

All-order calculations of the spectra of superheavy elements 113 and 114

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We apply a recently developed method [V. A. Dzuba, *Phys. Rev. A* **90**, 012517 (2014); J. S. M. Ginges and V. A. Dzuba, *ibid.* **91**, 042505 (2015)] to calculate energy levels of superheavy elements Uut ($Z = 113$), Fl ($Z = 114$), and Fl⁺. The method combines the linearized single-double coupled-cluster technique, the all-order correlation potential method, and configuration-interaction method. Breit and quantum electrodynamic corrections are included. The role of relativistic and correlation effects is discussed. Similar calculations for Tl, Pb, and Pb⁺ are used to gauge the accuracy of the calculations.

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I. INTRODUCTION

The study of the superheavy elements is an important area of research motivated by the predicted “island of stability” in the region $Z > 104$. Elements with nuclear charge up to $Z = 118$ have been synthesized (see, e.g., Refs. [1–5]) and evidence for the naturally occurring superheavy element 122 (E122) was reported [6].

The experimental study of atomic properties of superheavy elements has recently advanced to nobelium ($Z = 102$) and lawrencium ($Z = 103$). The ionization potential has been measured for lawrencium [7]; the ionization potential and frequencies of strong electric dipole transitions have been measured for nobelium [8,9]. Further progress towards heavier elements is very likely.

There are many theoretical works in atomic physics and quantum chemistry with attempts to predict the chemical properties of the superheavy elements and their electron structure and spectra (see, e.g., [10–12]). Superheavy elements 113 and 114 are of special interest due to their closeness to the hypothetical island of stability and relatively simple electron structure. The E113 atom can be considered as a system with one external electron above the closed-shell core that ends with the $7s^2$ subshell. Its lighter analog is Tl. The E114 atom can be considered as a system with two valence electrons. There are a number of calculations of electron spectra of elements 113 and 114 using multiconfiguration Dirac-Fock, coupled-cluster, and configuration-interaction methods and their combinations [13–20]. The results of different approaches agree on general trends caused by the interplay of relativistic and correlation effects. However, actual numbers for the energies often differ beyond the uncertainty claimed by the authors. Therefore, it is important to redo the calculations using the most advanced techniques, which should lead to more accurate and reliable results. In present paper we apply a recently developed technique [21] that combines the all-order correlation potential method [22], supplemented by ladder diagrams [23], with the configuration-interaction method [24]. The technique gives very accurate results for energy levels of Cs, Tl, Ba, Lu, Ra, and those ions of these elements that have one or two valence electrons above closed shells [21,23]. It was used to calculate energy levels of superheavy elements 119, 120, and 120⁺ [25–27]. We demonstrate that the method also works for Pb and Pb⁺. Then we apply it to calculate energy levels of E113, E114, and E114⁺.

II. METHOD OF CALCULATION

The method was described in detailed in our previous papers [21,23,26,27]. Here we repeat its main points with the focus on the details specific for the current calculations.

A. Atoms with one valence electron

Calculations are done in the V^{N-1} approximation, which means that the self-consistent potential is formed by the $N - 1$ electrons of the closed-shell core (the V^{N-1} potential). A complete set of single-electron orbitals is obtained by solving the equation

$$h_0\psi_0 = \epsilon_0\psi_0, \quad (1)$$

using the B -spline technique [28,29]. Here h_0 is the relativistic Hartree-Fock Hamiltonian

$$h_0 = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)mc^2 - \frac{Ze^2}{r} + V^{N-1}. \quad (2)$$

The B -spline basis set and Feynman diagram technique are used to calculate the all-order correlation potential (CP) $\hat{\Sigma}$ [22,23]. The CP operator $\hat{\Sigma}$ is defined in such a way that its expectation value for a valence state v is equal to the correlation correction to the energy of this state: $\delta\epsilon_v = \langle v | \hat{\Sigma} | v \rangle$. Perturbation theory expansion for $\hat{\Sigma}$ starts from the second order; we use the notation $\hat{\Sigma}^{(2)}$ for the corresponding CP. Then we include three classes of higher-order correlations in the all-order CP $\hat{\Sigma}^{(\infty)}$ [22]: (a) the screening of Coulomb interaction, (b) the hole-particle interaction, and (c) ladder diagrams [23]. States and energies of the valence electron are found by solving the equation [30]

