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Theoretical studies on the structures and properties of superheavy element compounds

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Abstract. An analysis of theoretical studies on the electronic structures and chemical properties of superheavy elements has been performed. It is noted that the specific features of calculations of molecular systems including superheavy element atoms are determined by the exceptional role of relativistic effects that should be taken into account at all stages of electronic structure modelling. The main approximations for relativistic Hamiltonians and general approaches to the solution of the many-electron problem for both superheavy element atoms and their compounds have been considered and compared. The results of modelling the chemical properties of superheavy elements by *ab initio* methods and density functional theory have been analysed. The bibliography includes 143 references.

I. Introduction

Recently, new superheavy elements (SHE) with atomic charges of $Z = 114$, 115, 116 and 118 have been synthesised in the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research (Dubna).[1–4] Of special interest were the registration and attempts at chemically identifying relatively long-living isotopes of these elements.[3,5] The lifetimes of the known SHE isotopes reach several seconds (^{283}E112), hours (^{267}Rf), and even days (^{268}Db); it is believed that the lifetimes of nuclei in the vicinity of the top of the 'island of stability' (Z = 114, N = 184) will range, in different estimates,[6–9] from 10^3 to 10^9 years. In addition to their fundamental importance for atomic physics and radiochemistry, studies of the properties of superheavy elements are of considerable interest for a number of other disciplines,[10] in particular, astrophysics [11] and meteoritic astronomy;[12] the possibility of their existence in nature is discussed in scientific literature.[13]

At present, superheavy elements are most reliably identified by gas and liquid chromatography and extraction, studies in solutions, *etc*.[14,15] However, the experimental investigation of their chemistry is difficult and labourious. Difficulties are due to the short lifetimes and small cross-sections of SHE formation in atomic reactions, because of which the amounts of substances available to analysis are very small; in many cases, individual atoms (atoms-at-a-time) are available. No wonder that the results of experiments are often ambiguous and sometimes contradictory. Since there is a good reason to assume that SHE significantly differ from their lighter analogues in valence structure and properties,[5,16,17] the most important source of information on the SHE chemistry are quantitative quantum mechanical calculations of the electronic structure of their compounds.

In the theoretical description of the electronic structures of molecular systems including SHE atoms, one should take into account the following features:

1. Relativistic effects (including spin-dependent interactions) cannot be treated as small corrections. Thus neglecting these effects leads to the overestimation of the calculated atomic radius of E112 by more than 40%, non-relativistic estimate of the atomic ionisation potential of this element is 4.2 eV lower than the relativistic one (the non-relativistic theory in this case incorrectly predicts the ground-state configuration of the ion) and the spin – orbit splitting of the 6d level, disappearing in the non-relativistic limit, exceeds 3 eV. According to the estimate,[18] the contribution of relativistic effects to the atomisation energy of the HsO_4 molecule is more than 9 eV. An important consequence is that high non-relativistic symmetry cannot be exploited in calculations (at least at all stages). Further, one cannot neglect the finite size of the atomic nucleus.

2. Electron correlation effects are of crucial importance. For example, the neglect or insufficiently exact description of these effects leads to the incorrect prediction of the type of the ground state of the Rf atom ([...]$7s^26d6p\ ^3D_2$ instead of

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[...]$7s^26d^2\ {}^3F_2$).[19] The chemical bond in the E112Au system (dissociation energy is of about 0.4 eV) is entirely determined by correlation effects,[20] their neglecting in modelling the structure of this system leads to the incorrect prediction of the non-bound character of the ground electronic term. As a result of the relativistic stabilisation of s-shells, one-electron energies 7s and 6d are close to each other (including those in elements with the filled 6d shell in the ground-state configuration), so that 6d electrons should be treated as valence electrons. At the same time, the regions of the spatial localisation of the 6d and outer core 6p shells strongly overlap, so that the correlation of 6d and 6p electrons significantly affects the properties associated with the valence shell. Therefore, to obtain the quantitative characteristics of chemical bonds in SHE compounds, one should correlate a rather large number of electrons. This particularly means that calculation schemes should, at least qualitatively, correctly describe the dependence of the system energy on the number of electrons (that is, should be 'size-extensive').

3. Because of the significance of both correlation and relativistic effects, one should not neglect their mutual influence (interference).

In view of the aforesaid, direct calculations on the properties of complex systems, which are of the particular practical interest from the viewpoint of present-day methods of chemical identification of SHE (for example, systems modelling an atom on the surface of a solid, complex ion in solution, *etc.*), cannot currently be performed using highly accurate *ab initio* methods. At the same time, such calculations of simpler systems have already been the major source of information on the properties of SHE, the nature of their chemical bonds with various elements and qualitative differences between SHE and their lighter analogues. In addition, in the lack of quantitative experimental data on SHE compounds, the results of precise calculations on small molecules and molecular ions offer a unique possibility of calibrating and testing the reliability of simpler methods for the description of the electronic structure, first of all, versions of the relativistic density functional theory, which is now the basic technique for modelling complex polyatomic structures (including those incorporating SHE atoms).

Of critical importance for the organisation of quantum mechanical calculations with realistic requirements for computer resources is the optimum and balanced choice of the following issues:

— models of particle interaction in an atom or a molecule, *i.e.*, of effective relativistic Hamiltonians (we recall that the exact expression for the many-electron relativistic Hamiltonian does not exist);

— an approximation of such Hamiltonian with a set of amplitudes (molecular integrals) by introducing a sufficiently complete finite set of one-electron basis functions (note that not all methods of the electronic structure theory require the transition to this representation);

— the scheme for solving the many-electron problem with the chosen Hamiltonian.

This paper considers theoretical studies on the chemical properties of SHE from the viewpoint of the comparative analysis of the methods used. Over the decade passed since the previous attempt has been made to give the overall picture of similar investigations,[21] their character has significantly changed: the main source of quantitative information on SHE chemistry today is the direct computational modelling of their compounds. In the recent reviews, primary attention was paid to experimental data [14, 15, 22] or specific approaches to quantum mechanical calculations of atoms and SHE compounds.[23, 24] New research into the chemistry of E112 (Refs 20, 25–27) and E114 (Ref. 5) were not reflected in the above reviews.

Section II describes basic models for relativistic Hamiltonians used in calculations on superheavy atoms and their molecules and the specific features of methods used to solve the relativistic many-electron problem; their knowledge is compulsory for assessing the reliability of the results of quantum mechanical calculations and predictions concerning the properties of SHE. A summary of these results and their short analysis are presented in Section III.

II. Relativistic many-electron Hamiltonians and methods for solving the many-electron problem

Let us start the consideration of the basic approximations for relativistic Hamiltonians used in the present-day electronic structure calculations of SHE compounds with those formulated within the four-component spinor representation, conventional for relativistic quantum mechanics. Provided that the standard form of the Dirac equation is used, the first and the second components in the non-relativistic limit are transformed to conventional spatial parts of spin-up and spin-down spinorbitals while the other (small) components disappear.

The Dirac–Coulomb Hamiltonian (see, for example, Ref. 28). The kinetic energy of each electron and its interaction with the nuclei are described by the Dirac Hamiltonian for a particle in an electrostatic field; the electron–electron interaction coincides with the conventional Coulomb repulsion. Taking into account the high speeds of electrons in the vicinity of SHE nuclei, one can readily realise that this non-relativistic model of electron–electron interaction is a rather rough approximation. Note that, at the stage of constructing the nuclear electrostatic potential, one can take into account the effects of finite nuclear sizes, which are of particular importance for SHE.

The Dirac–Coulomb–Breit Hamiltonian. Magnetic interactions of electrons and the effects of the finite velocity of electromagnetic field propagation (retardation effects) are additionally taken into account. These effects are described by rather sophisticated quantum mechanical operators.[28, 29] The Dirac–Coulomb–Breit model ensures sufficient accuracy of calculations for most physical and chemical properties of SHE compounds.

Problems with the direct modelling of the bound many-electron energy levels arising from the dissolution of these levels in the continuum of mixed electron–positron states (the Brown–Ravenhall disease [30]) are the common feature of the mentioned Hamiltonians. These problems are avoided using a stratagem equivalent to the prohibition of the creation of electron–positron pairs in quantum electrodynamics (no-pair approximation).

