Electron structure of superheavy elements Uut, Fl and Uup (Z=113 to 115).

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Abstract We use recently developed method of accurate atomic calculations which combines linearized single-double coupled cluster method with the configuration interaction technique to calculate ionisation potentials, excitation energies, static polarizabilities and valence electron densities for superheavy elements Uut, Fl and Uup (Z=113 to 115) and their ions. The accuracy of the calculations is controlled by comparing similar calculations for lighter analogs of the superheavy elements, Tl, Pb and Bi with experiment. The role of relativistic effects and correlations is discussed and comparison with earlier calculations is presented.

Keywords superheavy elements · elements E113, E114, E115 · element flerovium · relativistic and correlation effects in atoms

1 Introduction

Study of superheavy elements (SHE, nuclear charge Z > 103) is an important area of research motivated by the search of hypothetical stability island (see, e.g. [1,2,3,4,5]). Experimental work focuses mostly on production and detection of SHE and study of their chemical properties, while there is also some progress in the measurements of the atomic properties. The heaviest element for which ionization potential has been measured is lawrencium (Z = 103) [6]. There is good progress in the measurements of the frequencies of strong electric dipole transitions including hyperfine structure and isotope shift for nobelium (Z = 102) [7,8]. For heavier atoms the information about their atomic properties comes mostly from atomic calculations. The calculations may help in experimental progress and predict chemical properties of SHE. Apart from that the SHE represent an interesting objects from pure theoretical point of view due to strong interplay between correlation and relativistic effects. For example, strong relativistic effects often lead to breaking similarity in chemical properties between SHE and their lighter analogs (see, e.g. [9,10,11]).

In this paper we study SHE Uut, Fl and Uup (Z=113, 114 and 115). These elements are in the vicinity of the hypothetical stability island and have relatively simple electron structure. They can be considered as atoms with three (Uut, Uup) or four (Fl) valence electrons. For such systems accurate calculations are possible. The atoms were studied before mostly by multi-configuration Hartree-Fock and and coupled cluster methods [12,13,14,15,16,17]. In this paper we apply a recently developed method which combines linearized single-double coupled cluster (SD) and configuration interaction (CI) methods. We present detailed study of the energy levels, ionization potentials, static scalar polarizabilities, and electron densities for the superheavy elements and their ions. We discuss the role of relativistic and correlation effects.

2 Method of Calculation

Atomic calculations always start from calculating the energy and the wave function of the ground state. Then they may proceed to calculation of excited states, their lifetimes, transition amplitudes, etc. Since there are no experimental data on atomic properties of superheavy elements considered in
this paper we should decide which properties should be calculated with higher priorities. Ionization potential (IP) and polarizability of an atom are obviously important parameters since they determine its interaction with environment and thus, its chemical properties. This can be illustrated by the following example. A way of detecting SHE and studying their chemical properties (e.g., volatility) is by observing the SHE absorption to an inert surface. The energy of the interaction of the SHE with the surface is given by the formula [21]

\[ E(x) = -\frac{3}{16} \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{\alpha_{at}}{(\varepsilon_{slab} + 1)^2} x^3 \]  

(1)

where \( \alpha_{at} \) is atomic polarizability and \( \varepsilon_{at} \) is its ionization potential; \( \varepsilon \) is the dielectric constant of the substance of the slab, \( \varepsilon_{slab} \) is the ionization potential of the slab atom, and \( x \) is the surface-atom distance.

Other important characteristics of SHE include frequencies of strong electric dipole transitions from the ground state since they are likely to be measured first. It is also instructive to have other excited states and electron densities and compare them to lighter analogs of SHE to study the role of relativistic effects.

Obtaining reliable results for superheavy elements (SHE) require accurate treatment of relativistic and many-body effects. The inclusion of the most important relativistic effects associated with the Dirac equation is pretty straightforward. These relativistic effects are responsible for the difference between SHE and lighter atoms. Inclusion of other relativistic corrections such as Breit interaction, quantum electrodynamic (QED) corrections are also important for accurate results but they bring little difference in electron structure of SHE compared to lighter atoms. The main challenge for the calculations and largest uncertainty in the results comes from the treatment of the correlations. Accurate results can be obtained for atoms with simple electron structure with few valence electrons. The highest accuracy can be achieved for Fr-like and Ra-like atoms and ions which have only one or two valence electrons well separated from the core in space and on energy scale [22,23,24,25,26]. In this paper we consider atoms and ions with three and four valence electrons from 13th to 15th groups of the periodic table. The method of treating correlations is presented in next section.

Note that while accurate treatment of correlations is very important for accurate results, the correlations for SHE are very similar to those of the lighter atoms and usually do not cause any significant difference in the atomic properties of SHE.

