*,[15] this justifies the use of the non-relativistic expression for kinetic energy in Eqn (1) (see also Ref. 22 for a more correct analysis). The smoothness of pseudospinors greatly simplifies the task of their approximation in molecular calculations, especially when the spinors are expanded in a basis of simple analytical (*e.g.*, Gaussian) functions. At the same time, this operation necessarily distorts the description of the correlations of explicitly treated electrons; the correlation energy can be overestimated relative to that evaluated with the true spinors (*i.e.*, within the frozen core all-electron approximation).[23] It is worth noting that the use of small-core pseudopotentials reduces this effect because the nodal structure of the valence pseudospinors in the outer core region is partially retained. The use of radially nodeless outer-core pseudospinors is not so dangerous because it leads to correlation treatment errors mainly in the regions close to the nuclei where the strong central field predominates over electron–electron interactions.

The most straightforward and well-defined procedure of semilocal pseudopotential construction had been developed by the group of Pitzer.[15,24] One starts with the construction of numerical pseudospinors from large components of valence four-component atomic spinors in such a way that the pseudospinors have no radial nodes in the vicinity of the atomic nuclei coinciding with the (appropriately re-normalized) large component out of the 'core region'. Then the components of the pseudopotential for the given l and j values are evaluated through the inversion of the Hartree-Fock-like equations for the pseudospinor and the corresponding one-electron energy. The resulting pseudopotential is called shape-consistent because the shapes of the original spinors in the valence region are exactly reproduced by the pseudospinors.

Unfortunately, the extension of the described procedure to the cases of 'small cores' where several pseudospinors have the same orbital and total orbital momenta is not straightforward since (a) such pseudospinors, except for lowest-energy outer-core ones, have radial nodes that block the possibility of the direct inversion of the Hartree–Fock-like equation and (b) the potentials corresponding to outer-core and valence pseudospinors with the same j and l (say, $6s_{1/2}$ and $7s_{1/2}$ for superheavy atoms) would differ significantly. According to the original formulation of the procedure, the pseudopotential components should be generated only from the nodeless core-like pseudospinors, thus ensuring an accurate description of the outer core shells at the expense of the valence shells. In 1997, Nash *et al.*[25] published a complete set of such pseudopotentials for superheavy elements (up to E118), which were rather extensively used in molecular calculations.[26–29] A detailed comparison of the results of relativistic pseudopotential and all-electron calculations for simple SHE-containing molecules [26,28] revealed no essential difference between the two sets of predicted chemical bond properties provided that the same scheme of electron correlation treatment was used in both cases.

For chemical applications, it would be obviously more natural to optimize the description of valence rather than of outer-core shells. A technique enabling one to extract the components of shape-consistent pseudopotentials directly from the valence pseudospinors with radial nodes has been developed by Titov *et al.*;[19,22] the accuracy of calculations with such 'valence-optimized' pseudopotentials can be much higher than that attainable within the original scheme. The applications of this approach to the calcula-

tions of systems containing superheavy element E112 were reported in Refs 9 and 10.

Let us mention here also another solution for this problem through the introduction of the semi-local energy-adjusted pseudopotentials,[18] which are also successfully used in molecular calculations on superheavy element compounds. In this case, the procedure of fitting the energies of low-lying atomic states is used to generate the components of semilocal pseudopotentials. This technique is simple and, focusing on low-energy excitations, allows one to obtain pseudopotentials well suited to describe the properties associated with the valence shell. At the same time, it is not well grounded mathematically and is not free from arbitrariness, thus sometimes leading to unexpectedly large errors.[19,22] Numerical parameters of the energy-adjusted relativistic pseudopotentials for elements 111 through 114 and 119 can be found in Refs 30–33. It should be noticed here that the pioneering high-level *ab initio* calculations on polyatomic systems comprising E112 and E114[30,32] were performed with energy-adjusted pseudopotentials. The careful comparative study by Han and Hirao[26] demonstrated that their accuracy in applications to E111-containing molecules can be slightly inferior to that of conventional small-core shape-consistent pseudopotentials[25]; however, not enough data is yet available to draw conclusions.