In addition to the huge number of variables (electron coordinates) and the presence of four components in the spinors, difficulties with directly solving the many-electron problem for the molecules of SHE compounds stem from several specific problems that have no analogues in non-relativistic quantum mechanics. These include:

— variational collapse, *i.e.*, dramatic lowering of energy estimates in finite basis set calculations, which can be eliminated by the introduction of the derivatives of large-component basis functions with respect to spatial coordinates into the basis for small components (maintaining the kinetic balance);

— pseudo-variational collapse, *i.e.*, strong distortions of the relative positions of energy levels at the insufficiently accurate description of the effects of spin – orbit interactions on the core electron shells.[31]

Quasirelativistic effective Hamiltonians. The technique of eliminating the small component from explicit treatment is widely used in the relativistic quantum mechanics of molecules. The methods employing this technique are referred to as quasirelativistic or two-component methods. Many-electron Hamiltonians in quasirelativistic approaches are represented by effective operators[32] in subspaces spanned by the Pauli spinors (spinors for which only large components are non-zero). The transformation of full Hamiltonians to their effective counterparts results in considerable formal complications. The most popular methods of constructing quasirelativistic effective Hamiltonian, the regular approximation technique and the Douglas – Kroll transformation, are described.[33 – 37]

The rapid increase in the efficiency of four-component computational methods was observed in the last years;[38, 39] as a result, quasirelativistic approximations gradually loose their importance as independent models of molecular electronic structure. The practical importance of techniques implying the transformation to two-component spinors relates mainly to the theory of relativistic core pseudopotentials.

Relativistic core pseudopotential model. The possibilities of applying the above many-electron Hamiltonians to electronic structure studies on SHE compounds in the nearest future are restricted because of extremely high computational expenses. The approaches based on the relativistic core pseudopotential (effective potential) model seem to be more promising. The many-electron problem for all electrons of a molecule is replaced by that for a subsystem of valence electrons with the effective Hamiltonian acting within the space of two-component spinors. The kinetic energies of valence electrons and interactions between them are represented by the same operators as in non-relativistic quantum mechanics, while the interactions of these electrons with the nuclei and core shells are described by one-electron pseudopotential operators. The latter operators bear all information about relativistic effects including that on magnetic and retarded interactions between the valence and core electrons and on finite nuclear sizes.[40] The information about the deviation of effective interactions between the valence electrons from the non-relativistic Coulomb repulsion is lost; however, the resulting errors are of no importance for most applications in the quantum chemistry of SHE. We would like to stress that the meaning of the term 'valence electrons' does not always coincide with that accepted by chemists. To reach the accuracy level required by the most applications in physical chemistry, one should usually explicitly consider part of electronic shells conventionally referred to as core shells (6s6p shells for transactinides); in these cases, the term 'small-core' pseudopotentials is used.

Atomic core pseudopotentials are usually derived from solutions of the Hartree – Fock equations within the framework of the Dirac – Coulomb(– Breit) model [Dirac – Fock(– Breit) equations] for an isolated atom. The pseudopotential is usually defined in such a way that the solutions of the corresponding equations with the pseudopotential (pseudospinors) exhibit the maximum similarity with true atomic spinors in the spatial region associated with the valence shells but have no radial nodes in the core region (in the vicinity of the nuclei). Such pseudopotentials are named shape-consistent.[41 – 44] As an alternative, the pseudopotential parameters are often adjusted by fitting the calculated atomic energy spectra (energy-adjusted pseudopotentials[45]). The problem of restoring the pseudopotential operator from a finite set of numbers, atomic state energy values, is mathematically incorrect, so that its solution should be considered as a kind of an art, it leaves room to arbitrariness and is risky of errors.[46]

The major advantages of the pseudopotential model over the all-electron approaches stem from a relatively small number of electronic variables and a more simple and regular structure of wavefunctions in the core region. This opens up a possibility of working with much smaller basis sets at a given accuracy of the results.

The eigenstates of all of the above Hamiltonians cannot be classified according to their spin multiplicities and irreducible representations of molecular point groups. The relativistic symmetry described by the full relativistic symmetry group[47, 48] or its subgroup, double symmetry group,[49, 50] is lower than its non-relativistic counterpart; the consequence is a considerable increase in the volume of computations (sometimes, by orders of magnitude) in comparison with the non-relativistic case.

Scalar relativistic Hamiltonians provide an adequate description of spin-independent relativistic effects while neglecting spin-dependent ones. A scalar relativistic Hamiltonian has the same symmetry properties as its non-relativistic counterpart; this allows the considerable reduction of the volume of calculations. The derivation of the scalar analogue of the Dirac – Coulomb(– Breit) Hamiltonian is associated with rather complicated transformations;[51] in the case of quasirelativistic Hamiltonians it will suffice to reject the spin-dependent terms. A scalar version of the relativistic pseudopotential model is extremely easy to define: it is immediately obtained by averaging atomic pseudopotential operators over possible mutual orientations of the orbital and spin angular momenta. The deviation of the full Hamiltonian with pseudopotentials from the scalar one is called the effective spin – orbit operator; it is a sum of one-body operators. Let us emphasise that it implicitly incorporates contributions from the main two-body spin-dependent interactions.

The applicability of the scalar relativistic approach in itself to studies of SHE compounds is restricted mainly to closed-shell-like electronic states.

Below we summarise essential features of the main relativistic Hamiltonian models for electron subsystems of atoms and molecules using the elementary Robinson Crusoe's 'good – evil' scheme.[52]

Good	Evil
The Dirac – Coulomb Hamiltonian	
A rather simple model describing the main relativistic effects.	The neglect of magnetic two-electron interactions leads to accuracy restrictions, which are most significant just for SHE. At a given accuracy level, computations are much more (by orders of magnitude) complicated in comparison with the non-relativistic case.
The Dirac – Coulomb – Breit Hamiltonian	
A consistent model of particle interaction in a molecule ensuring, in principle, sufficient accuracy of the calculated properties of SHE compounds.	Direct application to molecular electronic state calculations is extremely difficult even with additional rough approximations.

Good	Evil
Scalar relativistic models	
Significant simplification of a solution of the many-electron problem by exploiting higher non-relativistic symmetry (point group + spin).	The results of calculations should be corrected with regard to spin-dependent interactions (exceptions are provided by closed-shell systems).
Core pseudopotential model	
Convenience of work with non-relativistic kinetic energy; applicability of slightly modified methods of conventional quantum chemistry.	Association with the frozen-core approximation; roughly approximate treatment of the effective interactions of valence electrons as two-body Coulomb interactions.
The construction of more accurate approximations for the valence part of wavefunction through saving computational efforts for the description of core shells.	The extraction of the core shells is ambiguous.
Possibility of the implicit inclusion of magnetic interactions, retardation and finite nuclear size effects with minimum computational expenses.	The necessity of constructing different basis sets for different forms of pseudopotentials.

***Ab initio* (first-principle based) methods.** The main approaches to the solution of the many-electron problem for the chosen model of relativistic Hamiltonian in the calculations of SHE compound properties can be divided into two groups. The approaches of the first group imply the construction of an approximate wavefunction for the electron subsystem of an atom or a molecule; methods of the second group are based on the electronic density functional formalism. The computational tools of the first group allow the systematic extension of the calculation scheme (an increase in the size of the basis set, account for the higher excitations of reference configurations, *etc.*), which should, at least in principle lead to the convergence of the results to 'exact' ones (exact for the given Hamiltonian model). However, huge computational efforts required for the quantitative prediction of the properties of SHE compounds within these approaches restricts their applicability mainly to studies of small molecules. The direct application of these methods to studying systems of the greatest applied interest (liquid-phase structures, atoms on a surface, *etc.*) is problematic; however, the methods are indispensable for the analysis of specific features of chemical bonds formed by SHE atoms and for checking the reliability of methods belonging to the second group (versions of the density functional theory) in applications to SHE compounds.