2.1 Treating the correlations. The SD+CI method.

For accurate treatment of correlations we use the combinations of the single-double (SD) coupled cluster method and the configuration interaction (CI) technique developed in Ref. [27] (the SD+CI method). Here we give its brief summary.

All atomic electrons are divided into two categories, the core electrons, which occupy the closed-shell core of the atom, and valence electrons, which occupy outermost open shells. The wave function of the valence electrons is assumed to be in the form

\[ \Psi(r_1, \ldots, r_{N_v}) = \sum_i c_i \Phi_i(r_1, \ldots, r_{N_v}), \]  

(2)

where \( N_v \) is the number of valence electrons (\( N_v = 3 \) for Tl, E113, Bi and E115, \( N_v = 4 \) for Pb and E114), \( \Phi_i(r_1, \ldots, r_{N_v}) \) is a single-determinant basis state constructed from single-electron orbitals \( \phi_i \). For example, for two valence electrons

\[ \Phi_i(r_1, r_2) = \frac{1}{\sqrt{2}} (\phi_i(r_1)\phi_0(r_2) - \phi_0(r_1)\phi_i(r_2)). \]  

(3)

The expansion coefficients \( c_i \) in (2) are found by solving the eigenvalue problem for the effective CI Hamiltonian,

\[ \hat{H}^{CI} = \sum_i \hat{h}_1(r_i) + \sum_{i < j} \hat{h}_2(r_i, r_j), \]  

(4)

\( \hat{h}_1 \) and \( \hat{h}_2 \) are one and two-electron parts of the Hamiltonian. The one electron part is given by

\[ \hat{h}_1 = c \alpha p + (\beta - 1)mc^2 + V_{core} + \hat{\Sigma}_1, \]  

(5)

where \( \alpha \) and \( \beta \) are Dirac matrixes, \( V_{core} \) is the self-consistent potential of the atomic core (including nuclear part), \( \hat{\Sigma}_1 \) is the single-electron correlation operator responsible for the correlation interaction of a valence electron with the core.

Two-electron part of the Hamiltonian is

\[ \hat{h}_2(r_1, r_2) = \frac{e^2}{|r_1 - r_2|} + \hat{\Sigma}_2(r_1, r_2), \]  

(6)

where \( \hat{\Sigma}_2 \) is the correlation correction to the Coulomb interaction between valence electrons caused by core electrons.

The \( \hat{\Sigma}_1 \) and \( \hat{\Sigma}_2 \) operators represent core-valence correlations. They can be calculated in the lowest, second order of the many-body perturbation theory (MBPT). Inclusion of the second-order \( \hat{\Sigma} \) into the CI calculations leads to significant improvement of the accuracy of the calculations compared to the CI method with no \( \hat{\Sigma} \). Further improvements in accuracy is achieved when \( \hat{\Sigma}_1 \) and \( \hat{\Sigma}_2 \) are calculated to all orders using the SD approach [27,28]. This approach also includes core-core correlations. The SD equations for the core do not depend on valence electrons and remain the same regardless of whether the SD and CI methods combined together or not. These equations can be found elsewhere (see,
Electron structure of superheavy elements Uut, Fl and Uup (Z=113 to 115).

The SD equations for valence states in the SD+CI method can be written in the form

\[ (\varepsilon_0 + \varepsilon_b - \varepsilon_m - \varepsilon_n) \rho_{mnab} = \sum_{rs} g_{mnrs} \rho_{rsvb} + \sum_{rc} g_{cnvb} \rho_{ncbc} = \]  
\[ \sum_{cd} g_{cdvb} \rho_{mbnr} + \sum_{rc} g_{cnvb} \rho_{ncbc} + \sum_{rc} \tilde{g}_{cnmb} \rho_{mbnr} \]  
\[ \sum_{rc} g_{cnvb} \rho_{ncbc} + \sum_{rc} \tilde{g}_{cnmb} \rho_{mbnr} \]  
\[ \sum_{rc} g_{cnvb} \rho_{ncbc} + \sum_{rc} \tilde{g}_{cnmb} \rho_{mbnr} . \]  

Here parameters \( g \) are Coulomb integrals

\[ g_{mnab} = \int \int \psi^\dagger_m(r_1) \psi^\dagger_n(r_2) \frac{e^2}{r_1r_2} \psi_b(r_1) \psi_b(r_2) dr_1 dr_2 . \]

parameters \( \varepsilon \) are the single-electron Hartree-Fock energies, \( \varepsilon_0 \) is an external parameter related to the energy of valence state of interest \[27\]. Coefficients \( \rho_{ij} \) and \( \rho_{ijkl} \) are the expansion coefficients found by solving the SD equations. The tilde above \( g \) or \( \rho \) means the sum of direct and exchange terms, e.g.,

\[ \tilde{\rho}_{mbrc} = \rho_{mbrc} - \rho_{rbcm} . \]

Indexes \( a, b, c \) numerate states in atomic core, indexes \( m, n, r, s \) numerate states above the core, indexes \( i, j, k, l \) numerate any states.