Apparently a better and more universal way to increase the accuracy of relativistic calculations with small-core pseudopotentials is to use different potentials $u_{lj}(r)$ for outer core and valence shells with the same l and j, thus going beyond the semilocal model (2). This can be done by invoking the generalized relativistic pseudopotential concept (see Refs 19 and 22 and references cited therein), which provides a generalization of the conventional 'shape-consistent' approach. It allows one to attain the highest accuracy of calculated electronic densities in the valence region and chemical and spectroscopic properties when treating outermost core shells explicitly, so that its error is negligible in comparison with those inevitably arising from the approximations used to describe electron correlation. To date, the generalized pseudopotentials were generated only for several SHE (E104, E105, E112–E114); examples of their applications in high-level relativistic molecular calculations can be found in the works by Mosyagin *et al.*[8] and Petrov *et al.*[34]

III. Chemical properties of elements 112 and 114

1. Synthesis and experimental studies.

Element 112 was first produced in 1996 at GSI† (Darmstadt, Germany) by Hofmann *et al.*[35] in a cold-fusion reaction:

$$^{70}\mathrm{Zn} + {}^{208}\mathrm{Pb} \longrightarrow {}^{278}\mathrm{E112}^{*} \longrightarrow {}^{277}\mathrm{E112} + \mathrm{n},$$

$$^{277}\mathrm{E112}\ (\alpha,\ 0.7\ \mathrm{ms}) \longrightarrow {}^{273}\mathrm{E110}\ (\alpha,\ 0.2\ \mathrm{ms}).$$

The synthesis was than confirmed at GSI in 2000 and at RIKEN (Japan) in 2004 by Morita *et al.*[36] The alpha-decay chains from ^{277}112 have been studied using a quantum tunneling model and the results[37] corroborated those obtained at RIKEN and GSI.

† Gesellschaft für Schwerionenforschung (GSI), Helmholtzzentrum für Schwerionenforschung GmbH.

In 1998, the Flerov Laboratory of Nuclear Reactions (FLNR) in collaboration with other research centres started a programme on producing SHE using ^{48}Ca nuclei in 'warm' fusion reactions with actinide targets. The ^{238}U (^{48}Ca,3n) ^{283}E112 reaction was used in their first experiments and as large as 5 min half-life was suggested for the parent isotope decaying by spontaneous fission.[38] However, the further detailed analysis of decay branches at GSI, LBNL and FLNR[39] had led to some uncertainties and the necessity of searching other ways to synthesize the ^{283}E112 isotope.

In April–May 2006 in Dubna, a FLNR–PSI (the Paul Scherrer Institute, Switzerland) team performed experiments probing the synthesis of ^{283}E112 as a daughter in the nuclear reaction ^{242}Pu (^{48}Ca,3n) ^{287}E114. The on-line thermochromatography studies of the reactivity of E112 were focused on the adsorption of E112 atoms on a gold surface held at temperatures from $+35$ °C to -190 °C in comparison with that of Hg (which was deposited on the warmest plates) and Rn (which was deposited on the coldest plates).[5] In this experiment, two ^{283}E112 atoms were unambiguously identified and the adsorption properties showed that E112 is a more volatile homologue of mercury, but definitely not an inert gas (whereas the analysis of the data obtained in experiments in 2003–2005 indicated that E112 had noble-gas properties). In April 2007, this experiment was repeated and further 3 atoms of ^{283}E112 were identified. The result of 2006 was confirmed and indicated that the adsorption properties of element 112 are in perfect agreement with those expected for the heaviest member of Group 12.[40] In the further experiments with ^{244}Pu, the long-living ^{284}E112 and ^{285}E112 were also produced.

The obtained parent isotopes, ^{287}E114, ^{288}E114 and ^{289}E114 were also studied in a gas thermochromatographic experiment in 2007–2008 showing a surprisingly inert behaviour of E114 compared to E112 (three events of the E114 nucleus decay were found at about -80 °C), which was in contradiction with the known theoretical data on the interactions of E114 with metal atoms including gold.[41]

2. Properties of free atoms

Much information on the chemical properties of E112 and E114 can be extracted from the results of calculations on free atoms and atomic ions. A detailed study of the atomic ground, excited and ionized states of E112 and E114 by highly accurate relativistic *ab initio* many-body techniques as well as the exhaustive bibliography of earlier calculations is presented in Refs 42–44. Certain qualitative conclusions concerning the differences between these elements and their lighter homologues can be drawn from a simple one-electron picture that can readily be obtained by the relativistic Hartree–Fock (Dirac–Fock) method (Fig. 1). On passing from the 6th row elements to the transactinides, an increase in relativistic contraction and the stabilization of s-shells is observed. A remarkable property of the one-electron picture for element 114 is the huge spin-orbit splitting of the valence 7p level; the $7p_{3/2}-7p_{1/2}$ gap is at least three times larger than its $6p_{3/2}-6p_{1/2}$ counterpart for Pb and the doubly degenerate $7p_{1/2}$ level is significantly lower than the $6p_{1/2}$ level in Pb. Thus, one might expect that the closed-shell configurations of E112 ($[...]6d^{10}7s^2$) and E114 ($[...]6d^{10}7s^27p_{1/2}{}^2$) are extremely stable; indeed, accurate *ab initio* calculations show that the first ionization potentials for these SHE and the lowest excitation energy (which is usually interpreted by chemists as 'promotion