The most widely used approaches imply the representation of the many-electron wavefunction by linear combinations of the Slater determinants (antisymmetrised products of one-electron spinors usually called molecular spinors). As a rule, molecular spinors or their individual components are constructed as linear combinations of a finite number of basis functions by solving the many-electron problem within a certain simple approximation (in most cases, conventional self-consistent field methods or its generalisations). One should distinguish two versions of this procedure:

— in the simplest case, trivial one-particle spinors with only one non-zero large component are generated using a scalar relativistic Hamiltonian; in two-component models, these are spinorbitals (spatial functions usually considered real, multiplied by spin-up or spin-down factors); this structure of spinors dramatically simplifies all calculations;

— spin-dependent components of the Hamiltonian are taken into account just in the first stage of calculations. In this case, all components of molecular spinors can be non-zero and complex; with the same formal parameters of the expansion of the many-electron wavefunction, this leads to much more difficult computations than in the first version. At the same time, the accuracy of the results obtained for large amplitudes of spin-dependent interactions, characteristic of SHE, is considerably better.

The choice of the basis set for the expansion of one-electron function is the key point of the computational procedure. On the one hand, bases should be sufficiently compact, because computational expenses rapidly grow with an increase in their size; on the other hand, they should ensure the desired accuracy of the results. These two controversial requirements lead to the necessity of the careful optimisation of the basis sets.[53, 54]

As a rule, bases are composed of individual (primitive) or contracted Gaussian functions. Numerical (defined on a grid) and Slater bases are used more rarely.

Let us specify the main types of basis sets used in the computational quantum chemistry of superheavy elements.

Even-tempered bases, *i.e.*, sets of primitive Gaussian functions with exponential parametres forming geometrical progressions [55, 56] are used mainly in relativistic calculations of free atoms and ions.[16, 57] The applicability of such bases to studies on molecules of heavy element compounds is restricted by their too large sizes necessary for attaining acceptable accuracy of the results. They can be used for constructing contracted bases (see below).

Segmented contracted bases remain the most common type of basis sets in calculations of SHE molecules. An initial set of primitive Gaussians is divided into non-overlapping groups, and one linear combination of functions of each group is used as a basis orbital.[58] If several basis functions are constructed from the same set of primitive Gaussians as their linear combinations, the contraction scheme is named general contraction. The most widespread implementations of this scheme are atomic natural orbitals [59] and correlation-consistent bases.[60–62] Their use allows the reduction of basis set sizes without deteriorating the accuracy of calculations (unfortunately, at the expense of more complicated algorithms and an increased number of primitive Gaussians the integrals of which should be evaluated).

Nowadays a number of methods and software packages have been developed for calculations of heavy element compounds; however, only part of them can be considered reliable tools for studying SHE-containing molecules. Let us specify the approaches that are used until now in the calculations on SHE compounds and discuss their main advantages and disadvantages.

Relativistic versions of the coupled cluster method (see Refs 23, 63, 64 and references therein) appear to be the most promising computational tool for SHE studies. The method is based on the use of the following Ansatz for many-electron stationary state wavefunctions (Ψ_μ)

$$\Psi_\mu = \exp(T)\psi_\mu .$$

Here ψ_μ denotes model wavefunctions that can be represented by single Slater determinants or linear combinations of a few determinants. The cluster operator T is a linear combination of

excitation operators with a given number of substitutions, as a rule, single and double [Coupled Cluster Singles plus Doubles (CCSD)], or additionally triple [Coupled Cluster Singles plus Doubles plus Triples (CCSDT)]; the weights of excitation operators (cluster amplitudes) are optimised. As a result, the expansion of the wavefunction usually includes all Slater determinants that can be constructed from the chosen set of one-electron functions; however, the contributions of these determinants are not independent parameters and are expressed through a rather small number of cluster amplitudes. An advantage of the specified approach is its exact size consistency; its main shortcomings arise from the complexity of non-linear equations for cluster amplitudes, the instabilities of procedures of their solution, frequently occurring and sometimes incurable in principle, and the rapid growth of computational expenses with an increase in the number of correlated electrons and the size of the basis set. It is particularly difficult to build cluster expansions in the cases of quasidegeneracies, for several open shells, *etc*.

The configuration interaction method is conceptually more simple and implies the direct optimisation of coefficients in a linear combination of the Slater determinants (or products of their symmetry adaptation, configuration state functions or simply configurations [50]) representing the many-electron wavefunction according to the variational principle. The number of independent coefficient is only less by one than the number of determinants (configuration state functions) included into the calculation; therefore, the latter number cannot be too large. In practice, one starts with a rather restricted initial set of reference determinants and takes into account only the determinants that can be generated from the reference by means of no more than double excitations.[65] To reduce the dimension of the problem more, configurations (determinants) can be selected using the perturbation theory.[66–69] Systematic studies of heavy element compounds by means of the relativistic configuration interaction method have been carried out since the late 1970s (see Ref. 70 for a review). Configurations with multiple open shells can be included into the reference without any conceptual or technical difficulties; therefore, the configuration interaction method is a universal tool for studying small (first of all, diatomic) molecules. However, a serious drawback of the mentioned approach as applied to complex systems containing SHE atoms is the lack of size consistency: the resulting correlation energy estimates qualitatively incorrectly depend on the number of electrons in the system. The potentialities of numerous stratagems used to reduce deviations from size consistency [71–74] are quite restricted.

The many-body perturbation theory can also provide a basis for creating effective technologies of calculating the properties of SHE-containing molecules. Conventional formulations of the perturbation theory with an unperturbed wavefunction represented by a single Slater determinant imply the use of molecular spinors that do not factorise into spatial and spin parts.[63] Otherwise, spin-dependent interactions will be considered entirely as perturbation; taking into account their huge amplitudes for SHE, one cannot expect good convergence of the perturbation expansions. Certain possibilities for working with spinorbitals are provided by multidimensional (quasidegenerate) perturbation theories implying the construction of a many-electron effective Hamiltonian in a space of a small dimension (model space).[75,76] Unfortunately, the experience of applying such schemes to studies of SHE compounds is unknown.

Combined computational schemes. The relative simplicity of calculations with scalar relativistic Hamiltonians because of their high symmetry has determined the popularity of computational procedures combining high-level (*e.g.* coupled cluster) scalar calculations with the evaluation of contributions from spin-dependent interactions within the framework of much simpler approximations (in most cases, by the configuration interaction method taking into account a small number of configurations).[77–80] Since considerable part of correlation effects is neglected in the course of computing corrections, combined schemes are reliable only where the deviations from the additivity of correlation and spin-dependent effects are small.

Relativistic density functional theory. Methods of the non-relativistic density functional theory (DFT) are exceptionally economical and generally reliable tools for theoretical studies on the properties of compounds of elements of the upper rows of the Periodic table. The relativistic version of the density functional theory (RDFT) is now considered as the most practical approach to the analysis of the ground electronic states of SHE-containing molecular systems. Below we consider the main features of various RDFT-based methods from the point of view of their applicability to the description of SHE compounds.

According to one of the formulations of the relativistic counterpart of the Hohenberg–Kohn–Sham theorem,[81,82] the ground-state energy of a many-electron system within the no-pair approximation and in absence of an external magnetic field is a functional of the total electron density ρ and magnetisation density $\mathbf{m}$, a vector quantity with the direction differing at different points in the space. It is usually supposed that the energy functional depends only on the length of the vector $\mathbf{m}$ (let us denote it m), and the contributions from orbital currents associated with the spatial motion of electrons but not with their spins are neglected (see Ref. 83 and references therein). To reveal the correlation with the conventional DFT, it would be convenient to go from ρ and m to their combinations, generalised spin densities

$$\rho_+ = \frac{\rho + m}{2},$$

$$\rho_- = \frac{\rho - m}{2}.$$

These quantities resemble conventional spin densities ρ_α and ρ_β widely used in approximate expressions for non-relativistic energy functionals. However, in contrast to ρ_α, ρ_β associated with the spin projection onto the chosen axis, the generalised spin densities are independent of the choice of the spin quantisation axis.

Practical applications of RDFT usually imply that kinetic energy and densities ρ and $\mathbf{m}$ are represented through auxiliary one-electron functions (molecular spinors), which are assumed to have integer occupation numbers; in this case, the central problem of the method is formulated as that of universally approximating the sum of exchange and correlation energy components, an exchange-correlation functional $E_{xc}[\rho, \mathbf{m}]$. Auxiliary spinors should obey the relativistic Kohn–Sham equations for an electron in the field of a density-dependent potential. This approach invokes certain associations with the single-determinant approximation for the wavefunction; this by no means reduces the conventional RDFT version to the latter approximation.