Equations \[7\] are solved iteratively starting from

\[ \rho_{mnij} = \frac{g_{mnij}}{\varepsilon_i + \varepsilon_j - \varepsilon_m - \varepsilon_n} . \]  

The right-hand side of \[7\] contains only terms which do not change in the iterations. Corresponding \( \rho_{ij} \) and \( \rho_{ijkl} \) coefficients are found by solving the SD equations for the core (see Ref. \[27\] for more details).

After solving the SD equations, matrix elements for the \( \hat{\Sigma}_1 \) and \( \hat{\Sigma}_2 \) operators can be found by

\[ (mn) \hat{\Sigma}_1 (ij) = \sum_{bn} \tilde{g}_{mban} \rho_{nbij} + \sum_{bc} \tilde{g}_{mbcn} \rho_{nbc} . \]  

and

\[ (mn) \hat{\Sigma}_2 (ij) = \sum_{cd} \tilde{g}_{cdvb} \rho_{mbnr} + \sum_{rc} \tilde{g}_{cnvb} \rho_{mbnr} + \sum_{rc} \tilde{g}_{cnmb} \rho_{mbnr} . \]  

A complete set of single-electron states is needed for solving the SD equations \[7\] and for construction of the many-electron valence states \[3\]. We use the same B-spline technique \[29\] in both cases. Forty B-spline states of the order of nine are calculated in a box of radius 40 \( a_g \) in the \( V^{N-M} \) potential \[30\]. Here \( N \) is total number of electrons and \( M \) is number of valence electrons. We include partial waves up to \( l_{\text{max}} = 6 \). Thirty lowest states in each partial wave are used for solving the SD equations for the core and for valence states. The SD equation for valence states are solved for few (usually three) states above the core in each partial wave up to \( l_{\text{max}} = 2 \). The second-order correlation potential \( \hat{\Sigma} \) is used for higher states. Fourteen states above the core in each partial wave up to \( l_{\text{max}} = 4 \) are used in the CI calculations. With this choice of the parameters the basis is sufficiently saturated.

2.2 Study of relativistic effects

Dominating relativistic effects \( (\sim (Z\alpha)^2) \) are included by solving Dirac-like equation for single-electron orbitals. Breit and quantum electrodynamics (QED) corrections are also included (see below). Choosing single-electron orbitals in the form

\[ \Psi(r) = \frac{1}{r} \left( \frac{f(r) \Omega_{\kappa,m}(n)}{\pm \alpha \kappa} \right) \]  

leads to the following form of the Dirac equation (we use atomic units)

\[ \frac{\partial f}{\partial r} + \frac{\kappa}{r} f - [2 + \alpha^2(e - \hat{V})] g = 0 , \]

\[ \frac{\partial g}{\partial r} - \frac{\kappa}{r} g + (e - \hat{V}) f = 0 . \]  

Here \( n \equiv r/r, \kappa = (-1)^{l+j+1/2}(j+1/2) \) defines electron orbital angular momentum \( l \) and total angular momentum \( j \), \( \alpha \) is the fine structure constant, and \( \hat{V} \) is the potential. Potential includes nuclear and electron parts. Electron part includes direct and exchange terms. Fine structure constant \( \alpha \) serves as a measure of relativistic effect. Non-relativistic limit corresponds to \( \alpha = 0 \). Varying the value of \( \alpha \) in \[12\] and corresponding computer codes allows us to study the role of relativistic effects in atoms. For example, it was used to search for the manifestations of the hypothetical space-time variation of the fine structure constant in atomic spectra (see, e.g., \[31\]–\[33\]).

We include Breit interaction in the zero momentum transfer approximation. Corresponding Hamiltonian is

\[ \hat{H}^B = -\frac{\alpha_1 \cdot \alpha_2 + \langle \alpha_1 \cdot n \rangle \langle \alpha_2 \cdot n \rangle}{2r} . \]  

Here \( r = |\mathbf{r}|, \mathbf{r} \) is the distance between electrons, and \( \alpha \) is the Dirac matrix. The Hamiltonian \[13\] includes magnetic interaction and retardation. Similar to Coulomb interaction, we determine the self-consistent Hartree-Fock contribution arising from Breit interaction by adding Breit term to the self-consistent Hartree-Fock potential.

\[ \hat{\Psi} = V^C + V^B . \]  

Here \( V^C \) is the Coulomb potential, \( V^B \) is the Breit potential. Iterating Hartree-Fock equations with the Breit term in the
Vergies (Lamb shifts) are accounted for by the use of the ra-
pole rescaling procedure \[35,36\]. However, in practice they
potential corresponds to the inclusion of the important re-
action, the relaxation effect is important and included by
arguing with external field. E.g., second-order Stark
shift is given by \( \delta E = \frac{1}{2} \alpha \varepsilon^2 \), where \( \varepsilon \) is atomic energy, \( \alpha \)
is polarisability and \( \varepsilon \) is electric field. For atoms with total
angular momentum \( J \geq 1 \) polarisability is given by the sum
of two terms
\[
\alpha = \alpha_0 + \alpha_2 \frac{3M^2 - J(J + 1)}{J(2J - 1)},
\]
(16)
where \( \alpha_0 \) is scalar polarisability, \( \alpha_2 \) is tensor polarisability and
\( M \) is projection of \( J \).