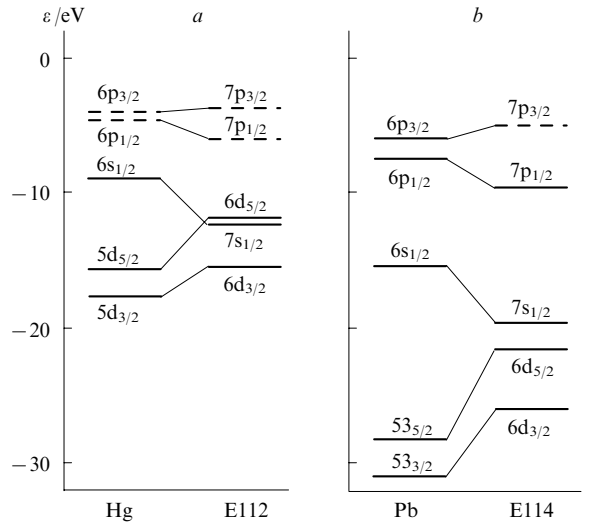


Figure 1. One-electron relativistic Hartree–Fock energies (ε) for free Hg, E112 (*a*), Pb and E114 atoms (*b*).

energy') for E114 are significantly larger than the corresponding quantities for their lighter homologues (Table 1). Many years ago this observation gave rise to the hypothesis of the rare-gas-like behaviour of E112 and E114 (Ref. 4), the hypothesis concerning E114 become popular after the series of thermochromatographic experiments.[12, 13]

Table 1. Ionization potentials (IP) and lowest excitation energies (EE) of free Hg, eka-Hg, Pb, and eka-Pb atoms (eV).

Hg		E112 (calculated)	Pb		E114 (calculated) [a]
experiment	calculated		experiment	calculated [a]	
Ionization potentials					
10.44	10.45 [b]	11.97 [b]	7.42	7.35	8.54
Excitation energies					
4.67	4.68 [c]	4.44 [c]	0.97	0.93	3.27

[a] From Ref. 43, [b] from Ref. 42, [c] from Ref. 44

The (sub)valence $d_{3/2}$ levels of SHE atoms are markedly destabilized in comparison with that in the sixth-row elements. In E112, one-electron energy associated with these spinors is higher than the 7s energy; in contradistinction to Hg^+, the ground state configuration of $E112^+$ is d^9s^2 rather than $d^{10}s^1$ (Ref. 42). This feature suggests the transition-metal-like behaviour of E112 in certain situations.

In spite of the stabilization of the $7p_{1/2}$ level of E114, the $7s-7p_{1/2}$ energy gap is much wider than the $6s-6p_{1/2}$ gap in lighter homologues, so that we may presume that the oxidation number +4 should not be readily accessible for this element.

3. Molecular and cluster calculations

Numerous relativistic electronic structure calculations for molecular systems [6–11, 29, 30, 34] along with the experimental data allowed one to reject the hypothesis of the rare-gas-like nature of E112 revealing a certain analogy between the chemical behaviour of this element and mercury. The most accurate calculations employing the small-core generalized pseudopotential model and the relativistic coupled cluster technique with extensive basis sets has been performed for the smallest eka-mercury-containing molecule, E112H. The results obtained [8, 9] suggest that the chemical bond in this molecule should be at least as strong as (and much shorter than) the Hg–H bond in the corresponding diatomic. These studies have also demonstrated the crucial role of the proper account for the spin-dependent relativistic effects in the chemistry of E112, while this is formally considered as an s element; the scalar relativistic approximation failed to properly describe the E112–H bond.[9, 45]

Since successful experiments on the chemical identification of E112 (Ref. 5) have employed thermochromatography on the gold surface, theoretical modeling of E112–Au chemical bonding was of particular interest. Fig. 2 *a* presents the Hg–Au and E112–Au interaction energies in diatomic species as functions of internuclear separations. These data were obtained within the accurate shape-consistent pseudopotential model optimized for the description of valence shells;[9, 19] the non-collinear relativistic DFT technique [46] with the non-empirical hybrid exchange-correlation functional PBE0 [47] was used to solve the many-electron problem. The shapes of the two curves do not differ strongly; E112–Au bond is somewhat longer and weaker than the Hg-Au bond. Other relativistic *ab initio* and DFT calculations [6, 9, 48] yield qualitatively similar pictures. A remarkable similarity of the equilibrium structures of $Hg-Au_n$ and $E112-Au_n$ complexes with $n \leqslant 4$ has been demonstrated.[10] For instance, both $HgAu_2$ and $E112Au_2$ were predicted to be linear and all low-energy structures for $n = 3$ and 4 to be planar. The deformation of the Au clusters upon the attachment of Hg (eka-Hg) is never strong. The E112–Au bonds are always slightly longer (by 0.05–0.09 Å) than the corresponding Hg–Au bonds. The $E112-Au_n$ binding energies ranging from 0.39 to 0.47 eV comprise 68%–75% of the corresponding values for $HgAu_n$. Extrapolating this ratio to larger systems and making use of the experimental adsorption energy of Hg on Au surface, one can derive an estimate of E112/gold