It is worth noting that the unrestricted optimisation of molecular spinors within the Kohn–Sham scheme offers the

possibility of the qualitatively correct description of the fragmentation of the system under study, including the cases of homolytic bond break. However, in many cases the unrestricted solutions of the Kohn–Sham equations will have lower symmetry than that determined by the relativistic symmetry group of the system.

Molecular spinors are usually approximated by linear combinations of a finite set of basis functions. The results of calculations using all DFT approaches employing the Kohn–Sham formalism are much more stable with respect to the incompleteness of the basis set in comparison to methods discussed above. However, excessive reckoning upon this stability is unjustified.[84]

Basis sets for all-electron calculations are usually composed of numerical solutions of the Kohn–Sham problems for free atoms (atomic spinors).[85,86] This allows the minimisation of the size of the core-like basis subset. At the same time, the extension of such bases by combining spinors obtained for different atomic charge conditions is neither very simple nor efficient. The combination of numerical core-like spinors with analytical (Slater) valence-like basis functions appears to have better prospects.[83,86] Computational schemes implementing these RDFT versions are extremely cumbersome; this imposes serious restrictions on the basis set quality in calculations on complex systems. The calculations employing the core pseudopotential model are almost always performed with Gaussian bases, often close to saturated.

Exchange-correlation functionals. The hierarchy of approximations for the exchange-correlation functional is conveniently represented by 'Jacob's ladder', the scheme proposed by Perdew:[87] from the terrestial world of the Hartree primitive independent particle model to the heavens of the quantitative prediction of chemical properties. Lifting from one rung to the next one is associated with the qualitative complication of the computational scheme and an increase in the accuracy of the results.

The first rung corresponds to local functional models: E_{xc} is a spatial integral of the exchange-correlation energy density, which is a function of charge density and magnetisation density. The local approximation in no case ensures an acceptable accuracy of the description of chemical properties for heavy elements; typical errors in bond energy estimates are 50% and more.[88,89] The second rung is associated with the gradient approximation (of the exchange-correlation energy density at each spatial point depends not only on the densities ρ and **m**, but also on their gradients). Lifting to the third rung additionally assumes the dependence of the exchange-correlation energy density on the density of kinetic energy (the so-called meta-gradient models). The next rung is associated with functionals depending explicitly not only on electron density and its derivatives, but also on the auxiliary spinors. Among these functionals, hybrid functionals bearing terms proportional to exact (Hartree–Fock) exchange energy are most popular and efficient.

Present-day all-electron RDFT computational technologies usually correspond to two lowest rungs of Jacob's ladder. Relativistic expressions for local components of E_{xc} and gradient corrections differ from their non-relativistic counterparts.[90,91] However, it is not clear whether this fact has any practical consequences: taking into account the specified differences considerably changes the properties of the core shell but has almost no effect on the properties important for chemistry, bond energies, molecular equilibrium geometries, *etc*.[92] Calculations within the core pseudopotential approximation employ functionals from all four of the above rungs.

It would be useful to distinguish non-empirical exchange-correlation functionals derived mainly from asymptotic and other requirements that the exact functional must satisfy and semiempirical ones parametrised by fitting the results of DFT calculations to experimental or very accurate computed data for a more or less representative set of atomic and molecular systems. Since all of the known semiempirical functionals were optimised without taking into account data on SHE compounds (and normally any data on heavy element compounds), their use in the studies of such compounds is conceptually a risky extrapolation. The adequacy of one or another model is sometimes estimated based on the accuracy of the results of its application to SHE analogues from the sixth row;[93] however, qualitative changes in the properties of analogues and the aggravation of the dependence of computed results on the particular choice of an approximate functional on going from the sixth to the seventh row [57,94,95] casts serious doubts about the reliability of this approach. A reasonable alternative consists in adjusting the approximate functional using scalar relativistic calculations on rather simple systems [20,26] with subsequently transferring these functionals to fully relativistic calculations.

Collinear approximation. Changes in the orientation of the magnetisation density vector from one point to another complicates the work with exchange-correlation functionals expressed through density functions ρ, **m** or ρ_+, ρ_-. This had lead to the use of the collinear approximation, in which only one **m** component is retained, parallel to the chosen axis [when $\mathbf{m} = (m_x, m_y, m_z)$ is replaced by $(0,0,m_z)$, the generalised spin densities change to their conventional analogues ρ_α, ρ_β]. Since the spin projection on the chosen axis, which determines the splitting of density into the spin components, in the relativistic case is not a good quantum number, the values of the energy functional depend on the mutual orientation of this axis and the molecule. The errors introduced by the collinear approximation and the dependence of the results obtained on the chosen direction of the spin quantisation axis in many cases are not catastrophic. They disappear for closed shells and are negligibly small for compounds of elements 111, 112, 113 bearing light elements and gold.[20,96] In contrast, for systems with considerable spin densities associated with one-electron states with strong spin–orbit splittings, errors in relative energy estimates and changes in these values upon the rotation of the spin projection of the quantisation axis may exceed 0.1 eV.[97] For linear molecules, the errors are minimised where the quantisation axis coincides with the molecular symmetry axis. With the development of efficient computer implementations of the non-collinear methods,[97,98] the use of collinear approximation will, probably, become senseless.

Relativistic density functional theory in combined computational schemes. The incorporation of operators associated with spin-dependent (magnetic) relativistic effects into the one-electron Kohn–Sham Hamiltonian in addition to the exchange-correlation potential ensures the simultaneous account for spin-dependent relativistic and correlation effects, as well as their mutual influence (interference) within the RDFT approach. This enables one to overcome the main problem of RDFT in its applications to SHE compounds, namely, the poorly controlled accuracy of describing electron correlations. The estimation of the energy correction for the spin-dependent interactions by means of RDFT followed by its incorporation into the results of highly accurate scalar relativistic calculations appears to be a more correct procedure than the combined schemes mentioned above: in contrast to the restricted configuration interaction method, DFT has no

tendency to systematically underestimating the effects of correlation. Rare applications of a combination of scalar coupled cluster calculations with the RDFT evaluation of spin–orbit corrections seem to be highly promising.[20, 99]

The main features of relativistic electronic structure calculations estimated in the 'good–evil' terms are presented below.

Good	Evil
Ab initio methods	
Systematic improvement of the results with the extension of the computational scheme (in principle, up to exact results within the chosen Hamiltonian model). Because of this feature, *ab initio* methods are indispensable as benchmarks for optimising the simpler computational schemes. Reliable approaches to describing states with complex open shells and the formation/cleavage of multiple chemical bonds. Efficient exploitation of symmetry properties. Direct applicability of numerous versions of the methods to excited state studies.	Huge computational expenses, cumbersome computer implementations, slow convergence of the results with the extension of the basis set and the improvement of the level of correlation treatment block the application of methods to the quantitative evaluation of the properties of SHE-containing systems. One should choose between the unequal-footing treatment of the Coulomb and magnetic interactions ('orbital' formulations) and the extremely complicated computational procedures ('spinor' formulations). Non-trivial maintenance of the size consistency of results necessary in investigations of systems with a large number of electrons.
Relativistic density functional methods	
Possibility of incorporating magnetic interactions in the same manner and at the same level as scalar relativistic effects and the Coulomb interactions. Exceptionally low expenses (especially within the pseudopotential approximation), stability with respect to the basis set quality. As a consequence, practical applicability to studies of SHE-containing polyatomic systems. Unrestricted optimisation of auxiliary molecular spinors offers the possibility of qualitatively correctly describing the fragmentation of a system. Adequate accounting for the mutual influence (interference) of magnetic interactions and correlations, which is important for evaluating the corrections for magnetic interactions to the results of high-level scalar relativistic calculations.	Strong dependence of the results on the particular choice of the exchange-correlation functional model; the possibility of functional adjustment is restricted by the lack of reliable data on SHE compounds. Certain association with the single-configuration approximation for wavefunctions, because of which applications to complex open-shell ground states are risky. The extension of the theory to excited states is at least non-trivial.