We also present in Table 1 the results of coupled-cluster
(CC) calculations of the energy levels of TI, Pb and Bi taken
from the works devoted to superheavy elements E113 \[12\],
E114 \[17\] and E115 \[18\]. All calculations are done with
the same method and probably with the same set of computer
codes. The most detailed data are presented for Pb. Com-
parison shows that both calculations have very similar devia-
tions from the experimental data. On the other hand, the
difference between two calculations is significantly smaller
than the difference between theory and experiment at least for
the lowest states. This is important observation since the
calculations are done with the use of very different tech-
niques. Good agreement between different calculations adds
to the reliability of the results.

2.3 Calculation of polarizabilities

Polarisability is an important characteristic of an atom defin-
ing its interaction with external field. E.g., second-order Stark
shift is given by \( \delta E = \frac{1}{2} \alpha \varepsilon^2 \), where \( E \) is atomic energy, \( \alpha \)
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where \( \alpha_0 \) is scalar polarisability, \( \alpha_2 \) is tensor polarisability and
\( M \) is projection of \( J \).

When many-electron atom is treated by a configuration
interaction technique all atomic electrons are divided into
two groups. Most go to the closed-shell core, and few re-
maining are treated as valence electrons. As a consequence,
there are three contributions to the scalar polarisability, core
contribution, core-valence contribution, and valence con-
tribution
\[
\alpha_0 = \alpha_e + \alpha_{cv} + \alpha_v.
\]
(17)

Core-valence contributions arise due to the interference be-
tween core and valence terms. Calculation of the core polar-
isability is affected by the presence of the valence electrons
due to the Pauli principle. States, occupied by valence elec-
trons must be excluded from the summation over complete
set of states.

Another consequence of dividing electrons into core and
valence categories is the effect of core polarisation by exter-
valence potential is the potential arising
from the electric formfactor. As for the case of the Breit in-
teraction, the relaxation effect is important and included by
iterating the Hartree-Fock equations with the radiative poten-
tial added to the Hartree-Fock potential. Table 1 compares
calculated ionisation potentials and lowest excitation ener-
gies of TI, Pb and Bi with experimental data. Correlations
and relativistic effects are included in all calculations
as has been described above. The difference between theory
and experiment is on the level of \( \sim 1\% \).

Table 1 Calculated and experimental ionization potentials (IP, in
\( \text{cm}^{-1} \)) and excitation energies (EE, in \( \text{cm}^{-1} \)) for the ground and lowest
excited states of TI, Pb and Bi atoms. Other theoretical data are taken
from Ref. \[12\] for TI, Ref. \[17\] for Pb and Ref. \[18\] for Bi. Experimental
values are taken from the NIST database \[33\].

| Atom | State | \( E_{\text{calc}} \) | \( E_{\text{expt}} \) |
|------|-------|-----------------|-----------------|
| TI   | \( 6s^26p\) | \( ^2P_{1/2} \) | 49228 | 48575 | 49266 |
| EE   | \( 6s^26p\) | \( ^2P_{1/2} \) | 7897 | 7710 | 7793 |
| Bi   | \( 6s^27p\) | \( ^1S_0 \) | 26713 | 26456 | 26478 |
| Pb   | \( 6s^25p\) | \( ^1S_0 \) | 35456 | 35161 | 36118 |
| Bi   | \( 6p^3\) | \( ^2D_{5/2} \) | 34648 | 36672 |
| Pb   | \( 6p^3\) | \( ^2P_{3/2} \) | 40932 | 38746 | 42318 |

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Table 1 compares calculated ionisation potentials and lowest excitation energies of TI, Pb and Bi with experimental data. Correlations and relativistic effects are included in all calculations as has been described above. The difference between theory and experiment is on the level of \( \sim 1\% \).