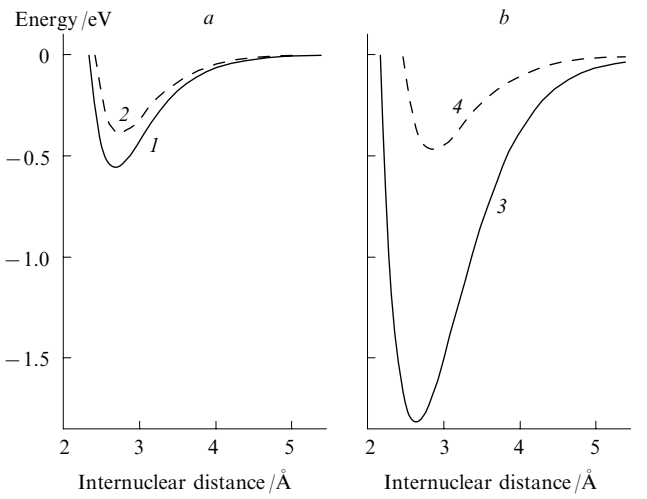


Figure 2. Interaction energies of Hg, E112 (*a*), Pb and E114 (*b*) atoms with Au in diatomic molecules.
(*1*) HgAu, (*2*) E112Au, (*3*) PbAu, (*4*) E114Au.

adsorption energy (*ca*. 0.7 eV), which is compatible with the experimental results.[5]

At the moment, a comparison of pseudopotential studies on the interaction of eka-Hg with gold atoms and clusters with results from the corresponding all-electron calculations is necessarily restricted to DFT methods. This comparison [see, *e.g.*, fully relativistic ('four-component') DFT studies (Ref. 11 and references cited therein) and a recent review [14]] shows general agreement, quantitative differences arise mainly from the use of different approximations for exchange-correlation functionals; furthermore, early all-electron calculations [6] were affected by the basis set restriction errors.

The studies of interactions with non-metals generally confirm that E112 is a true homologue of mercury. Early calculations of eka-Hg fluorides by the scalar relativistic coupled cluster method with configuration–interaction corrections for spin-orbit effects [30] predict the existence of both $E112F_2$ and $E112F_4$ somewhat resembling the corresponding mercury fluorides (see Ref. 49 for the experimental observation of HgF_4). While $E112F_2$ is markedly less stable than HgF_2, $E112F_4$ is expected to be much more stable with respect to the abstraction of F_2 in comparison with mercury tetrafluoride. The latter fact can be interpreted as a manifestation of the transition-element nature of eka-Hg.

It is generally assumed that the use of DFT-based methods in studies of weak van-der-Waals interactions is at least risky; this determines the particular importance of the pseudopotential models enabling one to focus on the description of the outer electronic shells and to make use of high-level many-body correlation techniques without catastrophic computational expenses. The coupled cluster/pseudopotential calculations on the dimer of E112 have shown [29, 34] that the van-der-Waals radius of eka-Hg is smaller, and the bond in the dimer is stronger, than those in Hg_2. It might be worth noting here that, according to relativistic pseudopotential calculations by Gaston *et al.*[50] the cohesive energy of solid element 112 is slightly larger than that of mercury and an order of magnitude larger than those of solid noble gases.

Electronic structure simulation shows that, in agreement with the qualitative argumentation based on the atomic one-electron picture, the Pb–E114 homology appears to be much more formal than the Hg–E112 one; there is no doubt that E114 is a rather inert element and the difference between its chemical properties and those of lead are much more pronounced than the difference between the properties of E112 and mercury. An illustration concerning the important case of E114–Au interactions is given in Fig. 2*b*: the difference between E114–Au and Pb–Au interaction energy functions is huge and the E114–Au bond energy in the diatomic molecule is only 1/3–1/4 of the Pb–Au bond energy.