III. Calculations of the electronic structure and properties of superheavy element compounds

Sufficiently wide experience has been accumulated in calculations of the electronic structure of SHE atoms and molecules of their compounds. Unfortunately, difficulties with summarising this experience are caused by the extremely limited possibility of comparing the results of calculations with the experimental data; the key reliability criteria here are the validity of the approximations in solving the many-electron problem and the convergence of the results with the extension of the calculation scheme. Of special importance is the agreement between the results obtained within significantly differing theoretical approaches.

Preliminary remarks: calculations of free atoms. Studies on the electronic structures of SHE atoms and ions were started in the late 1960s–early 1970s, with the development of software for relativistic calculations by the self-consistent-field Dirac–Slater (with the simplified exchange operator)[100, 101] and Dirac–Fock[102, 103] methods. The early calculations of SHE were discussed in detail in the reviews.[104, 105] These calculations were undertaken mainly with the aim of determining the ground-state configuration of SHE, which was often quite different from the configuration of the lighter analogues.[105, 106] Later, calculations of SHE (see Refs 107–109) were carried out by the Dirac–Fock multiconfiguration method,[103, 110] which describes the effects of mixing of low-energy valence configuration, and by many-body perturbation theory,[111] which also takes into account the effects of core–valence correlation. Recently, the relativistic coupled-cluster method (see review [63] and references cited therein) has become the most efficient tool for studying the electronic structures of SHE atoms.[112, 113] In some cases, calculations were performed taking into account not only relativistic (Breit) interactions between the electrons, but also radiation corrections.[114] These theoretical approaches used in combination have allowed researchers to predict many properties of SHE atoms with a very high degree of reliability. They generally confirmed the periodicity of filling of electron shells, but gave some unexpected results. In particular, the ground-state configuration of the eka-gold (E111) atom was found to be $6d^9 7s^2$ rather than $6d^{10} 7s^1$, as was expected by analogy with the Au atom (ground-state configuration $5d^{10} 6s^1$).

Relativistic *ab initio* calculations of molecules including SHE atoms, which take into account spin-dependent components of the Hamiltonian at all stages (including the construction of the set of one-electron molecular spinors) and describe electron correlation at the high level of theory have still remained relatively exotic because of their extreme laboriousness. The problem is slightly simplified for closed-shell systems provided that the Kramers-restricted version of the Dirac–Fock(–Breit) method is used as the starting point. Nash[115] studied properties of E112, E114, and E118 atoms and diatomic molecules using mentioned approach within the model of small-core (1s ... 5f) shape-consistent relativistic pseudopotentials. Electron correlations were described within the framework of the second order Møller–Plesset perturbation theory (MP2) and the coupled-cluster [CCSD and CCSD (T)] method using the Gaussian (6sd6p2pf1g) basis set. Based on the estimates for atomic polarisabilities, ionisation potentials, and bond energies in the $E112_2$, $E114_2$ and $E118_2$ dimers and their comparison with the corresponding properties of

6p-elements, it was concluded that element 112 (eka-mercury) is similar in its properties to mercury but is more inert, element 114 (eka-lead) is much more inert than lead, and element 118 (eka-radon) is much more reactive than radon (and, possibly, E112 and E114). Note that the first two conclusions agree with the data of successful recent experiments on the thermochromatographic detection of E112 (Ref. 3) and E114 (Ref. 5). It is believed that the chemical properties of 7p elements should strongly differ from those of their 6p analogues because of the larger spin–orbit splitting of the 7p sublevel. Note that the choice of the most consistent *ab initio* relativistic calculation scheme in the work [115] was coupled with restrictions in the basis set size, which affected, in particular, the accuracy of the description of the van-der-Waals dimer $E112_2$ (see more below).

A similar computational technology was used to estimate the molecular constants of E111H.[116] It was shown that the accuracy of the results of calculations with the small-core (1s ... 5f) shape-consistent pseudopotential is comparable with the accuracy of the best calculations by four-component methods; the additional explicit account of the dependence of the wavefunction on the coordinates of 5f electrons only slightly changed the results of calculations. A change to energy-adjusted pseudopotentials has led to the underestimation of the contributions of spin–orbit interactions to molecular properties.

A simpler approach in which spin-dependent components of the Hamiltonian are excluded at the stage of constructing one-electron spinors (*i.e.* molecular spinorbitals are used) seems to be a reasonable compromise between the calculation expenses and the accuracy of the results. In particular, calculations of the diatomic E112H molecule were performed within the framework of such computational technology using the relativistic coupled cluster singles plus doubles method [25] and the generalised core pseudopotential model.[44] The results of calculations indicate that the chemical bond in this molecule should be at least as strong, as and much shorter than, the Hg–H bond. In combination with the recent experimental data,[3] this allowed the authors to close the discussion about the possible analogy between the properties of E112 and inert gases. Despite the fact that the E112–H bond is formally associated with the interaction of atomic *s* shells, the account of spin–orbit interactions was found to be necessary even for the qualitatively correct reproduction of the bond properties.

Combined schemes offer an important and rather inexpensive source of information about the chemical properties of SHE. Thus characteristics of the ground states of molecules of E111–E114 compounds were studied by Seth *et al.*[17, 77–80] using the small-core pseudopotential approach. The scalar relativistic problem was solved by the methods of the many-body theory [from MP2 to the coupled-cluster CCSD(T) method], and the effects of spin–orbit interactions were included by means of corrections found from the results of calculations by the relativistic configuration interaction method taking into account a rather limited set of configurations. The realisation of this scheme in calculations of the E111N, E111Li, and E111F systems [117] has demonstrated the non-additivity of the contributions of electron correlation and relativistic effects to the energy, force constants, bond lengths, and dipole moments of molecules. Spin–orbit interactions were found to be significant only for dissociation energy estimates; these effects were of special importance in the case of the high electronegativity of the light atom. Spin–orbit interactions stabilise the bond in E111Li and weaken it in E111F. The results of a similar study of E112 hydride and fluoride molecules and ions and changes in the properties of E111 and E112 compounds on going to their lighter analogues are documented.[77] It was shown that, with the inclusion of relativistic effects, the calculated bond lengths E111– H and E112– H in the systems E111H and $E112H^+$ shorten by more than 0.4 Å and become comparable to those in copper and zinc hydrides. The $E112H^+$ ion should be the most stable hydride among the elements of the zinc subgroup (according to the most reliable estimates, the dissociation energy of $E112H^+$ is more than 4 eV). It was predicted that E112 in the oxidation state +4 should form stable fluoride and chloride; the energies of the decomposition

$$E112F_4 \longrightarrow E112F_2 + F_2,$$

$$E112F_4 \longrightarrow E112 + 2F_2,$$

were found to be 129.5 and 250.1 kJ mol^{-1}, respectively. The stability of MF_2^-, MF_4^-, and MF_6^- (M = Cu, Ag, Au, E111) ions was studied [78] by calculating energies of the reactions

$$MF_n^- \longrightarrow MF_{n-2}^- + F_2.$$

Element 111 should be the most stable in the oxidation states +3 and +5; relativistic effects favour the stabilisation of the higher oxidation states of the studied elements. Calculations of E113 hydrides and halides in the oxidation states +1 and +3 were reported.[79] On the whole, the properties of E113 correspond to its position in the aluminium subgroup of the Periodic table (eka-thallium); the electronegativity of the element appears to be a little higher than it could be supposed based on extrapolation along the subgroup. This is assigned to the effects of spin–orbit interactions. The equilibrium structures of the $E113X_3$ (X = H, F, Cl) molecules are T-shaped rather then symmetrical triangular; this is explained by 6d electrons of E113 participating in the bonding. Compounds of E113 in the oxidation states +3 and +5 are thermodynamically unstable; it was supposed that only the anionic complex $E113F_4^-$ can exist.

Schwerdtfeger and Seth [118] compared the results of calculations for molecules of element 114 di- and tetrahydrides and halides [bond lengths, valence bond angles, energies of decomposition with the abstraction of a diatomic hydrogen or halogen molecules (X_2)] by the Dirac–Fock method and within the MP2 approach using scalar-relativistic pseudopotentials. They have shown that the abstraction of X_2 from $E114X_4$ with the inclusion of relativistic effects is exothermic and the oxidation state +4 is unstable. Element 114 should be chemically more inert than its lighter analogues (Pb, Sn and Ge); the only stable oxidation state of E114 should be +2.