We also present in Table 1 the results of coupled-cluster (CC) calculations of the energy levels of TI, Pb and Bi taken from the works devoted to superheavy elements E113 [12], E114 [17] and E115 [18]. All calculations are done with the same method and probably with the same set of computer codes. The most detailed data are presented for Pb. Comparison shows that both calculations have very similar deviations from the experimental data. On the other hand, the difference between two calculations is significantly smaller than the difference between theory and experiment at least for the lowest states. This is important observation since the calculations are done with the use of very different techniques. Good agreement between different calculations adds to the reliability of the results.
random-phase approximation (RPA). The RPA equations for single-electron orbitals $\phi$ can be written as

$$\langle \hat{H}^{\text{HF}} - \varepsilon \rangle \delta \phi = - (\hat{F} + \delta V)\phi,$$

(18)

where $\hat{H}^{\text{HF}}$ is the Hartree-Fock Hamiltonian, $\delta \phi$ is the correction to the single-electron orbital $\phi$ due to external field, $\hat{F}$ is the operator of the external field, and $\delta V$ is the correction to the self-consistent Hartree-Fock potential due to the external field. In case of calculation of the static polarizabilities, the external field is static electric field and $\delta V$ is the electric dipole operator, $\hat{F} \equiv d = - er$.

Core contribution to the polarisability is given by

$$\alpha_c = \frac{2}{3} \sum_{an} \frac{\langle a|\hat{d}|n\rangle \langle a|\hat{d} + \delta V|n\rangle}{\varepsilon_a - \varepsilon_n}$$

(19)

Summation goes over core states $a$ and complete set of single-electron states above the core $n$. Note that the RPA correction is included into only one of two matrix elements (see, e.g. Ref. [39] for more detailed discussion).

Expression (19) does not take into account the presence of valence electrons. States occupied by valence electrons must be excluded from the summation over excited states $n$ in (19). This is not a trivial task since states $n$ are just single-electron basis states but not real physical states. The solution within the CI approach is the following. Recall that the many-electron wave function for valence electrons has the form (23). Then fractional occupation number $w_n$ for a single-electron orbital $\phi_a$ can be found as a sum

$$w_n = \sum_{ia} \phi_{ia}^2$$

(20)

where additional index $n$ for expansion coefficients means that summation goes only over those states $\Phi_i$ in (23) which contain single-electron orbital $\phi_a$ in the definition of $\Phi_i$ (e.g., formula (23) for the two-valence-electrons case). Final occupation number for the orbital $\phi_a$ is the ratio of $w_n$ to the maximum possible number of electrons in state $n$ which is $2J_n + 1$. In the end, the sum of the core and core-valence contributions to atomic polarisability can be written as

$$\alpha_c + \alpha_{cv} = \frac{2}{3} \sum_{an} \frac{\langle a|\hat{d}|n\rangle \langle n|\hat{d} + \delta V|a\rangle}{\varepsilon_n - \varepsilon_a} \left(1 - \frac{w_n}{2J_n + 1}\right).$$

(21)

Valence contribution to the polarisability is given by

$$\alpha_{cv} = \frac{2}{3} \sum_{n} \frac{|\langle 0|\hat{D}^{\text{RPA}}|n\rangle|^2}{E_n - E_0}.$$ 

(22)

The summation goes over complete set of many-electron valence states $N$ which are the eigenstates of the CI hamiltonian and have a form of (23). $E_n$ is the energy of state $N$, $E_0$ and $J_0$ are the energy and total angular momentum of the state $|0\rangle$, $\hat{D}^{\text{RPA}}$ is the many-electron operator of electric dipole moment, $\hat{D}^{\text{RPA}} = \sum_N |\hat{d} + \delta V\rangle$.

Performing summation over many-electron states in (22) is a challenging task since most if not all of the eigenstates of the CI Hamiltonian need to be included for accurate results. We use the technique introduced by Dalgarno and Lewis [40] to perform the summation. In this approach a correction to the ground state many electron wave function is introduced in a form

$$|\tilde{0}\rangle = \sum_N |N\rangle \frac{\langle N|\hat{D}^{\text{RPA}}|0\rangle}{E_N - E_0}.$$ 

(23)

Since all states $N$ and $0$ in (23) are the eigenstates of the CI Hamiltonian, the correction (23) satisfies the equation

$$\langle \hat{H}^{\text{CI}} - E_0 |0\rangle = - \hat{D}^{\text{RPA}} |0\rangle.$$ 

(24)

In the CI technique the correction $|\tilde{0}\rangle$ has a form of (23) and equation (24) is reduced to the system of linear equations for expansion coefficients $c_i$. After solving the equations we calculate valence part of the polarisability using the formula

$$\alpha_{cv} = \frac{2}{3} \sum_{J_n} \frac{|\langle 0|\hat{D}^{\text{RPA}}|\tilde{0}\rangle|^2}{(2J_n + 1)}.$$ 

(25)

Calculation of tensor polarisability $\alpha_2$ (see Eq. (16) is similar. There is no core contribution because total angular momentum of the closed shell core is zero. Calculation of the valence contribution involves performing the same summation as in (22). It can be done ones for both polarizabilities, $\alpha_0$ and $\alpha_2$. The formula for $\alpha_2$ differs from (22) by angular coefficients only and can be found elsewhere (see, e.g. Ref. [39]).