To give more insight into the interactions of eka-lead with gold, we calculated equilibrium structures and energies of small E114–Au_n complexes using the non-collinear two-component relativistic DFT and accurate semilocal small-core shape-consistent pseudopotentials cited above. Two different approximations for the exchange-correlation functional were employed: the Becke–Perdew functional B88P86 (Refs 51 and 52) with the VWN5 expression for the local correlation energy density [53] and the PBE0 hybrid functional.[47] Both approximations predict the linear (E114–Au–Au) structure for the most stable complex

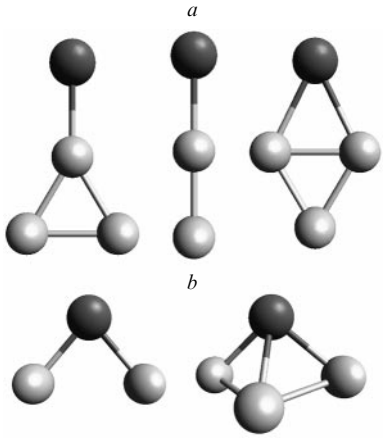


Figure 3. Low-energy structures of the complexes 114–Au_n (*a*) and Pb–Au_n (*b*).
$n = 2, 3$.

with $n = 2$ and the existence of two low-energy planar isomers for E114–Au_3, which can be considered as the E114 atom 'adsorbed' on the stable (D_{3h}) isomer of Au_3. No resemblance with the corresponding complexes of Pb can be found (see Fig. 3): calculations within the same approximation predict that the minimum energy configuration of $PbAu_2$ is an isosceles triangle and that the $PbAu_3$ equilibrium structure is non-planar (strongly deformed tetrahedron with C_s symmetry). Furthermore, the deformations of the Au_2 and Au_3 clusters upon attachment of an eka-lead atom are moderate (the changes in Au–Au bond lengths do not exceed 0.02 Å for $n = 2$ and 0.06 Å for $n = 3$), whereas the equilbrium Au–Au distance in $PbAu_2$ is about 1 Å longer than that in Au_2, *i.e.*, the Au–Au bond is to a certain degree broken. The formation of the $PbAu_3$ complex is accompanied by at least partial cleavage of one of the three Au–Au bonds (equilibrium distance increases by 1.4 Å). The deformation of the Au_n fragment can be considered as a measure for the strength of a covalent bond between Au_n and the adatom, so this finding is consistent with the binding energy estimates that are about 2–2.5 eV for Pb complexes and below 0.8 eV for their eka-Pb containing counterparts. To summarize, the differences between the interactions of Pb and eka-Pb with gold clusters are really dramatic, and one should not hope to exploit the homology for extracting an estimate for the E114–Au adsorption energy from the corresponding experimental value for Pb and the results of the comparative analysis of $PbAu_n$ and $E114Au_n$ based on the homology concept, as is done for eka-mercury.[10, 11]

In contrast, the equilibrium geometries found for the mentioned complexes of E114 exhibit striking similarity with those for another closed-shell SHE atom, E112, and mercury. Moreover, $E114Au_n$ and $E112Au_n$, $n = 2$ and 3, are characterized by comparable SHE detachment energies. These facts, as well as the conditions of experimental studies (in most experiments, E114 and E112 belong to the same decay chain) seem to indicate the usefulness of the direct comparison E112–Au_n *vs.* E114–Au_n in the cluster simulation of SHE adsorption on the gold surface.

In Table 2 we summarize the results of cluster simulation of E112 and E114 adsorbed on the (100) surface of an Au crystal. These results were obtained using the same relativistic electronic structure model as above; it is worth-

Table 2. SHE atom detachment energies (eV) for $E112Au_n$ and $E114Au_n$ complexes simulating the SHE adsorbed on the (100) surface of Au.

'Bridge' position						'Hollow' position					
n	the number of Au atoms in layers	B88P86		PBE0		n	the number of Au atoms in layers	B88P86		PBE0	
		E112	E114	E112	E114			E112	E114	E112	E114
8	6+2	0.39	0.56	0.45	0.50	9	4+5	0.14	0.33	0.15	0.24
16	8+6+2	0.33	0.55	0.39	0.45	13	4+5+4	0.57	0.68	0.64	0.57
26	12+8+4	0.33	0.55	0.39	0.49	25	12+9+4	0.33	0.50	0.36	0.40

Note. The structures of the Au clusters are depicted by the numbers k, l, m of atoms in the first (surface), second and (for larger clusters) third layer, respectively, as $k+l+m$.

while noting that the use of the pseudopotential approach enabled us to practically exclude the problem of basis set truncation errors (the employed uncontracted Gaussian bases appear to be nearly saturated at the DFT level). Since the relaxation effects upon the formation of surface complexes are expected to be negligible for both superheavy atoms (*cf*. Ref. 10), the Au–Au distances in the clusters were always kept at their bulk values. Three types of SHE adatom positions on the surface, mono-coordinate ('on-top'), two-coordinate ('bridge'), and four-coordinate ('hollow'), were considered; in each case, only the distance between the surface and the adatom was optimized. A detailed study of 'on-top' complexes was skipped since the corresponding SHE detachment energies were found to be significantly smaller than those for 'bridge' and 'hollow' coordination.