Combined schemes with the solution of the scalar relativistic problem by the coupled-cluster method using large one-electron basis sets and estimation of the contributions of spin-dependent interactions within the collinear version of relativistic DFT were applied [20, 99] to the study of E112H, E112Au, and $E112_2$ molecules. The characteristics obtained for the latter system, *viz.*, bond length R_e = 3.38 Å and dissociation energy D_e = 0.084 eV, significantly differ from those found in the above-mentioned work [115] (R_e = 3.07 Å and D_e = 0.187 eV). This is explained first of all by the considerably better flexibility of the basis system and the elimination of atomic basis set superposition errors in the combined calculations. The equilibrium distance in $E112_2$ was found to be almost 0.2 Å shorter than, and D_e, almost twice as great as, those in Hg_2.

Electronic structure calculations within the framework of the all-electron four-component formalism ignoring electronic

correlation (*i.e.*, using the Dirac–Fock method) can be performed rather easily even for polyatomic systems but do not give quantitative estimates of many important properties (in particular, energetic). At the same time, a comparison of the results of such calculations for SHE and their lighter analogues along with the data of modelling the electronic structure without relativistic effects can possibly give helpful information. A series of works published by Malli [18,119–121] presents the results of electronic structure calculations of rutherfordium tetrachloride $RfCl_4$, seaborgium hexabromide $SgBr_6$, hassium and osmium tetroxides HsO_4 and OsO_4, and eka-plutonium fluoride E126F. Atomisation and bond break energies, vertical ionisation potentials, and electron affinities were discussed. The Mulliken atomic charges were considered characteristic of the degree of bond ionicity (covalence), which served as the qualitative estimate of volatility (the lower ionicity, the higher volatility). Calculations of the same properties in the non-relativistic approach allowed the author to conclude about rather significant changes in atomisation energies (more than twofold for HsO_4) because of relativistic effects. It was noticed that the ground states of all of the studied systems are strongly bound. In addition, the results of these studies confirm the adequacy of the frozen (1s ... 5d) core approximation for SHE atoms.[120]

Another way to restrict the volume of calculations within the all-electron model is the scalar relativistic approximation. The experience of its application to calculations of SHE compounds was sometimes regrettable, and the corresponding results should be considered with extreme caution. Nakajima and Hirao [122] estimated the energy, bond length, and frequency of harmonic vibration E112–H in the E112H molecule and $E112H^+$ and $E112H^-$ ions using the Douglas–Kroll transformation to two-component scalar Hamiltonians. As was shown by the next, more accurate calculations,[20,25] one of the results was the substantial underestimation of the bond energy in the neutral molecule. The complete inefficiency of the scalar relativistic approach in the study of element 114 dihydride can be seen from the results of calculations by the relativistic configuration interaction method with and without the inclusion of spin–orbit interactions.[123] Filatov and Cremer [124] determined the static polarisability of MO_4 (M = Ru, Os and Hs) tetroxides within the scalar version of the zero-order regular approximation. The many-electron problem was solved by the Hartree–Fock and MP2 methods using the contracted Gaussian basis set [17s13p11d7f]. The calculated polarisabilities decrease in the order $RuO_4 > OsO_4 > HsO_4$, which is different from that found earlier by relativistic DFT calculations.[25,126] It was concluded that the models of MO_4 adsorption on the silica surface should be revised [125] and that both electrostatic and dispersion interactions should be taken into account.

Relativistic density functional theory forms the basis for a vast majority of studies on polyatomic systems including SHE. A series of such calculations with the inclusion of all electrons within the limits of the four-component spinor formalism [85,89] was published by Pershina and co-authors.[21,88,93,125,127–133] These works utilised rather simple approaches for the relativistic exchange-correlation functional, local-density [134] and generalised gradient [135,136] approximations. The contribution of the gradient component to the exchange-correlation potential was estimated [129] only as a perturbation theory correction. The basis sets were formed of numerical atomic spinors; they included the minimum set of functions and only one or two sets of polarisation functions. This was insufficient for obtaining quantitative estimates of energy characteristics (see Ref. 84). In some cases, basis functions were optimised (the varied parametres were atomic charges in generating atomic spinors). Large systems were studied using the frozen-core approximation.

A great number of publications were devoted to the comparative analysis of the interaction of E112 (eka-mercury) and mercury atoms with metal atoms, first of all gold, their clusters, and metal surface.[93,127,132,137] The aim of these studies was to estimate the energy of E112 adsorption on the surface of metals (Au, Ag, Cu, and Pd); this property was necessary for interpreting the results of experiments on the thermochromatographic identification of E112 atoms. Molecular constants of E112M and HgM (M = Cu, Ag, Au, Pd) diatomic systems were calculated.[127] It was concluded that the bond energy of E112 with metal atoms is 15–20 kJ mol^{-1} lower than the energy of the corresponding bonds of the mercury atom and that the bond energy decreases in the order Pd > Cu > Au > Ag coinciding with the decrease in the enthalpy of mercury adsorptions on the metal surface. The bond lengths in E112M molecules are larger than those in HgM, on the average, by 0.06 Å. The effective atomic charges and dipole moments found suggest that the degree of bond covalence substantially increases on going from HgM to E112M.

The adsorption of E112 and Hg atoms in different positions on the Au(100) surface was studied.[88,93,137] The gold surface was simulated by Au_9, Au_{13} and Au_{16} clusters including 4, 8 and 9 surface atoms, respectively, and one or two additional atomic layers. More complex cluster models (up to 50 Au atoms) including those with the cluster surrounding in the crystal lattice simulated by static potentials, were considered.[137] The bond energies calculated with the local and gradient exchange-correlation functionals differed almost twofold. To reach the agreement between the experimental adsorption energy of the mercury atom on the gold surface (1.01 eV), the DFT version was used with the local functional known to strongly overestimate bond energies.[85,127,133] The difference in adsorption energies of E112 and Hg should be [93] from 10 to 15 kJ mol^{-1}.

Calculations of the dipole polarisabilities and ionisation potentials of mercury and E112 atoms made it possible to estimate dispersion interactions of these atoms with an inert surface of an insulator (silica) and characteristic adsorption temperatures on this surface, and sublimation energies of individual atoms.[132] The predicted drastic decrease in the enthalpy of sublimation of E112 and an increase in the energy of adsorption of its atoms on an inert surface in comparison with those of mercury atoms was explained by the increase in dispersion interactions because of the relativistic contraction of s and p shells of E112.

The main results of calculations of the electronic structures and properties of SHE molecules and ions: BhO_3Cl, HsO_4, RfL_6^{2-}, $Rf(H_2O)_8^{4+}$, $Db(H_2O)_8^{5+}$, $Db(IT)_6^-$, DbL_6^-, SgO_4^{2-} and $Sg(H_2O)_6^{6+}$ (L = F, Cl, Br) and compounds of their analogues, transition 4d and 5d elements, were reviewed.[24] On the basis of the calculated effective atomic charges, ionisation potentials, dipole moments, polarisabilities and dissociation energies, an attempt has been undertaken at estimating adsorption enthalpies of MO_3Cl (M = Bh, Re, Tc) and MO_4 (M = Hs, Os, Ru) on the silica surface, energy of formation and stability constants of the ML_6^{2-} (M = Rf, Hf, Zr; L = F, Cl) and ML_6^- (M = Db, Ta, Nb, Pa; L = F, Cl, Br) complexes in aqueous solutions, energies and constants of hydrolysis of $M(H_2O)_6^{5+}$ (M = Db, Ta, Nb, Pa) and the protonation of MO_4^{2} (M = Sg, W, Mo) within simple physical and chemical models invoking

the known experimental data. It was concluded that BhO_3Cl possessed the lowest volatility in the subgroup; the volatility of HsO_4 is little higher or comparable with that of OsO_4; the stability constants of halide complexes change in the order Zr > Hf > Rf and Pa ≫ Nb > Db > Ta. The trends in the constants of hydrolysis (Nb > Ta > Db ≫ Pa) and protonation (Sg > W > Mo) found in the subgroups agree with the known experimental data.