Table 2: Contributions to the static scalar polarizabilities $\alpha_0 = \alpha_c + \alpha_{cv}$, $\alpha_0$, $\alpha_{cv}$ of the ground state of Tl, Pb and Bi atoms (in $a_0^3$) and comparison with earlier calculations or measurements. See formula (17) and discussion below it for definitions of $\alpha_c$, $\alpha_{cv}$, and $\alpha_{cv}$. 

| Atom | State | $\alpha_c$ | $\alpha_{cv}$ | $\alpha_0$ | Present work Other |
|------|-------|------------|---------------|------------|-------------------|
| Tl   | $6s^26p$ | $2P_{1/2}^0$ | 4.98 | -0.11 | 42.91 | 47.78 | 49.2(41), 51.6(42), 51.3(5.4) | [43] |
| Pb   | $6s^26p^2$ | $1S_0^0$ | 3.63 | -0.44 | 40.85 | 40.04 | 47.3(41), 47.1(7.0) | [44], 46(11) | [45] |
| Bi   | $6p^3$ | $2P_{3/2}^0$ | 11.22 | -5.43 | 38.83 | 44.62 | 50(12) | [45] |
valence, give significant contribution to the scalar polarizability and there is good agreement between present calculations and available experimental data and earlier calculations. Judging by the differences in results the accuracy of present calculations is within few percent.

2.4 Density of valence electrons

In the configuration interaction calculations many-electron wave function for the valence electrons has a form of \( \Phi_i \) in which single-determinant basis states \( \Phi_i \) are constructed from single-electron states of the form \( \Phi_n^\alpha \). Therefore, density of valence electrons as a function of distance can be calculated as

\[
\rho_v(r) = \sum_{i=1}^{N_v} \sum_{\alpha=1}^{n_i} f_n^\alpha(r) + \alpha^2 g_n^\alpha(r).
\] 

This expression is the most accurate one. It includes correlations and relativistic effects. To study the effect of correlations one should compare (26) with the electron density calculated in the HF approximation using the \( V^N \) potential (all atomic electrons are included into the self-consistent HF procedure),

\[
\rho_v(r)^{HF} = \sum_{n=1}^{N_v} \left( f_n^\alpha(r) + \alpha^2 g_n^\alpha(r) \right),
\] 

where \( f_n \) and \( g_n \) are single-electron HF wave functions of the valence electrons. Non-relativistic limit for the density can be obtained if the calculations are conducted with \( \alpha = 0 \).

3 Results and discussion

Calculated energy levels, \( g \)-factors and ionization potentials of superheavy elements E113, E114 and E115 and their ions are presented in Tables 3, 4, 5. The results of earlier calculations are also presented for comparison. As it was discussed above we expect that the accuracy of our calculated energies is about 1%. In most of cases the difference with other results is slightly larger, varying from about 1% to few percents. Since other calculations must also have uncertainty, the results are rather in agreement with each other. Note, that the agreement for E114 is significantly better than for E113 (see Tables 3 and 4).

The \( g \)-factors are useful for identification of states. We can see from the data in the tables that the values of calculated \( g \)-factors are close to corresponding non-relativistic values given by

\[
g_{NR} = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}.
\]

This allows us to use non-relativistic labelling of the states.

### Table 3 Calculated excitation energies (\( E \), cm\(^{-1} \)), ionisation potentials (I.P.) and \( g \)-factors for the lowest states of the E113 atom and E113\(^+\) and E113\(^{++}\) ions.

| State     | This work | Other \([12]\) |
|-----------|-----------|----------------|
| E113, I.P. = 7.37 eV |           |                |
| 7s\(^2\)7p | \( 1^P_{1/2} \) | 0.6667 | 0 |
| 7s\(^2\)7p | \( 3^P_{1/2} \) | 24758 | 1.3333 | 22528 |
| 7s\(^2\)8s | \( 1^S_{1/2} \) | 36665 | 1.9997 | 35124 |
| 7s\(^2\)8p | \( 1^P_{1/2} \) | 44346 | 0.6667 |
| 7s\(^2\)8p | \( 3^P_{1/2} \) | 47104 | 1.3333 |
| 7s\(^2\)7d | \( 1^D_{3/2} \) | 48768 | 0.8000 |
| 7s\(^2\)7d | \( 3^D_{5/2} \) | 49176 | 1.2000 |
| 7s\(^2\)9s | \( 3^S_{1/2} \) | 49774 | 2.0000 |
| 7s\(^2\)9p | \( 3^P_{1/2} \) | 51375 | 0.6667 |
| 7s\(^2\)6f | \( 3^P_{2/2} \) | 52225 | 0.8571 |
| 7s\(^2\)6f | \( 5^P_{2/2} \) | 52231 | 1.1429 |
| 7s\(^2\)9p | \( 5^P_{2/2} \) | 52485 | 1.3333 |
| E113\(^{++}\), I.P. = 23.6 eV |           |                |
| 7s\(^2\) | \( 3^P_0 \) | 60042 | 0.0000 | 61245 |
| 7s\(^2\) | \( 3^P_0 \) | 63187 | 1.3969 | 66868 |
| 7s\(^2\) | \( 2^P_2 \) | 97312 | 1.4999 | 82208 |
| 7s\(^2\) | \( 3^P_2 \) | 104560 | 1.1024 | 107182 |
| E113\(^{++}\), I.P. = 33.5 eV |           |                |
| 7s | \( 3^S_{1/2} \) | 0 | 2.0000 |
| 7p | \( 1^P_{1/2} \) | 70054 | 0.6667 | 74779 |
| 7p | \( 3^P_{1/2} \) | 117593 | 1.3333 | 111044 |