In spite of certain quantitative differences between the results obtained with the two approximate exchange-correlation functionals, one can notice that the detachment energies for eka-lead are in the same range as, and normally somewhat larger than, for eka-Hg. At first glance, this conclusion disagrees with the results of the thermochromatographic experiments performed in FNLR.[12,13] However, one should not forget that all of the studied clusters are far too small for the quantitative simulation of bulk metal properties. One should also take into account that the present model by construction describes an ideal surface; the role of various defects in increasing the measured adsorption energy can be important and different for the two SHE. Nevertheless, on the basis of our calculations we must refute the hypothesis of rare-gas-like chemical behaviour of E114.[12,13] Our conclusions essentially coincide with that drawn from the results of very recent all-electron four-component DFT calculations.[54]

The evidences for the relative chemical inertness of eka-Pb in comparison with Pb and essential differences in the chemical behaviour of these two elements are obviously not restricted to the case of their interaction with gold; let us refer to the review[14] and cite here only a couple of examples. The dissociation energies for eka-lead monohalides and monooxide seem to be always smaller than the halved values for the corresponding Pb compounds.[27] Detailed electronic structure calculations of hydrides, fluorides and chlorides of eka-Pb (Ref. 32) appear to confirm the impossibility of involving the 7s shell of E114 into the bond formation, suggesting the instability of oxidation number +4 readily accessible for lead. However, none of the results of high-level *ab initio* or DFT calculations within the relativistic pseudopotential or all-electron model give evidence for the true chemical inertness similar to that of rare gases.

IV. Conclusion

The relativistic pseudopotential approach gives rise to universal and computationally efficient tools for electronic structure calculations on superheavy-element compounds featuring the strongest effect of relativity in chemistry. A somewhat suspicious stratagem consisting of the replacement of the conventional relativistic many-electron problem by a formally non-relativistic problem for a much smaller number of electrons, boxing up all information on the effects of relativity into spin-dependent one-electron pseudopotential operators, seems to lead to full success. Advanced pseudopotential models leaving both valence and outer core electronic shells for explicit treatment (small-core pseudopotentials) are capable of ensuring 'chemical' accuracy for most chemical properties of compounds including the 'hyper-relativistic' case of SHE, so that the errors arising from the use of approximate methods for solving the electron correlation problem are always much larger than those stemming from the pseudopotential approximation itself. Bearing nearly exhaustive information concerning the effects of relativity on chemically active electronic shells, pseudopotentials can also properly account for finite nuclear charge distributions, which are of particular importance for SHE.

Because of the presence of spin-dependent one-electron operators (effective spin-orbit potentials), the outer core/valence effective Hamiltonians used within the relativistic pseudopotential approach have much lower symmetry than the conventional non-relativistic (or scalar relativistic) Hamiltonians; the most important feature is the lack of the spin symmetry efficiently used to reduce computational efforts in the scalar-relativistic and non-relativistic cases. For superheavy elements, the amplitudes of the effective spin-orbit interactions are huge (this corresponds to very large spin-orbit splittings in atoms), and non-relativistic symmetry usually cannot be efficiently exploited even as an approximate one. This fact gives rise to several conceptual and computational difficulties; let us cite here the problem of formulating the spin density functional theory and a very limited usability of the spinorbital (one-component spinor) representation. Briefly speaking, the use of relativistic pseudopotentials does not make the simulation of superheavy element compounds as simple as that of lighter elements.

Electronic structure calculations employing accurate small-core pseudopotential models, along with all-electron

calculations and experimental studies, have given some insight into the chemistry of eka-mercury and eka-lead. One can affirm that the chemical behaviour of eka-Hg should exhibit certain similarity with that of mercury, though eka-Hg is generally somewhat more inert and its transition-metal-like features are more apparent. The properties of E114 and its lighter homologue, Pb, seem to differ much more; the former element is quite inert while the latter is a typical metal. This is readily explained by the specific closed-shell structure of the E114 atom associated with the huge spin-orbit splitting of the valence p-shell and apparently having no analogues in the Periodic Table. At the same time, numerical simulation does not confirm the hypothesis of the rare-gas-like chemical behaviour of E114.

The data reviewed above confirm that the variation of p-element properties within the seventh row should differ significantly from that in the previous rows because of the predominant role of spin-dependent relativistic effects (spin-orbit interactions) in SHE. Going from 112 to 114, a distinct part of the period is closed with the full occupation of the $7p_{1/2}$ subshell strongly separated in energy from the $7p_{3/2}$ one, and the next part associated with the filling of the $7p_{3/2}$ subshell extends to E118.

Let us finally notice that the differences in the chemical properties of SHE and their lighter homologues should not be directly associated with the effects of relativity. One should also bear in mind the increase in the main quantum number of the outer electronic shell on going from the sixth to the seventh row. It is the relativistic contraction that largely counterpoises the expansion of the electron charge distribution upon the addition of a new electronic shell, thus in a sense reducing the difference in the properties of E112 and Hg.