The role of relativistic effects in calculations of the electronic structures, volatility, and adsorption properties of HsO_4, OsO_4 and RuO_4 was studied in detail [131] by comparing the results of fully relativistic and non-relativistic DFT calculations. It was shown that the inclusion of relativistic effects leads to the strengthening of chemical bonds in the molecules, *i.e.*, to an increase in atomisation energies and the shortening of equilibrium distances; it also leads to an increase in the degree of bond covalence, an increase in ionisation potentials and a decrease in dipole polarisabilities. The enthalpies of adsorption on an inert surface and adsorption temperatures estimated from molecular ionisation potentials and dipole polarisabilities slightly (within 0.5 kJ mol^{-1} and 1 K) varied upon the account of relativistic effects, which was due to the mutual compensation of the changes in ionisation potentials and polarisabilities. The theoretically predicted changes in volatility in the series $RuO_4 < OsO_4 < HsO_4$ differ from the data of gas-adsorption chromatography [138] and the results of earlier calculations for the same group of compounds.[125]

The analysis of the electronic structures of $RfCl_4$ and chlorides of its analogues from the titanium subgroup is presented.[130] The agreement between the experimental and the calculated bond lengths M–Cl and frequencies of the symmetrical valence vibration ν_1 for the $ZrCl_4$ and $HfCl_4$ molecules evidenced for the satisfactory reliability of the predicted properties of the $RfCl_4$ molecule. It was shown that the difference between the atomisation energies of $RfCl_4$ calculated in the collinear and non-collinear approximations was insignificant (0.04 eV).

Bond energies, interatomic distances and vibrational frequencies of diatomic molecules E114X and PbX (X = O, Pd, Pt, Au) and element 114 and lead dimers have been estimated.[133] It was shown that the bond energies strongly depend on the choice of the approximation for the exchange-correlation functional; the corresponding dependence for bond lengths and vibrational frequencies is not so pronounced. The reliability of the method used can be judged from the agreement between the calculated molecular characteristics and the experimental data (the difference between the calculated dissociation energies of Pb_2 and PbO is 32%–74% and 14%–37%, respectively, depending on the model of the exchange-correlation functional); this was considered satisfactory. It was concluded that element 114 is more inert than lead. Nevertheless, the estimate for the bond energy in E114–Au (0.81 eV with the gradient model of the exchange-correlation functional) was found to be much larger than the corresponding value for the E112–Au found in the similar approach, from 0.27 (Ref. 24) to 0.41 eV.[88] With regard to the known experimental evidence about the ability of E112 and the corresponding inability of E114 to adsorb on the gold surface (Refs 3 and 5), the latter result does not seem plausible.

It is evident that the transformation from the four-component to the two-component formulation of relativistic DFT is possible without a significant loss in the accuracy of the most calculated characteristics of SHE compounds. Liu and coworkers [92, 139] compared the results of four-component and two-component (zero-order regular approximation) calculations of MH, M_2 (M = E113, E114, E115, Tl, Pb, Bi), and MX (M = E114, Pb; X = F, Cl, Br, I, O, O_2) molecules. It was shown that, even using this simple version of the two-component theory, one can sufficiently reliably describe the valence properties of SHE. On the contrary, the reliability of a number of gradient exchange-correlation functionals in describing electronic correlation in Tl_2 and $E113_2$ was considered questionable. Note that these calculations provided new evidence for the inertness of element 114.

Calculations of the electronic structure of Rg complexes and complexes of copper subgroup metals (Cu, Ag, Au) with small molecules were described;[140] they were performed with scalar relativistic corrections taken into account within the limits of the zero-order regular approximation. Energies of gas-phase reactions

$$[M(H_2O)_2]^+(gas) + L(gas) = [M(H_2O)L]^+(gas) + H_2O(gas),$$

where M = H, Cu, Ag, Au, Rg; L = NH_3, H_2S and PH_3 were calculated in the frozen-core approximation using local [134] and gradient [141] exchange-correlation functionals. The calculated values were used to estimate the Gibbs energies and equilibrium constants of the corresponding reactions in aqueous solutions based on the linear correlations found. It was concluded that Rg(I) is a very strong Lewis acid and an extremely soft ion according to the Pearson criterion.

Numerical experiments using different versions of the relativistic density functional theory with reliable models of core pseudopotentials have shown that the difference in the results of all-electron calculations are negligible in comparison to their change in going from one popular exchange-correlation functional to another. As a result, the popularity of these PDFT versions has increased dramatically as well as the number of studies of SHE compounds using these functionals. Note that almost in all such studies, basis sets were sufficiently flexible and errors due to their incompleteness did not play an important role.

Choi and Lee [95] presented the results of the electronic structure calculations of element 113–117 monohydrides and their analogues from the sixth period (Tl–At) within the framework of the collinear version of the relativistic density functional theory using various gradient and hybrid approximations for exchange-correlation functionals and small-core energy-adjusted pseudopotentials. It was shown that the best agreement with the data of numerical modelling at the evidently much higher level of theory [CCSD(T)] was reached using the hybrid B3LYP functional.[142] The account of spin–orbit interactions leads to the noticeable elongation of the E113–H bond and the reduction of its energy by 0.95 eV; the bonds in E114, E115, E116, and E117 hydrides are shortened and destabilised by 2.22, 0.41, 0.68, and 1.03 eV, respectively.

Mitin and van Wüllen [98] published the results of calculations of diatomic molecules including element 117 (eka-astatine) and its lighter analogues (Br, I, At) using the non-collinear DFT approximation and relativistic small-core pseudopotentials (78 core electrons for E117), both full (spin-dependent) and spin-averaged, with the explicit treatment of all electrons in the molecules. In the latter case, the transformation to two-component effective Hamiltonians was carried out within the limits of the zero-order regular approximation or by means of the Douglas–Kroll transformation. The exchange-correlation functionals were either gradient (B88P86, see Refs 135 and 136) or hybrid (B3LYP, see Ref. 142). The results for Br_2 and I_2 were considered consistent with the experimental data and with the results of two-and four-component relativistic calculations by the coupled cluster method [CCSD(T) version]. The

bond energies evaluated with the B3LYP functional proved to be a little underestimated and those with the B88P86 functional, overestimated. With the inclusion of spin–orbit interactions, the bond in the $E117_2$ considerably weakened (dissociation energy decreased from 1.7 ± 0.1 eV in scalar-relativistic to 0.6 ± 0.1 eV in fully relativistic calculations). Similar schemes were used to study E116 dihydrides and dihalides.[143] It was also shown that, with switching on spin–orbit interactions, the calculated bond angle in the $E116X_2$ (X = Br, I, At, E117) molecules increases from 100° (equilibrium structure symmetry C_{2v}) to 180° (symmetry $D_{\infty h}$).

Chemical bonding in diatomic molecules E112H and E112Au and the interaction of eka-mercury (E112) and mercury atoms with small gold clusters (2–10 atoms) were studied [20, 25] by two-component relativistic density functional theory calculations within the model of small-core shape-consistent relativistic pseudopotentials. The approximation for the exchange-correlation functional was selected based on the results of accurate calculations of diatomic systems at the scalar relativistic level. The parametres of equilibrium configurations and energy characteristics were calculated for the systems E112–Au_n and Hg–Au_n. It was shown that, in spite of the difference in the nature of chemical bonds Hg–Au and E112–Au (spin–orbit interactions stabilise only slightly the bond in the former case and provide about one half of the bond energy in the latter case), the equilibrium structures of $HgAu_n$ and $E112Au_n$ complexes are very similar; in the latter case, the minimum equilibrium distances between the 'adsorbed' atom and the nearest gold atom were found to be 0.05–0.09 Å longer. The ratio between the energies of the abstraction of E112 and Hg from the gold cluster varies within rather narrow limits (from 2 : 3 to 3 : 4), depending on the gold cluster. Taking into account this fact and the experimental value of the energy of mercury adsorption on the gold surface, the estimate for the corresponding energy for eka-mercury was found to be 0.7 eV.