$$(\hat{h}_0 + \hat{\Sigma})\psi_v = \epsilon_v\psi_v. \quad (3)$$

Here $\hat{\Sigma}$ can be either the second-order CP $\hat{\Sigma}^{(2)}$ or the all-order CP $\hat{\Sigma}^{(\infty)}$. Note that by iterating Eq. (3) we include one more class of higher-order correlations, the iterations of $\hat{\Sigma}$ (contributions proportional to $\hat{\Sigma}^2$, $\hat{\Sigma}^3$, etc.). The wave functions ψ_v of the valence electron found by solving Eq. (3) are often called Brueckner orbitals. Corresponding energies ϵ_v include correlations. Breit and quantum electrodynamic corrections are also included.

Table I presents the results of the calculations for the low s and p states of Tl and Pb⁺. The results for Tl are taken

TABLE I. Energy levels of Tl and Pb^+ calculated in different approximations. Final results are the sum of Σ^∞ and ladder contributions. Here % is the percentage deviation of the final theoretical result compared to experiment. The results for Tl are taken from Ref. [23]. The results for Pb^+ are obtained in the present work. Experimental numbers are taken from the NIST database [31].

State	RHF	$\Sigma^{(2)}$	Σ^∞	Ladder	Final	%	Expt.
Tl							
$6p_{1/2}$	42823	51597	50815	-1215	49600	0.68	49264
$6p_{3/2}$	36636	43524	42491	-794	41697	0.54	41471
$7s_{1/2}$	21109	23375	22887	-43	22844	0.25	22786
Pb^+							
$6p_{1/2}$	114360	123612	122547	-1421	121126	0.01	121245
$6p_{3/2}$	100731	109451	108108	-987	107121	0.04	107164
$7s_{1/2}$	58660	62793	61895	-104	61791	0.01	61796

from our earlier paper [23]; the results for Pb^+ are obtained in this work. The contributions of the ladder diagrams are presented separately because they are the latest addition to the method and it is important to emphasize their role. Tl and Pb^+ have similar electron structures, therefore it is natural to expect that the results are also similar. We see, however, that the results for Pb^+ are even slightly better than for Tl. This is probably due to the stronger Coulomb potential leading to a smaller relative value of the correlation correction. Indeed, the correlation correction to the energy is equal to the difference between the relativistic Hartree-Fock (RHF) results (column 2 in Table I) and the experimental values. We see that the absolute value of the correlation correction is larger for Pb^+ , while the relative value is smaller for Pb^+ than for Tl. In the end, the accuracy for the energy is on the level of 0.5%.

B. Atoms with two valence electrons

We use the configuration-interaction (CI) technique combined with the all-order methods to include core-valence correlations [21,24,26]. The effective CI Hamiltonian for the system of two valence electrons has the form

$$\hat{H}^{\text{CI}} = \hat{h}_1(r_1) + \hat{h}_1(r_2) + \hat{h}_2(r_1, r_2), \quad (4)$$

where \hat{h}_1 is the single-electron operator and \hat{h}_2 is the two-electron operator. The \hat{h}_1 operator is the sum of the RHF operator and the CP $\hat{\Sigma}_1$,

$$\hat{h}_1 = \hat{h}_0 + \hat{\Sigma}_1. \quad (5)$$

Here the CP $\hat{\Sigma}_1$ is the all-order CP considered in previous section. We introduce index 1 to stress that this is a single-electron operator.

The \hat{h}_2 operator is the sum of the Coulomb interaction and the correlation operator $\hat{\Sigma}_2$ [21],

$$\hat{h}_2(r_1, r_2) = \frac{e^2}{|r_1 - r_2|} + \hat{\Sigma}_2(r_1, r_2). \quad (6)$$

The $\hat{\Sigma}_2$ operator appear due to core-valence correlations and can be understood as screening of Coulomb interaction between valence electrons by core electrons. This is also the all-order operator that comes from solving the single-double

TABLE II. Calculated excitation energies E (cm^{-1}), g factors for the lowest states of the Pb atom, and %, the percentage deviations of the final theoretical results compared to experiment.