Thanks are due to Valeria Pershina and Elena Rykova for critical reading the manuscript. The work was partially supported by the Russian Foundation for Basic Research (Project Nos 07-03-01139 and 09-03-00655).

References

1. M Schädel *Angew. Chem., Int. Ed.* **45** 368 (2006)
2. Yu Oganessian *J. Phys. G: Nucl. Phys.* **34** R165 (2007)
3. Yu Ts Oganessian *Eur. Phys. J., D* **45** 17 (2007)
4. K S Pitzer *J. Chem. Phys.* **63** 1032 (1975)
5. R Eichler, N V Aksenov, A V Belozerov, G A Bozhinkov, V I Chepigin, S N Dmitriev, R Dressler, H W Gäggeler, V A Gorshkov, F Haenssler, M G Itkis, A Laube, V Ya Lebedev, O N Malyshev, Yu Ts Oganessian, O V Petrushkin, D Pigguet, P Rasmussen, S V Shishkin, A V Shutov, A I Svirikhon, E E Tereshatov, G K Vostokin, M Wegrzecki, A V Eremin *Nature (London)* **447** 72 (2007)
6. V Pershina, T Bastug, T Jacob, B Fricke, S Varga *Chem. Phys. Lett.* **365** 176 (2002)
7. V Pershina, T Bastug, C Sarpe-Tudoran, J Anton, B Fricke *Nucl. Phys. A* **734** 200 (2004)
8. N S Mosyagin, T A Isaev, A V Titov *J. Chem. Phys.* **124** 224302 (2006)
9. A Zaitsevskii, E Rykova, N S Mosyagin, A V Titov *Cent. Eur. J. Phys.* **4** 448 (2006)
10. E A Rykova, A Zaitsevskii, N S Mosyagin, T A Isaev, A V Titov *J. Chem. Phys.* **125** 241102 (2006)
11. C Sarpe-Tudoran, B Fricke, J Anton, V Persina *J. Chem. Phys.* **126** 174702 (2007)
12. S N Dmitriev, N V Aksenov, A V Belozerov, G A Bozhikov, V I Chepigin, R Dressler, R Eichler, H W Gäggeler, V A Gorshkov, R A Henderson, M G Itkis, A M Johnsen, J M Kenneally, V Ya Lebedev, O N Malyshev, K J Moody, Yu Ts Oganessian, O V Petrushkin, D Piguet, A Popeko, D A Shaughnessy, S V Shishkin, A V Shutov, M A Stoyer, N J Stoyer, A I Svirikhin, E E Tereshatov, G K Vostokin, M Wegrzecki, P A Wilk, A V Yeremin, in *The 3rd International Conference on the Chemistry and Physics of the Transactinide Elements (TAN07). (Book of Abstracts), Davos, Switzerland, 2007* p. 22
13. S N Dmitriev, in *The 7th International Conference on Nuclear and Radiochemistry (NRC7) (Book of Abstracts), Budapest, 2008* p. 264
14. A V Zaitsevskii, E A Rykova, A V Titov *Usp. Khim.* **77** 211 (2008) [*Russ. Chem. Rev.* **77** 205 (2008)]
15. Y S Lee, W C Ermler, K S Pitzer *J. Chem. Phys.* **67** 5861 (1977)
16. C Teichteil, M Pelissier, F Spiegelmann *Chem. Phys.* **81** 273 (1983)
17. Y S Lee, in *Relativistic Electronic Structure Theory* Vol. 2 (Ed. P Schwerdtfeger) (Amsterdam: Elsevier, 2004) Pt. 2, p. 352
18. P Schwerdtfeger, in *Theoretical Chemistry and Physics of Heavy and Superheavy Elements* (Eds U Kaldor, S Wilson) (Dordrecht: Kluwer Academic, 2003) p. 399
19. N S Mosyagin, A N Petrov, A V Titov, I I Tupitsyn, in *Recent Advances in the Theory of Chemical and Physical Systems* (Eds J P Julien, J Maruani, D Mayou, S Wilson, G Delgado-Barrio) (Dordrecht: Springer, 2006) p. 229
20. *Relativistic Electronic Structure Theory. Applications* (Ed. P Schwerdtfeger) (Amsterdam: Elsevier, 2004) Pt. 2
21. A N Petrov, N S Mosyagin, A V Titov, I I Tupitsyn *J. Phys. B* **37** 4621 (2004)
22. A V Titov, N S Mosyagin *Int. J. Quantum Chem.* **71** 359 (1999)
23. K Dyall *J. Chem. Inf. Comput. Sci.* **41** 30 (2001)
24. P A Christiansen, Y S Lee, K S Pitzer *J. Chem. Phys.* **71** 4445 (1979)
25. C S Nash, B E Bursten, W C Ermler *J. Chem. Phys.* **106** 5133 (1997)
26. Y K Han, K Hirao *Chem. Phys. Lett.* **328** 453 (2000)
27. W Liu, C van Wüllen, Y K Han, Y J Choi, Y S Lee *Adv. Quantum Chem.* **39** 325 (2001)
28. Y J Choi, Y S Lee *J. Chem. Phys.* **119** 2014 (2003)
29. C S Nash *J. Phys. Chem. A* **109** 3493 (2005)
30. M Seth, P Schwerdtfeger, M Dolg *J. Chem. Phys.* **106** 3623 (1997)
31. M Seth, P Schwerdtfeger, K Fægri *J. Chem. Phys.* **111** 6422 (1999)
32. M Seth, K Fægri, P Schwerdtfeger *Angew. Chem., Int. Ed.* **37** 2493 (1998)
33. I Lim, M Pernpointner, M Seth, P Schwerdtfeger, P Neogrady, M Urban *Phys. Rev. A* **60** 2822 (1999)
34. A N Petrov, N S Mosyagin, A V Titov, A V Zaitsevskii, E A Rykova *Phys. Atom. Nucl.* **72** 396 (2009)
35. S Hofmann, V Ninov, F P Hessberger, P Armbruster, H Folger, G Münzenberg, H J Schött, A G Popeko, A V Yeremin, S Saro, R Janik, M Leino *Z. Phys. A* **354** 229 (1996)
36. K Morita, K Morimoto, D Kaji, S Goto, H Haba, E Ideguchi, R Kanungo, K Katori, H Koura, H Kudo, T Ohnishi, A Ozawa, J C Peter, T Suda, K Sueki, I Tanihata, F Tokanai, H Xu, A V Yeremin, A Yoneda, A Yoshida, Y L Zhao, T Zheng *Nucl. Phys. A* **734** 101 (2004)
37. C Samanta, D N Basu, P R Chowdhury *J. Phys. Soc. Jpn.* **76** 124201 (2007)
38. Yu Ts Oganessian, A V Yeremin, G G Gulbekian, S L Bogomolov, V I Chepigin, B N Gikal, V A Gorshkov, M G Itkis, A P Kabachenko, V B Kutner, A Yu Lavrentev, O N Malyshev, A G Popeko, J Roháč, R N Sagaidak, S Hofmann, G Münzenberg, M Veselsky, S Saro, N Iwasa, K Morita *Eur. Phys. J., A* **5** 63 (1999)