An attempt to apply relativistic DFT in combination with small-core energy-adjusted pseudopotentials to an extended system was described.[27] The electronic structure of crystalline eka-mercury (E112) was calculated using several local and generalised gradient exchange-correlation functionals and contracted Gaussian basis sets. The parametres of the rhombohedral and hexagonal structures were optimised. Based on the comparison of total energies and band gap estimates (0.7–0.9 eV), the authors came to the conclusion that element 112 in the solid state should form hexagonal close-packed structure and exhibit the properties of a semiconductor.

The data on the basic publications in the computational quantum chemical modelling of the structure and properties of SHE-containing systems are presented in Table 1.

Table 1. Calculations of the electronic sructures and properties of systems including SHE atoms.

Element	Compounds, ions	Properties	Calculation method	Ref.
Rf (E104)	$RfCl_4$	$\{R\}_e$, D, atomic charges and volatility	Dirac–Fock	119
	$RfCl_4$	$\{R\}_e$, D	RDFT	130
	RfF_6^{2-}, $RfCl_6^{2-}$	stability constants of complex ions	RDFT	24
Db (E105)	$Db(OH)_6^-$, $DbO_nL_{2-n}^-$ (L = F, Cl, Br)	constants of hydrolysis	RDFT	24
Sg (E106)	$SgBr_6$	$\{R\}_e$, D, I, A, atomic charges and volatility	Dirac–Fock	120
	SgO_4^{2-}	protonation constants	RDFT	24, 128
Bh (E107)	$BhOCl_3$	$\{R\}_e$, D, I, μ, α, atomic charges, adsorption energy on the silica surface	RDFT	24, 127
Hs (E108)	HsO_4	$\{R\}_e$, D, atomic charges and volatility	Dirac–Fock	18
	HsO_4	α	H_{sc}/MP2	35
	HsO_4	$\{R\}_e$, D, I, μ, α, atomic charges, adsorption energy and temperatutre on the silica surface	RDFT	24, 132
Rg (E111)	RgH	R_e, D	H^{pp}/CCSD(T)	116
	RgF_2^-, RgF_4^-, RgF_6^-	$\{R\}_e$, D, k	H_{sc}^{pp}/CCSD(T) + Δ_{so}	78
	RgH, RgLi, RgF	R_e, D, k, μ	H_{sc}^{pp}/CCSD(T) + Δ_{so}	117
	$Rg[(H_2O)L]^+$ (L = NH_3, H_2S, PH_3)	stability constants of complexes in solution	H^{pp}/RDFT	140
E112	$E112_2$	R_e, D	H^{pp}/MP2, CCSD(T)	115
	$E112H$, $E112H^+$, $E112H^-$	R_e, D, k	H_{sc}^{pp}/MP2, CCSD(T)	122
	E112H	R_e, D	H^{pp}/CCSD	25
	E112H	R_e, D	H^{pp}/RDFT,	20
			H_{sc}^{pp}/CCSD(T) + Δ_{so}	20
	$E112H^+$, $E112F_2$, $E112F_4$	R_e, D, k, α	H_{sc}^{pp}/MP2, CCSD(T) + Δ_{so}	77
	E112H, E112Au	R_e, D	H^{pp}/RDFT,	20
			H_{sc}^{pp}/CCSD(T) + Δ_{so}	
	$E112_2$	R_e, D	H_{sc}^{pp}/CCSD(T) + Δ_{so}	99
	E112X (X = Cu, Ag, Au, Pd)	R_e, D, μ, atomic charges	RDFT	129
	E112–Au_n	D, energy of E112 adsorption on the Au(100) surface	RDFT	88, 93, 137
	E112–silica	I, A, energy of E112 adsorption on the silica surface	RDFT	132
	E112–Au_n (n = 2–10)	$\{R\}_e$, D, energy of E112 adsorption on the Au(111) surface	H^{pp}/RDFT	26
	E112, crystals	unit cell parameters, band structure	H^{pp}/RDFT	27

Table 1 (continued).

Element	Compounds, ions	Properties	Calculation method	Ref.
E113	E113H, E113F, $E113H_3$, $E113F_3$, $E113F_4^-$	$\{R\}_e$, D, k	H^{pp}/MP2, CCSD(T) + Δ_{so}	79
	E113H, $E113_2$	R_e, D, k	H^{pp}/RDFT	139
	E113H	R_e, D	H^{pp}/RDFT	95
E114	$E114_2$	R_e, D	H^{pp}/MP2, CCSD(T)	115
	E114H	R_e, D	H^{pp}/RDFT	95
	$E114H_2$	$\{R\}_e$, D	H^{pp}/configuration interaction	123
	$E114H_2$, $E114H_4$, $E114F_2$, $E114F_4$, $E114Cl_2$, $E114Cl_4$	$\{R\}_e$, D	H^{pp}/MP2 + Δ_{so}	118
	E114X (X = O, Pd, Pt, Au, E114)	R_e, D, k	RDFT	133
	$E114_2$, E114X (X = H, F, Cl, Br, I, O, O_2)	$\{R\}_e$, D, k	RDFT, H^{pp}/CCSD(T)	92
E115	E115H	R_e, D	H^{pp}/RDFT	95
	E115H, $E115_2$	R_e, D, k	H^{pp}/RDFT	139
E116	E116H	R_e, D	H^{pp}/RDFT	95
	$E116X_2$ (X = H, F, Cl, Br, I, At, E117)	$\{R\}_e$	H^{pp}/RDFT	143
E117	E117H	R_e, D	H^{pp}/RDFT	95
	$E117_2$	R_e, D, k	H^{pp}/RDFT	98
E118	$E118_2$	R_e, D	H^{pp}/MP2, CCSD(T)	115
	E118H	R_e, D	H^{pp}/RDFT	95
E126	E126F	R_e, D	Dirac–Fock	121

Note. Designations: R_e is bond length, $\{R\}_e$ is equilibrium structure of the polyatomic system, D is dissociation/atomisation energy, k is force constant and/or vibrational frequencies, I is ionisation potential, A is electron afinity, μ is dipole monent, Δ_{so} is polarisability, H^{pp} is relativistic preudopotential model, H_{sc} is scalar-relativistic approximation, Δ_{so} is correction for spin-dependent (spin–orbit) interactions.

IV. Conclusions

The development of relativistic quantum chemical computational technologies has ended the epoch when attempts at theoretically predicting the properties of superheavy element compounds were reduced to atomic structure calculations for SHE and the results obtained together with the data on the chemical properties of lighter analogues were used for risky extrapolations. Now it becomes possible to directly model the properties of sufficiently complex molecular systems including transactinide atoms. Nevertheless, one should not underestimate the complexity of this work. First of all, it is due to large amplitudes of relativistic effects, including spin-dependent ones. This reduces the possibilities of their treatment as perturbation theory corrections and substantially reduces the importance of non-relativistic symmetry classifications 'spin–point group representation', highly useful in non-relativistic electronic structure calculations. Serious technical problems are created by the necessity of the simultaneous description of relativistic effects and electron–electron correlations.

The largest volume of information on the systems containing superheavy elements, interesting for experimentalists, was obtained using various versions of relativistic density functional theory. These methods will probably remain the main tool of the theoretical chemistry of SHE in the nearest future. However, the latter approaches are essentially semiempirical. Approximate exchange-correlation functionals without adjustment parametres described in the literature should not mislead. We would like to remind that of several non-empirical functionals, one chooses that ensuring the best reproduction of some (most important) properties for a certain class of molecules. The situation with many SHE is characterised by the extreme scarcity or absence of experimental data on molecules containing these elements; the major if not the only, source of data for calibrating DFT schemes (the selection of the approximation for exchange-correlation functionals) in this case remains high-level *ab initio* calculations for the simplest systems, small molecules (including those that will hardly be synthesised or are of no interest from the chemical point of view).

Let us note in conclusion that the practical implementation of the electronic structure calculations of SHE compounds is impossible without invoking serious approximations. Attempts to retain the rigour and accuracy in one element of the computational scheme usually imply the necessity of more rough approximations in the other elements. For example, the explicit account of the dependence of the wavefunction or the electron density of the system on the coordinates of all electrons is coupled with the drastic restriction of the size of the 'valence' basis subset and the corresponding problems in reproducing the properties of chemical bonds. Therefore, a certain guarantee of the reliability of the calculated data can only be agreement of the results obtained within qualitatively different electronic structure models.

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