State	This work			Experiment	
	E	%	g	E	g
$6p^2 \ ^1S_0$	0		0.0000	0	0.0
$6p^2 \ ^3P_1$	7922	1.3	1.4999	7819	1.501
$6p^2 \ ^3D_2$	10940	2.6	1.2916	10650	1.269
$6p^2 \ ^3D_2$	21924	2.1	1.2085	21458	1.230
$6p^2 \ ^1S_0$	29177	1.0	0.0000	29467	0.0
$7s6p \ ^1S_0^o$	35109	0.4	0.0000	34959	0.0
$7s6p \ ^3P_1^o$	35536	0.7	1.3509	35287	1.349
$6p7p \ ^3D_1$	43236	0.7	0.6707	42919	
$6p7p \ ^1S_0$	44449	0.1	0.0000	44401	0.0
$6p7p \ ^3P_1$	44873	0.4	1.4690	44675	
$6p6d \ ^3F_2^o$	44986	1.0	0.7962	45443	0.798
$6p7p \ ^3D_2$	44997	0.4	1.1739	44809	
$6p6d \ ^1P_1^o$	46132	0.1	0.8186	46068	0.864
$6p6d \ ^3D_2^o$	46162	0.2	1.2715	46061	1.247
$6p6d \ ^3F_3^o$	46324	0.0	1.1184	46328	1.116
$7s6p \ ^3P_2^o$	48765	1.2	1.4814	48188	1.496
$8s6p \ ^1S_0^o$	48784	0.1	0.0000	48726	0.0
$8s6p \ ^3P_1^o$	48811	0.3	1.3238	48687	1.304
$7s6p \ ^1P_1^o$	49892	0.9	1.1014	49440	1.131
$6p8p \ ^3D_1$	51422	0.2	0.6690	51321	
$6p8p \ ^1S_0$	51683	0.2	0.0000	51786	

(SD) coupled-cluster equations [21]. Note that solving the SD equation produces both a single-electron CP $\hat{\Sigma}_1$ and a two-electron correlation operator $\hat{\Sigma}_2$. However, for many atomic systems, including those considered in present work and those considered previously [21,27], using the all-order CP $\hat{\Sigma}^{(\infty)}$, which was discussed in previous section, leads to better results than using the SD operator $\hat{\Sigma}_1$.

Table II shows the results of the calculations for Pb. We present energies and g factors and compare them to the experiment. The g factors are useful for identification of the states. A comparison with experiment shows that the accuracy for the energies is on the level of 1%–2% or better.

C. Breit and QED correction

Since we are considering heavy atoms it is important to include Breit and QED corrections. The Breit operator in the zero-energy-transfer approximation has the form

$$h^B = -\frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{n})(\boldsymbol{\alpha}_2 \cdot \mathbf{n})}{2r}, \quad (7)$$

where $\mathbf{r} = \mathbf{n}r$, r is the distance between electrons, and $\boldsymbol{\alpha}$ is the Dirac matrix.

We use the radiative potential method introduced in Ref. [32] to include QED corrections to the energies. The

TABLE III. Energy levels (in cm^{-1}) of superheavy elements Uut ($Z = 113$) and Fl^+ ($Z = 114$) calculated in different approximations. The notation is the same as in Table I and the numbers in parentheses are the error bars of the energy levels.

State	RHF	$\Sigma^{(2)}$	$\Sigma^{(\infty)}$	Ladder	Final	Ref. [20]
Uut						
$7p_{1/2}$	54901	61929	61953	-2183	59770(420)	59446
$7p_{3/2}$	31557	38498	36623	-497	36126(220)	34688
$8s_{1/2}$	22193	24653	23761	-32	23729(120)	22781
Fl^+						
$7p_{1/2}$	130420	138110	138105	-2333	135772(30)	137710
$7p_{3/2}$	89802	99170	96708	-667	96041(80)	97329
$8s_{1/2}$	60844	65316	63832	-82	63750(20)	63964

radiative potential has the form

$$V_{\text{rad}}(r) = V_U(r) + V_g(r) + V_e(r), \quad (8)$$

where V_U is the Uehling potential, V_g is the potential arising from the magnetic form factor, and V_e is the potential arising from the electric form factor. Both the Breit and QED operators are included in the Hartree-Fock iterations so that an important relaxation effect is taken into account [33–35].