Calculated IPs of the superheavy elements are compared with IPs of their lighter analogs and with other calculations in Table 5. The agreement of present results with experiment and with best earlier calculations is on the level of 1%.

Comparing the spectra of superheavy elements and their lighter analogs (see tables 3, 4, 5 and 1) reveals the difference which can be attributed to relativistic relaxation of the \( s \) and \( p_{1/2} \) states and increased fine structure intervals for \( p \) and \( d \) states. For example, ionization potentials of E113 and E114 are significantly larger than those of Ti and Pb. This is because IPs of these elements are the energies of removal of the external \( p_{1/2} \) electron from the atom. However, due to relativistic relaxation, the \( 7p_{1/2} \) states of E113 and E114 are deeper on the energy scale than the \( 6p_{1/2} \) states of Ti and Pb. In contrast, the IP of E115 is smaller than those of Bi. These is because these atoms have three external \( p \)-electrons which means that the \( p_{3/2} \) state is also occupied. The IP is the energy to remove the \( p_{3/2} \) electron. Due to larger fine structure, the \( 7p_{3/2} \) electron of E115 is higher on the energy scale than the \( 6p_{3/2} \) electron of Bi. Note that the E115\(^+\) ion has no \( 7p_{3/2} \) electron and its ionization potential is larger than for the case of E114\(^+\) due to larger \( Z \) (see Table 6).

Similar tendency can be observed for polarizabilities (see Tables 7 and 8). The polarizabilities of E113 and E114 are...
Relativistic effects move the 7\textsuperscript{115} atom (Fig. 3) due to the presence of the 7\textsuperscript{115} electron density. The picture is more complicated for the other states, which experience similar contraction causing little change in electron density. Both atoms have the 7\textsuperscript{115} states, most of which are also significantly more change to the electron density than correlations. The difference between first two lines is due to correlations while the difference between latter two lines is due to relativistic effects associated with Dirac equation \( \text{[12]} \). Comparing the graphs for E113 and E114 shows that the relativistic effects cause significantly more change to the electron density than correlations. Both atoms have the 7\textsuperscript{131/2} and 7\textsuperscript{11/2} valence states with two electrons in the 7\textsuperscript{131/2} state and one or two electrons in the 7\textsuperscript{11/2} state. Relativistic effects cause these states to contract towards the core. Configuration interaction brings admixture of other states most of which are also \textsuperscript{11/2} or \textsuperscript{131/2} states. They experience similar contraction causing little change in electron density. The picture is more complicated for the E115 atom (Fig. 3) due to the presence of the 7\textsuperscript{13/2} state. Relativistic effects move the 7\textsuperscript{11/2} and 7\textsuperscript{13/2} states in opposite directions, therefore, the change in total density is smaller while the effect of correlations is larger.

### 4 Conclusion

Accurate calculations of energy levels, ionization potentials, polarizabilities and densities of valence electrons of superheavy elements E113, E114 and E115 are presented. Similar calculations for lighter analogs of the superheavy elements are presented for comparison and for the control of accuracy. The accuracy for the energies is expected to be on the level of 1% and the accuracy for the polarizabilities is few per cent. The study of relativistic and correlation effects reveal that the difference in electron structure of superheavy elements Uut, Fl and Uup (Z=113 to 115).