39. W Loveland, K E Gregorich, J B Patin, D Peterson, C Rouki, P M Zielinski, K Aleklett *Phys. Rev. C* **66** 044617 (2002)
40. R Eichler, N V Aksenov, A V Belozerov, G A Bozhikov, V I Chepigin, R Dressler, S N Dmitriev, H W Gäggeler, V A Gorshkov, F Haenssler, M G Itkis, V Y Lebedev, A Laube, O N Malyshev, Yu Ts Oganessian, O V Petruschkin, D Piguet, P Rasmussen, A Serov, S V Shishkin, A V Shutov, A I Svirikhin, E E Tereshatov, G K Vostokin, M Wegrzecki, A V Yeremin *Angew. Chem., Int. Ed.* **47** 3262 (2008)
41. V Pershina, J Anton, B Fricke *J. Chem. Phys.* **127** 134310 (2007)
42. E Eliav, U Kaldor, Y Ishikawa *Phys. Rev. A* **52** 2765 (1995)
43. A Landau, E Eliav, Y Ishikawa, U Kaldor *J. Chem. Phys.* **114** 2977 (2001)
44. T H Dinh, V A Dzuba, V V Flambaum *Phys. Rev. A* **78** 062502 (2008)
45. T Nakajima, K Hirao *Chem. Phys. Lett.* **329** 511 (2000)
46. A V Mitin, C van Wüllen *J. Chem. Phys.* **124** 064305 (2006)
47. C Adamo, V Barone *J. Chem. Phys.* **110** 6158 (1999)
48. C Sarpe-Tudoran, V Pershina, B Fricke, J Anton, W-D Sepp, T Jacob *Eur. Phys. J., D* **24** 65 (2003)
49. X Wang, L Andrews, S Riedel, M Kaupp *Angew. Chem., Int. Ed.* **46** 837 (2007)
50. N Gaston, I Opahle, H W Gäggler, P Schwerdtfeger *Angew. Chem., Int. Ed.* **46** 1663 (2007)
51. A D Becke *Phys. Rev. A* **38** 3098 (1988)
52. J P Perdew *Phys. Rev. B* **33** 8822 (1986)
53. S H Vosko, L Wilk, M Nuisar *Can. J. Phys.* **58** 1200 (1980)
54. J Anton, T Jacob, V Pershina *GSI Annual Report 2008* (Darmstadt: GSI, 2009)