III. RESULTS AND DISCUSSION

Table III shows the results of calculations for Uut (E113) and Fl^+ superheavy elements in the same form as in Table I for Tl and Pb^+ . We include error bars for the energies of superheavy elements. The error bars are estimated by comparing the calculated and experimental energies for Tl, Pb, and Pb^+ and assuming that the errors for the heavy analogs of these atoms should be similar.

A comparison of the energies of superheavy elements and their lighter analogs shows some interesting trends. The total values of the correlation correction for superheavy elements and their lighter analogs are similar, but slightly smaller for the superheavy elements. This is probably due to relativistic relaxation, which leads to an increased energy interval between core and valence states. On the other hand, the contribution of ladder diagrams is larger for the ground states of E113 and Fl^+ than for Tl and Pb^+ . Ladder diagrams describe the residual Coulomb interaction between the valence electron and the core. A larger contribution probably reflects the fact that due to relativistic relaxation the superheavy elements in the ground state have smaller size than their lighter analogs. Since the total value of the correlation correction to the energies is very similar for heavy and lighter elements, we expect that the accuracy of the calculations is also very similar, i.e., $\sim 0.5\%$ for E113 and $\sim 0.1\%$ for Fl^+ .

The results of the present calculations are in a reasonable agreement with previous SD-CI calculations of Ref. [20] (see Table III). However, they are closer to the results of coupled-cluster calculations of Refs. [13,14]. This is true for both the ionization potential and excitation energies.

The results for Fl (E114) are presented in Table IV and compared with previous calculations of Refs. [18,20]. In most

TABLE IV. Calculated excitation energies E (cm^{-1}) and g factors for lowest states of superheavy element Fl . The numbers in parentheses are the error bars of the excitation energies.

State	This work		Other	
	E	g	E^a	E^b
$7p^2 \ ^1S_0$	0	0.0000	0	0
$7p^2 \ ^3P_1$	26780(350)	1.4995	27316	26342
$7p^2 \ ^3D_2$	29462(770)	1.1966	29149	28983
$8s7p \ ^1S_0^o$	43573(220)	0.0000	44036	43111
$8s7p \ ^3P_1^o$	43876(310)	1.3413	44362	43441
$7p8p \ ^3D_1$	51646(370)	0.6670	51834	51302
$7p8p \ ^1S_0$	52724(260)	0.0000	53149	52487
$7p8p \ ^3P_1$	54842(280)	1.4932	55414	54647
$7p8p \ ^3D_2$	55015(280)	1.1713	55191	54814
$7p7d \ ^3D_2^o$	55814(280)	1.1780	56988	
$7p7d \ ^1D_2^o$	55828(280)	0.8730	57413	
$7p7d \ ^3F_3^o$	55890(280)	1.1138	57481	
$7p7d \ ^1P_1^o$	55910(280)	0.8259	57244	
$9s7p \ ^1S_0^o$	57607(290)	0.0000	57367	
$9s7p \ ^3P_1^o$	57663(290)	1.3316		
$7p9p \ ^3D_1$	60198(300)	0.6669		
$7p9p \ ^1S_0$	60324(305)	0.0000		
$7p9p \ ^3D_2$	61272(310)	1.1769	57413	
$7p8d \ ^3F_2^o$	61612(310)	0.7717		
$7p6f \ ^1D_2$	61620(310)	0.9097		
$7p6f \ ^3G_3$	61650(310)	0.8357	60291	
$7p6f \ ^3F_3$	61653(310)	1.1917	60298	
$7p6f \ ^3G_4$	61655(310)	1.0838	60311	

^aReference [20].

^bReference [18].

of the cases the results of the present work are in between the two earlier results. However, the difference between all three sets of results is small, $\sim 1\%$. This is consistent with the estimate of accuracy based on similar calculations for Pb (see the previous section).

IV. CONCLUSION

We apply a recently developed advanced method of atomic structure calculation that combines three different all-order techniques to calculate energy levels of superheavy elements 113, Fl , and Fl^+ with the accuracy $\sim 1\%$. This represents some improvement to previous calculations and contributes to the reliability of the theoretical predictions of the spectra of superheavy elements.

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