### Table 5 Calculated excitation energies (\( E, \text{cm}^\text{-1} \)), ionisation potentials (I.P.), and g-factors for the lowest states of \textit{E115}, \textit{E115}\textsuperscript{+} and \textit{E115}\textsuperscript{++}.

| State       | This work   | Other     |
|-------------|-------------|-----------|
| \textsuperscript{115}Ip | 5.56 eV     |           |
| \textsuperscript{7p\textsuperscript{3}P\textsubscript{1/2}} | 0.0000     |           |
| \textsuperscript{7p\textsuperscript{3}S\textsubscript{1/2}} | 0.0000     |           |
| \textsuperscript{7p\textsuperscript{3}D\textsubscript{3/2}} | 0.0000     |           |
| \textsuperscript{8s\textsuperscript{1}S\textsubscript{1/2}} | 0.0000     |           |
| \textsuperscript{8s\textsuperscript{1}P\textsubscript{1/2}} | 0.0000     |           |
| \textsuperscript{8s\textsuperscript{1}P\textsubscript{3/2}} | 0.0000     |           |
| \textsuperscript{8s\textsuperscript{1}D\textsubscript{3/2}} | 0.0000     |           |

Figs. 1 and 2 show electron density of valence electrons of superheavy elements E113, E114 and E115 calculated in different approximations. Solid line represents the result of most accurate calculations using the CI wave function and formula \( \text{[26]} \). Dashed line shows the density in the relativistic Hartree-Fock approximation calculated using formula \( \text{[27]} \). Dotted line is the Hartree-Fock density calculated in the non-relativistic limit. The difference between first two lines is due to correlations while the difference between latter two lines is due to relativistic effects associated with Dirac equation \( \text{[12]} \). Comparing the graphs for E113 and E114 shows that the relativistic effects cause significantly more change to the electron density than correlations. Both atoms have the 7\textsuperscript{131/2} and 7\textsuperscript{11/2} valence states with two electrons in the 7\textsuperscript{131/2} state and one or two electrons in the 7\textsuperscript{11/2} state. Relativistic effects cause these states to contract towards the core. Configuration interaction brings admixture of other states most of which are also \textsuperscript{11/2} or \textsuperscript{131/2} states. They experience similar contraction causing little change in electron density. The picture is more complicated for the E115 atom (Fig. 3) due to the presence of the 7\textsuperscript{13/2} state. Relativistic effects move the 7\textsuperscript{11/2} and 7\textsuperscript{13/2} states in opposite directions, therefore, the change in total density is smaller while the effect of correlations is larger.

#### 4 Conclusion

Accurate calculations of energy levels, ionization potentials, polarizabilities and densities of valence electrons of superheavy elements E113, E114 and E115 are presented. Similar calculations for lighter analogs of the superheavy elements are presented for comparison and for the control of accuracy. The accuracy for the energies is expected to be on the level of 1% and the accuracy for the polarizabilities is few per cent. The study of relativistic and correlation effects reveal that the difference in electron structure of su-
Table 6  Ionization potential of Tl, Pb, Bi and superheavy elements E113, E114, E115 including ions (eV). Comparison with experiment and other calculations.

| Atom/ Ion | Expt. [38] | Present work | Other |
|-----------|------------|--------------|-------|
| Tl        | 6.108      | 6.022 [12], 6.096 [13] |       |
| Pb        | 7.416      | 7.312 [14], 7.35 [15], 7.349 [17], 7.484 [17] |       |
| Bi        | 7.285      | 7.272 [13], 7.29 [12] |       |
| E113      | 7.37       | 7.306 [13] |       |
| E113\(^+\) | 23.6       | 23.9 [12] |       |
| E113\(^++\) | 33.5       | 33.6 [12] |       |
| E114      | 8.37       | 8.28 [14], 8.54 [15], 8.539 [17] |       |
| E114\(^+\) | 17.0       | 17.2 [14], 16.871 [17] |       |
| E115      | 5.56       | 5.574 [18] |       |
| E115\(^+\) | 18.4       | 18.360 [18] |       |
| E115\(^++\) | 27.7       |       |       |

Table 7  Static scalar polarizabilities \(\alpha_0\) of SHE (in a.u.). Comparison with other calculations.

| Atom | Ground state | Present work | Other |
|------|--------------|--------------|-------|
| E113 \(7s^27p\) \(^2P_{1/2}\) | 28.8 | 29.85 [13] |       |
| Fl \(7s^27p\) \(^1S_0\) | 31.4 | 31.0 [16], 34.4 [19], 30.59 [20] |       |
| E115 \(7p\) \(^4P_{3/2}\) | 70.5 |       |       |

perheavy elements compared to their lighter analogs mostly come from relativistic effects associated with Dirac equation. Inclusion of Breit and QED effects is important for accurate results but cause little difference. The contribution of the correlations is similar for superheavy elements and their lighter analogs. Accurate treatment of the correlations represent the main challenge for the calculations. For atoms with relatively simple electron structure (no more than three valence electrons), as those considered in present paper, the calculations are done with sufficiently high accuracy.

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Electron structure of superheavy elements Uut, Fl and Uup (Z=113 to 115).

![Fig. 3](image)

**Fig. 3** Density of valence electrons for the ground state ($7p^3 \ ^4S_{3/2}$) of Uup (E115). See Fig. [I] for notations.

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